Université de Montréal

Partie 1: Synthèse de la triphénylphosphine liée au polystyrène non réticulé et son utilisation lors de la réaction de Mitsunobu

Partie 2: Cyclopropanation catalytique énantiosélective d'alcènes utilisant le diazométhane

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Cette thèse intitulée:

Partie 1: Synthèse de la triphénylphosphine liée au polystyrène non réticulé et son utilisation lors de la réaction de Mitsunobu

Partie 2: Cyclopropanation catalytique énantiosélective d'alcènes utilisant le diazométhane

présentée par:

Marc K. Janes

a été évaluée par un jury composé des personnes suivantes:

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[Taper le nom] , représentant du doyen de la FES

Résumé

La première partie de cet ouvrage porte sur la préparation et l'utilisation en synthèse d'un réactif phosphinique polymérique. Partant du concept de lier un réactif à un support pour en faciliter sa récupération ou son élimination, nous avons lié la triphénylphosphine au polystyrène non réticulé (soluble dans certains solvants). De cette manière, la réactivité du réactif en milieu réactionnel homogène est conservée, tout en ayant la possibilité de précipiter sélectivement ce dernier au moment de la purification. L'utilisation de ce réactif phosphinique polymérique dans la réaction de Mitsunobu a été utile pour constater la conservation de la réactivité de la triphénylphosphine malgré son support polymérique. Une plus grande régiosélectivité a même été observée, favorisant le réactif supporté, entre ce réactif et la triphénylphosphine lorsqu'il y a possibilité de réaction à deux sites différents.

La deuxième partie de cette thèse porte sur le développement d'une méthode catalytique asymétrique de cyclopropanation d'alcènes. Plusieurs systèmes ont été testés impliquant différents métaux de transition tous combinés à une panoplie de ligands chiraux. Le fruit de cette exploration a été la découverte de conditions réactionnelles qui permettent la synthèse de cyclopropanes énantioenrichis à partir d'esters cinnamiques et de diazométhane, en utilisant un catalyseur chiral composé de cuivre et d'un ligand bisoxazoline. Dans le but d'augmenter la portée de cette réaction, nous avons tenté brièvement d'utiliser le palladium comme substitut au cuivre, puisqu'il présente une réactivité accrue.

La troisième partie de cet ouvrage décrit la découverte d'une réaction de métallation anormale entre deux sels, l'un d'imidazolium et l'autre de palladium. Nous avons illustré

l'étendue de cette réaction. La métallation anormale survient en position C5 d'un arylimidazolium plutôt qu'à la position C2 laquelle aurait mené à la formation d'un carbène *N*-hétérocyclique. Un mécanisme réactionnel menant à la métallation anormale est postulé. Certains complexes anormaux synthétisés peuvent servir de catalyseurs pour des réactions de couplage et leur réactivité a été comparée à celle des catalyseurs générés *in situ*. Ces travaux ont eu un impact important, car la réaction entre deux sels tel que discuté ci haut, n'était pas connue. Devant l'abondance en catalyse de l'utilisation du palladium et de l'émergence du domaine des carbènes *N*-hétérocycliques (CNH), il a été important d'étudier ce système pour comprendre et prédire les interactions de types ligand-métal.

Mots-clés: Mitsunobu, triphénylphosphine polymérique, cyclopropanation énantiosélective, diazométhane, complexes anormaux de palladium.

Abstract

This work relates in first part to the preparation and synthetic applications of a phosphinic polymeric reagent. Based on the concept of binding a reagent to a support to facilitate its recovery or elimination, we bound the triphenylphosphine to non-crossed-linked polystyrene. In this manner, the reactivity of this soluble reagent was amenable to facile precipitation by modification of the medium. The use of this phosphinic reagent in the Mitsunobu reaction did not require excess reagent despite the fact that it is polymeric. Greater regioselectivity was observed using our reagent comparatively to triphenylphosphine with substrates bearing two possible reactive sites.

The second part of this thesis relates to the development of asymmetric catalytic methods for the cyclopropanation of alkenes. Several systems have been tested involving various transition metals and a variety of chiral ligands. The fruit of this exploration was the discovery of reaction conditions which allowed diazomethane and a chiral Cu-bisoxazoline catalyst to afford enantioenriched cyclopropanes from cinnamic esters as starting materials. With the aim of increasing the scope of this reaction, palladium was used as a substitute for copper in this reaction because of its high reactivity, but no enantioselectivity could be observed. Fortuitously, during the synthesis of the palladium catalyst involving N-heterocyclic carbene precursors, we discovered an abnormal metalation reaction.

The third part of this work describes the discovery and scope of an abnormal metalation reaction between an imidazolium salt and a palladium salt. The abnormal metalation occurs in the C5 position of an arylimidazolium salt rather than at the C2 position, which would have led to the formation of an N-heterocyclic carbene. A possible

mechanistic pathway is postulated for the formation of the abnormal complexes. Abnormal complexes can be used as catalysts for cross-coupling reactions, and their reactivity is compared with *in situ* generated catalysts.

Keywords: Mitsunobu, polymeric triphenylphosphine, enantioselective cyclopropanation, diazomethane, abnormal palladium complexes.

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$[\alpha]_D$	rotation optique; raie D du sodium
°C	degré Celsius
Å	Ångstrom
Ac	acétyle
AcO	acétate
Ad	adamantyle
Anal.	analyse
Ar	aryle
Bn	benzyle
br	broad
c	concentration
calcd ou calc.	calculated ou calculé
cat.	catalytique
CLPS	crossed-linked-polystyrene
CNH	carbène N-hétérocyclique
Cy	cyclohexyle
d	doublet
DCM	dichlorométhane
DEAD	diéthylazodicarboxylate
Dec.	décomposition
deg	degré
DMA	N,N-diméthylacétamide
DME	1,2-diméthoxyéthane
DMF	N,N-diméthylformamide
ee	excès énantiomérique
EI	electron impact

equiv	équivalent
ES	electrospray
Et	éthyle
EtOAc	acétate d'éthyle
FAB	fast atom bombardment
g	gramme
GC	gas chromatography
Hex	hexane
HRMS	spectre de masse à haute résolution
Hz	hertz
i	iso
IR	infra rouge
J	constante de couplage
L	litre
log	logarithme
LRMS	spectre de masse basse résolution
M	métal
m	méta
MAB	metastable atom bombardment
Me	méthyle
MeCN	acétonitrile
MeOH	méthanol
Mes	mésityle
mg	milligramme
MHz	mégahertz
min	minute
mL	millilitre
mmol	millimole

mol	mole
MOMCl	chlorométhylméthyle éther
n.d.	non disponible
n.r.	no reaction
NCPS	non-crossed-linked-polystyrene
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
OTf	O-triflate
PEG	poly(éthylèneglycol)
Ph	phényle
p	para
Pr	propyle
ppm	partie par million
psi	pound per square inch
Py	pyridine
q	quartet
qn	quintet
R	alkyle (sauf si spécifié)
R	rectus
RMN	résonance magnétique nucléaire
RT	room temperature
S	sinister
s	sec
SCG™	solubility controling group
sep	septuplet
SFC	supercritical fluid chromatography
t	tert
t	triplet

T	température
THF	tétrahydrofurane
TMAD	*N,N,N,N*-tetraméthylazodicarboxamide
TMS	tetraméthylsilane
TON	turnover number
T_r	temps de rétention
UV	ultra violet
δ	déplacement chimique
μL	microlitre
υ	longeur d'onde
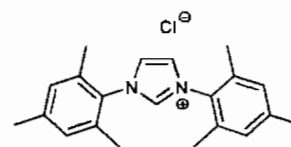
IMesHCl

SIMesHCl
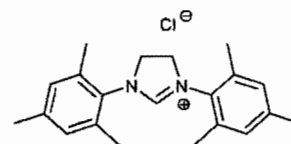
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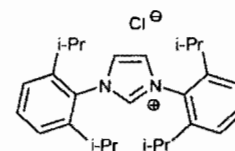
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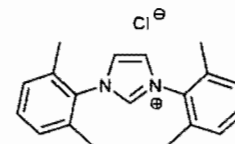
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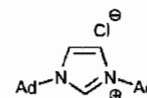
ICyHCl
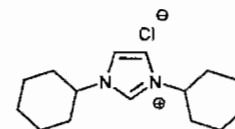
À ma conjointe Isabelle, ma famille et mes

fils Michaël, Anthony et Raphaël ...

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Chapitre 1 : Stratégies facilitant la purification à l'aide de supports polymériques pour la réaction de Mitsunobu

1.1. La réaction de Mitsunobu

La réaction de Mitsunobu est extrêmement utile en synthèse. Elle permet entre autre d'inverser la configuration absolue d'un centre chiral tout en produisant un alcool protégé en utilisant le nucléophile approprié (**Figure 1-1**).[1]

Le choix du nucléophile, du composé azo, de la phosphine et du substrat est très vaste, ce qui sous entend que la réaction de Mitsunobu est une réaction très générale. Son principal désavantage est l'utilisation d'une quantité stœchiométrique de phosphine qui est convertie en oxyde de phosphine lors de la réaction. De plus, le composé azo donne également de façon stœchiometrique un dérivé de l'hydrazine. Ces deux produits peuvent s'avérer difficiles à séparer du produit réactionnel.

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[1] (a) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380; (b) Mitsunobu, O. *Synthesis* **1981**, 1; (c) Hughes, D. L. *Org. Prep. Proced. Int.* **1996**, *28*, 127; (d) D. L. Hughes, *Org. React.* **1992**, *42*, 335; (e) O. Mitsunobu, "Synthesis of alcohols and ethers", dans *Comprehensive Organic Synthesis* (Eds.: B. M.Trost, I. Fleming), Pergamon, Oxford, **1991**, vol. 6; (f) O. Mitsunobu, "Synthesis of amines and ammonium salts", in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, vol. 6, pp. 65-101; (g) B. R. Castro, *Org. React.* **1983**, *29*, 1.

Pour faciliter la séparation des sous-produits résultant de la phosphine, des stratégies empruntées à la chimie combinatoire dont la chimie sur support solide ont été utilisées. Le pionnier de l'utilisation de supports solides en synthèse est Merrifield.[2,3] Il a imaginé une résine de polystyrène réticulé chlorométhylé sur laquelle il est possible de greffer des groupements nucléophiles en déplaçant les chlorures benzyliques. Cette résine est obtenue par co-polymérisation du styrène chlorométhylé et du divinylbenzène.
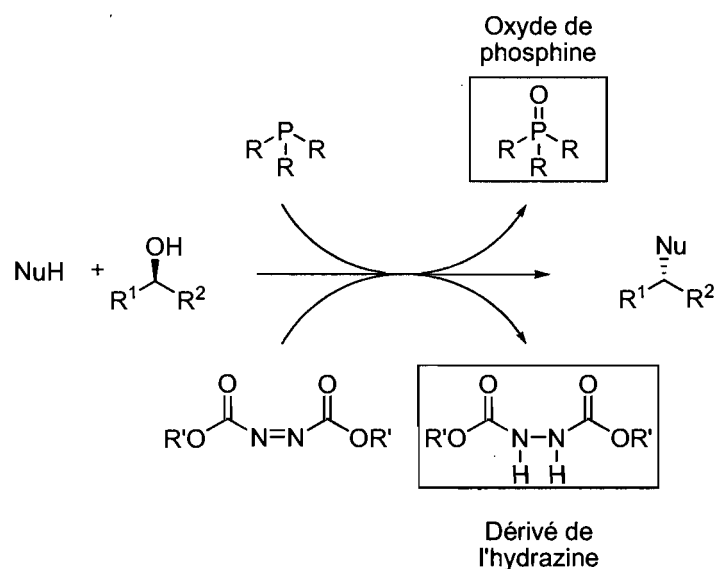
Figure 1-1. Sous-produits compliquant la purification du produit de réaction dans la réaction de Mitsunobu.

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[2] Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.

[3] (a) Thompson, L. A.; Ellman, J. A. *Chem. Rev.* **1996**, *96*, 555; (b) Toy, P.; Janda, K. D. *Acc. Chem. Res.* **2000**, *33*, 546; (c) Seeberger, P. H.; Haase, W.-C. *Chem. Rev.* **2000**, *100*, 4349.

1.2. Stratégies facilitant la purification en synthèse organique

Depuis ces travaux historiques, a émergé un nouveau domaine de recherche ayant pour but le besoin de faciliter la purification de produits réactionnels. Plusieurs stratégies ont été alors élaborées avec cette perspective. La **Figure 1-2** illustre trois stratégies générales. La première (stratégie A) consiste à greffer le substrat sur un support et à effectuer les transformations désirées à l'aide de réactifs en solution. Le rinçage du support élimine les impuretés et les sous-produits et permet d'isoler le produit désiré pur toujours lié au support. Cette liaison produit-support est scindée lors d'une étape de clivage qui doit évidemment préserver le produit. Les réactions doivent obligatoirement être complètes pour l'obtention de produits purs.

Une deuxième approche (stratégie B) consiste à conserver le substrat en solution et à greffer les réactifs au support. Le produit final de la réaction se retrouve en solution et les réactifs liés au support. L'étape de clivage n'est donc pas nécessaire. Les deux stratégies A et B nécessitent un excès de réactifs dû à la nature hétérogène (donc moins réactive) des systèmes.

La troisième stratégie (stratégie C) contourne en partie ce problème. La réaction a lieu avec le substrat et les réactifs en solution sans support. Ensuite, la solution réactionnelle résultante est « filtrée » sur un support solide auquel des agents de piègeage ont été fixés. Ces agents de piègeage servent à la capture sélective des sous-produits en se liant à eux.[4] Il est toujours possible que la capture soit incomplète.

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[4] Revue sur le sujet: Eames, J.; Watkinson, M. *Eur. J. Org. Chem.* **2001**, 1213.
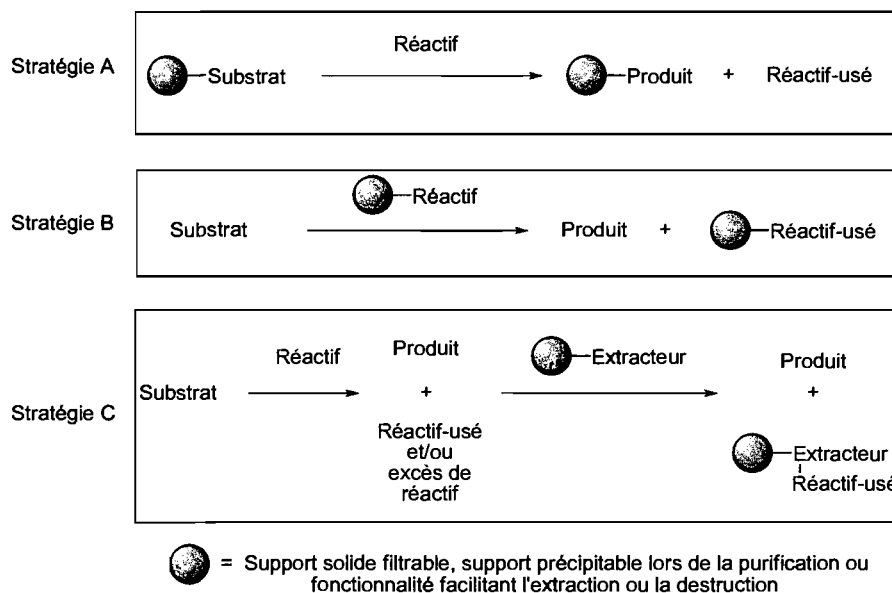
Figure 1-2. Stratégies possibles facilitant la purification par l'utilisation de supports.

Il est toujours possible de coupler la stratégie B (**Figure 1-2**) avec l'utilisation d'un réactif lié à support polymérique qui est soluble dans le milieu réactionnel mais qui précipite lors de l'ajout d'un co-solvant suite à la réaction afin d'optimiser la réactivité par rapport à l'utilisation de réactifs hétérogènes. Ce support peut être couplé à des réactifs ou même des catalyseurs.[5] Il existe plusieurs supports solubles pour la fixation de réactifs (**Figure 1-3**).

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[5] Pour un article de revue, voir: Dickerson, R. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325.

1.3. Les supports solubles polymériques

poly(styrène)   poly(vinyle alcool) poly(étylène imine)   poly(acide acrylique)

poly(oxyde de méthylène)   poly(éthylèneglycol)   poly(oxyde de propylène)
(PEG)

cellulose   poly(acrylamide)   PEG avec
3,5-diisocyanato-chlorure de benzyle

PEG avec
3-nitro-3-azapentane-1,5-diisocyanate
(après hydrogénation)

poly(vinyle alcool)-
poly(1-vinyl-2-pyrrolidinone)

poly(N-isopropylacrylamide)-
poly(dérive d'acide acrylique)

poly(styrène)-
poly(monosaccharides substitués
avec des vinyls)

Figure 1-3. Supports polymériques solubles pour la fixation de réactifs.

À partir de ces stratégies, une multitude de solutions ont été proposées pour résoudre le problème des sous-produits de phosphines et d'oxyde de phosphines dans les réactions de Mitsunobu. Ford a été le premier à lier une phosphine à un support solide de type polystyrène réticulé. L'inconvénient majeur provient de la nature insoluble du support et du grand excès du réactif, nécessaire pour obtenir des rendements satisfaisants.[6]

Hodge a synthétisé une version soluble de ce polymère (**Figure 1-4**).[7] Malheureusement, il ne démontre pas de supériorité par rapport à sa version non soluble pour la conversion d'alcools en chlorures. De plus, cette version du polymère réticule lors de son entreposage et devient alors insoluble. Bergbreiter a travaillé avec un poly(éthylène) comme support pour la phosphine et la réactivité observée se compare à celle du réactif de Ford pour la conversion d'alcools en chlorures.[8] Janda a pour sa part travaillé avec du poly(éthylène glycol) (PEG)[9,10] comme support et l'a expérimenté dans des réactions de réduction d'azotures[11] et pour la réaction de Mitsunobu. Dans ces deux cas, les réactions se sont montrées plus rapides que celles impliquant le support de polystyrène réticulé. Charette, de son côté, a mis au point une version soluble de la triphénylphosphine, synthétisée à partir du polystyrène non réticulé disponible commercialement.[12] Lors d'expériences comparatives effectuées à l'aide de la réaction de Staudinger/Aza-Wittig, ce réactif soluble a démontré une réactivité supérieure à son analogue réticulé. De plus, il s'est avéré aussi réactif que la triphénylphosphine non liée. L'extraction de la triphénylphosphine liée

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[6] Bernard, M.; Ford, W. T. *J. Org. Chem.* **1983**, *48*, 326.

[7] Harrison, C. R.; Hodge, P.; Hunt, B. J.; Khoshdel, E.; Richardson, G. *J. Org. Chem.* **1983**, *48*, 3721.

[8] Bergbreiter, D. E.; Blanton, J. R. *J. Chem. Soc., Chem Commun.* **1985**, 337.

[9] Sieber, F.; Wentworth, P.; Jr.; Toker, J. D.; Wentworth, A. D.; Metz, W. A.; Reed, N. N.; Janda, K. D. *J. Org. Chem.* **1999**, *64*, 5188.

[10] Wentworth, P.; Jr.; Vandersteen, A. M.; Janda, K. D. *Chem. Commun.* **1997**, 759.

[11] (a) Staudinger, H. *Helv. Chim. Acta* **1919**, *2*, 635; (b) Cooper, R. D. G. *Pure Appl. Chem.* **1987**, *59*, 485.

[12] Charette, A. B.; Boezio, A. A.; Janes, M. K. *Org. Lett.* **2000**, *2*, 3777 (incluse dans l'annexe I).

s'effectue par précipitation à l'aide de solvants tels l'éther ou le méthanol, d'où peuvent être extraits les produits réactionnels avec des rendements élevés surtout dans les cas de formation d'imines via la réaction de Staudinger/Aza-Wittig.
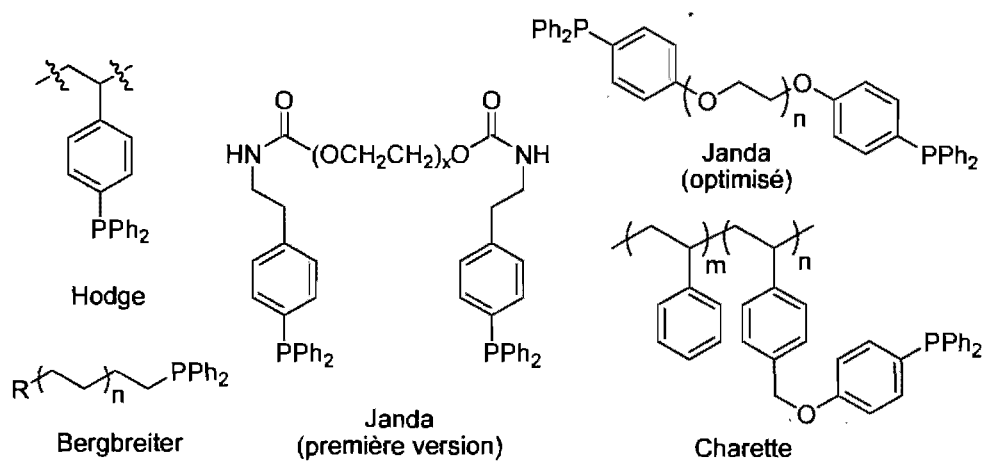
Figure 1-4. Phosphines liées à des supports polymériques solubles.

1.4. Réactifs non polymériques facilitant l'étape de purification et utiles pour la réaction de Mitsunobu

Les phosphines d'Hanessian, Kiankarimi, Ley (**Figure 1-5**) et celle de Flynn peuvent être éliminées soit par traitement acide ou basique selon le cas.[13,14] De plus, celle de Flynn, peut aussi l'être par filtration sur une colonne échangeuse d'ions, une fois l'ester *t*-butylique hydrolysé.[15,16] La phosphine de Routledge, quant à elle, porte un éther-couronne et ses sous-produits peuvent être captés au moment de la purification par une résine pourvue de fonctions ammonium.[17] La phosphine proposée par Yoakim est une phosphine portant un carboxylate « masqué » que l'on « démasque» après la réaction et qui est éliminée par extraction en conditions basiques.[18] Celle de Parlow est conçue de sorte qu'il faut faire intervenir une réaction de Diels-Alder avec un réactif sur un support solide, pour l'éliminer.[19] La phosphine de Curran comprend des groupes fluorés qui permettent son extraction à l'aide de techniques appropriées.[20] Plus récemment, une phosphine munie de groupements fonctionnels permettant le contrôle de la solubilité (un phosphonium) a été développée par Charette *et al.* puis utilisée avec succès dans la réaction de Mitsunobu.[25]

[13] Hanessian, S.; Ducharme, D.; Massé, R.; Capmau, M.L. *Carbohydr. Res.* **1978**, *63*, 265.

[14] Smith, C. D.; Baxendale, I. R.; K. Tranmer, G. K.; Baumann, M.; Smith, Lewthwaitec, R. A.; Ley, S.V. *Org. Biomol. Chem.*, **2007**, *5*, 1562.

[15] Kiankarimi, M.; Lowe, R.; McCarthy, J. R.; Whitten, J. P. *Tetrahedron Lett.* **1999**, *40*, 4497.

[16] (a) Starkey, G. W.; Parlow, J. J.; Flynn, D. L. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2385; (b) Flynn, D. L. *Med. Res. Rev.* **1999**, *19*, 408.

[17] Jackson, T.; Routledge, A. *Tetrahedron Lett.* **2003**, *44*, 1305.

[18] Yoakim, C.; Guse, L.; O'Meara, J. A.; Thavonekham, B. *Synlett* **2003**, 473.

[19] Lan, P.; Porco Jr., J. A.; South, M. S.; Parlow, J. J. *J. Comb. Chem.* **2003**, *5*, 660.

[20] Q. Zhang, Z. Luo, D. P. Curran, *J. Org. Chem.* **2000**, *65*, 8866.
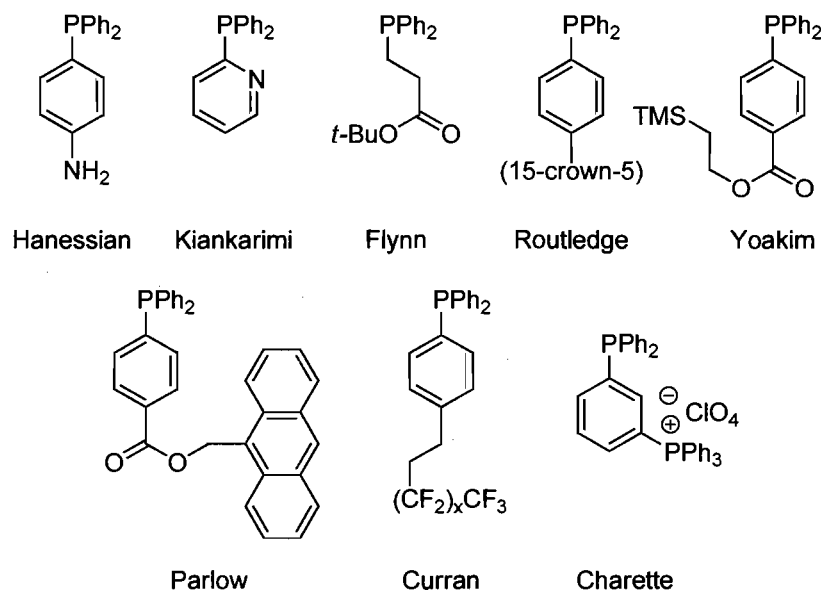
Figure 1-5. Phosphines liées à des supports non polymériques utilisées lors de la réaction de Mitsunobu.

Le composé azo (traditionnellement le diéthylazodicarboxylate (DEAD)) est aussi utilisé en quantité stœchiométrique dans la réaction de Mitsunobu (**Figure 1-1**). Son sous-produit, un dérivé de l'hydrazine, est très polaire. De fait, il est généralement plus facile de le séparer du produit réactionnel que l'oxyde de phosphine, en utilisant des méthodes traditionnelles de purification. Conséquemment, moins d'efforts ont été déployés dans le but de faciliter son élimination. Quelques exemples de stratégies ont été développés dans le but de faciliter quand même la purification par l'élimination facilitée du composé azo (**Figure 1-6**). Le DBAD et ses sous-produits sont détruits en produits volatiles par traitement en milieu acide.[21] D'autre part, le DNAD et ses sous-produits sont polymérisés en fin de réaction et filtrés.[22] Par ailleurs, le FDEAD et ses sous-produits sont extraits en fin de réaction par

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[21] Kiankarimi, R.; Lowe, R.; McCarthy, J. R.; Whitten, J. P. *Tetrahedron Lett.* **1999**, *40*, 4497.

[22] Barrett, A. G. M.; Roberts, R. S.; Schröder, J. *Org. Lett.* **2000**, *2*, 2999.

lavages avec des solvants fluorés.[23] Les BadMAD et BadEAD et leurs analogues réagis portent un groupe adamantyle pouvant être lié à une cyclodextrine pour élimination.[24] Finalement, le SCG™-DEAD est le DEAD lié à un phosphonium soluble dans le milieu réactionnel, servant à sa précipitation lors de la purification.[25]
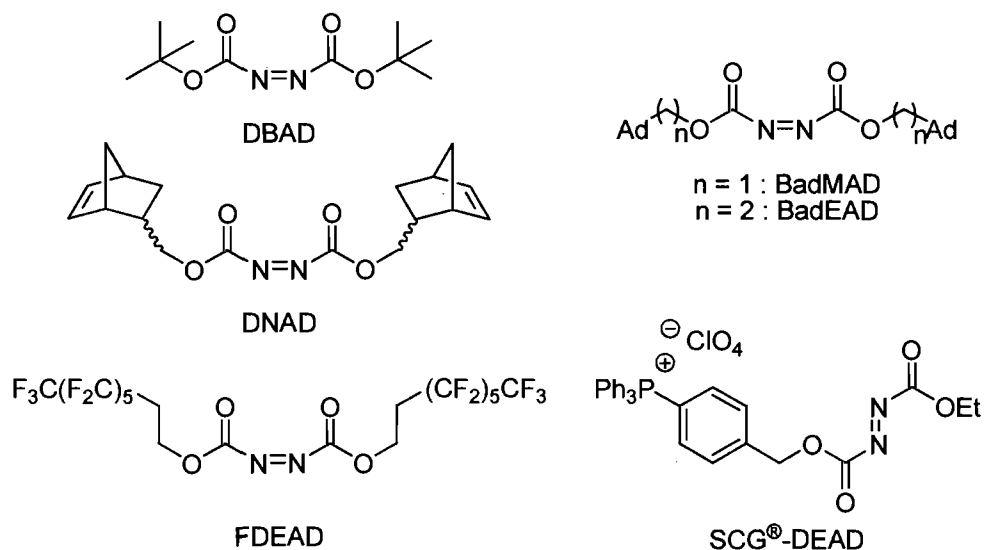
Figure 1-6. Composés utilisés dans des stratégies pour éliminer les sous-produits dérivés des composés hydrazine.

[23] (a) Dandapani, S.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3855. (b) Dobbs, A. P.; McGregor-Johnson, C. *Tetrahedron Lett.* **2002**, *43*, 2807.

[24] Dandapani, S.; Newsome J. J.; Curran, D. P. *Tetrahedron Lett.* **2004**, *45*, 6653.

[25] Charette, A. B.; Poupon, J.-C.; Boezio, A. A. *Brevet déposé et résultats non publiés.*

1.5.   Recherche proposée

En chimie organique de synthèse, un des aspects qui consomme le plus de temps et de ressources est la purification des produits réactionnels bruts dans le but d'obtenir des composés organiques de pureté élevée. Parfois, il est nécessaire d'utiliser plusieurs méthodes de purification successives pour atteindre ce but. Les difficultés rencontrées dans certaines voies de synthèse en proscrivent parfois l'utilisation. Des stratégies pour diminuer le fardeau de purification ont été dévelopées telles que décrites dans le présent chapitre. L'utilisation de groupes servant de point d'ancrage permet d'extraire sélectivement des composés liés d'un mélange complexe. Tel que vu, les groupes fonctionnels sensibles aux acides et/ou aux bases ainsi que les polymères sont souvent liés à des réactifs ou des substrats dans le but de faciliter l'extraction de ces réactifs ou substrats.

Les phosphines sont des réactifs très souvent utilisés en synthèse organique. Suite au processus réactionnel dans lequel elles prennent part, elles sont généralement oxydées irréversiblement en produits inertes. Cette oxydation constitue souvent une force motrice importante dans un procédé chimique mais des stratégies doivent être adoptées pour éliminer les sous-produits réactionnels du produit réactionnel désiré.

Vu l'importance en chimie des phosphines et particulièrement de la triphénylphosphine, vu la difficulté de purification et l'émergence de supports polymériques solubles, nous avons entrepris de développer une alternative à la triphenylphosphine qui comporte un élément facilitant   les   purifications   dans   les   réactions   impliquant   ce   réactif.

Chapitre 2 : Mitsunobu reaction using triphenylphosphine linked to non-cross-linked polystyrene (published article)

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2.1. Article

The Mitsunobu reaction of alcohols has been extensively used in organic synthesis for the preparation of esters, alcohols, aryl ethers, amine, and thioethers.[1] This reaction was found to be particularly effective to invert the configuration of chiral secondary alcohols since a clean S_N2 process is generally observed. Over the past decade, many efforts were directed toward replacing triphenylphosphine and diethyl or diisopropyl azodicarboxylate (which are respectively converted into triphenylphosphine oxide and the related dialkylhydrazino dicarboxylate) by other reagents to facilitate the isolation and purification of the desired

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[1] (a) Mitsunobu, O. *Synthesis* **1981**, 1; (b) Hughes, D. L. *Org. React. (N.Y.)* **1992**, *42*, 335; (c) Hughes, D. L. *Org. Prep. Proced. Int.* **1996**, *28*, 127.

product.[2] One alternative strategy that has been contemplated is to use solid supported reagents[3,4] that could be simply filtered after the reaction. However, possible problems encountered with solid-supported reagents in Mitsunobu reactions include their lower reactivity due to the sterically less accessible reactive center. Furthermore, the slower reaction kinetics imparted by the biphasic system is generally circumvented by using a large excess of the reagent; such a solution is obviously not desirable and practical in Mitsunobu reactions. In this context, the Mitsunobu inversion reaction of secondary alcohols using a solidsupported triphenylphosphine has never been reported thus far.[5] In principle, the use of soluble polymer supports[6] could circumvent these problems if the reaction site is readily accessible and if the polymeric reagent retains the reactivity of free triphenylphosphine. We recently reported[7] the synthesis of triphenylphosphine linked to a non-cross-linked polystyrene[8] (**Figure 2-1**), and we have shown its effectiveness in the Staudinger-Aza-Wittig reaction. The polymer was easily prepared in three steps from commercially available non-cross-linked polystyrene, and it could be quantitatively recovered after the reaction. In this note, we show that this soluble polymerbound

[2] For alternatives to PPh3 or DEAD: (a) Kiankarimi, M.; Lowe, R.; McCarthy, J. R.; Whitten, J. P. *Tetrahedron Lett.* **1999**, *40*, 4497; (b) Oneill, I. A.; Thompson, S.; Murray, C. L.; Kalindjian, S. B. *Tetrahedron Lett.* **1998**, *39*, 7787 and references therein.

[3] For the preparation and use of cross-linked polystyrene supported triphenylphosphine, see: Bernard, M.; Ford, W. T. *J. Org. Chem.* **1983**, *48*, 326.

[4] For the preparation and use of cross-linked polystyrenesupported DEAD, see: Arnold, L. D.; Assil, H. I.; Vederas, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 3973.

[5] (a) Pelletier, J. C.; Kincaid, S. *Tetrahedron Lett.* **2000**, *41*, 797; (b) Barrett, A. G.; Roberts, R. S.; Schröder, J. *Org. Lett.* **2000**, *2*, 2999.

[6] Previous soluble polymer (PEG) bound phosphines: (a) Wentworth Jr., P.; Vandersteen, A. M.; Janda, K. D. *J. Chem. Soc., Chem. Commun.* **1997**, 759; (b) Sieber, F.; Wentworth, P., Jr.; Toker, J. D.; Wentworth, A. D.; Metz, W. A.; Reed, N. N.; Janda, K. D. *J. Org. Chem.* **1999**, *64*, 5188.

[7] Charette, A. B.; Boezio, A. A.; Janes, M. K. *Org. Lett.* **2000**, *2*, 3777 (incluse dans l'annexe I).

[8] For recent examples of non-cross-linked polystyrene-supported reagents, see: (a) Enholm, E. J.; Gallagher, M. E.; Moran, K. M.; Lombardi, J. S.; Schulte, J. P. *Org. Lett.* **1999**, *1*, 689; (b) Enholm, E. J.; Schulte, J. P. *Org. Lett.* **1999**, *1*, 1275.

phosphine is highly effective in the Mitsunobu reaction of secondary alcohols and in S_N2' nucleophilic substitution of Baylis-Hillman adducts.
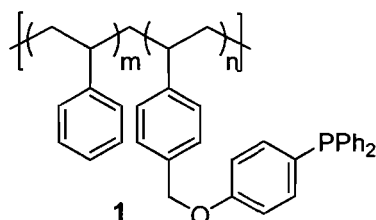
Figure 2-1. NCPS-PPh₃.

The Mitsunobu reaction on menthol was selected to optimize the efficiency of polymer **1** in these transformations and to monitor its sensitivity to steric hindrance of the starting alcohol. Interestingly, even though it is a fairly hindered secondary alcohol, menthol has been shown to react well with $Ph_3P/DEAD/p\text{-}NO_2C_6H_4COOH$[9] to produce the *p*-nitrobenzoate **2** in 83% yield.[10] The solvent optimization when polymer **1** was used as the triarylphosphine clearly indicated that either toluene or THF were suitable solvents (**Table 2-1**). Both were much superior to benzene which is often used in these reactions. The optimal concentrations were between 0.05 and 0.1 M but sometimes, stirring was easier under dilute conditions. Diisopropyl azodicarboxylate was also examined, and it gave a yield similar to that obtained with the diethyl derivative (75% conversion).

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[9] (a) Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017; (b) Saïah, M.; Bessodes, M.; Antonakis, K. *Tetrahedron Lett.* **1992**, *33*, 4317 and references therein.
[10] Dodge, J. A.; Trujillo, J. I.; Presnell, M. *J. Org. Chem.* **1994**, *59*, 9, 234.

As expected, the use of tetramethylazodicarboxamide (TMAD)[11] did not lead to any significant amount of the desired product, and the starting material was recovered quantitatively.

Table 2-1. Optimization of the Reaction Conditions for the Mitsunobu Reaction of Menthol.[a]
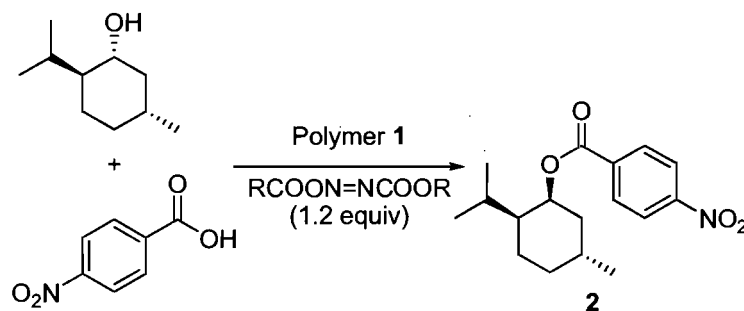
entry	solvent (concn)	R	Conversion[b] (%)
1	PhH (0.1 M)	Et	50
2	PhH (0.1 M)	Et	38[c]
3	PhH (0.05 M)	Et	57
4	THF (0.1 M)	Et	70
5	toluene (0.1 M)	Et	72
6	toluene (0.05M)	Et	75 (67)[d]
7	toluene (0.05 M)	i-Pr	75

[a] All the reactions were carried out as described in the general procedure. [b] Conversions were determined by ^{1}H NMR of the crude reaction product that was extracted out of the precipitated polymer. c In this entry 2.0 equiv of DEAD were used. [d] The yield in parentheses corresponds to the isolated yield of chromatographically pure ester.

[11] (a) Ito, S.; Tsunoda, T. *Pure Appl. Chem.* **1999**, *71*, 1053; (b) Tsunoda, T.; Uemoto, K.; Nagino, C.; Kawamura, M.; Kaku, H.; Ito, S. *Tetrahedron Lett.* **1999**, *40*, 7355.

Two other alcohols were tested, and the results were compared to those obtained with triphenylphosphine or triphenylphosphine bound to a cross-linked polystyrene (PPh$_3$-CLPS) (**Figure 2-2**). 2-(S)-Octanol could be converted into its benzoate antipode very effectively with the soluble phosphine polymer. Conversely, the transformation was slightly less efficient if the analogous cross-linked phosphine was used. In a similar fashion, ethyl (S)-lactate could be transformed into the (R)-p-nitrobenzoate derivative in 71% yield. In both cases, none of the starting alcohols were detected by ^{1}H NMR in the crude reaction mixture after extraction of the product out of the polymer. The isolation of the desired product required addition of methanol to precipitate the polymer. The lower isolated yield could be a consequence of the product being trapped in the polymer upon precipitation since the yield is highly dependent on the extraction procedure.

1	83%
PPh$_3$-NCPS	65%

1	71%
PPh$_3$	91%
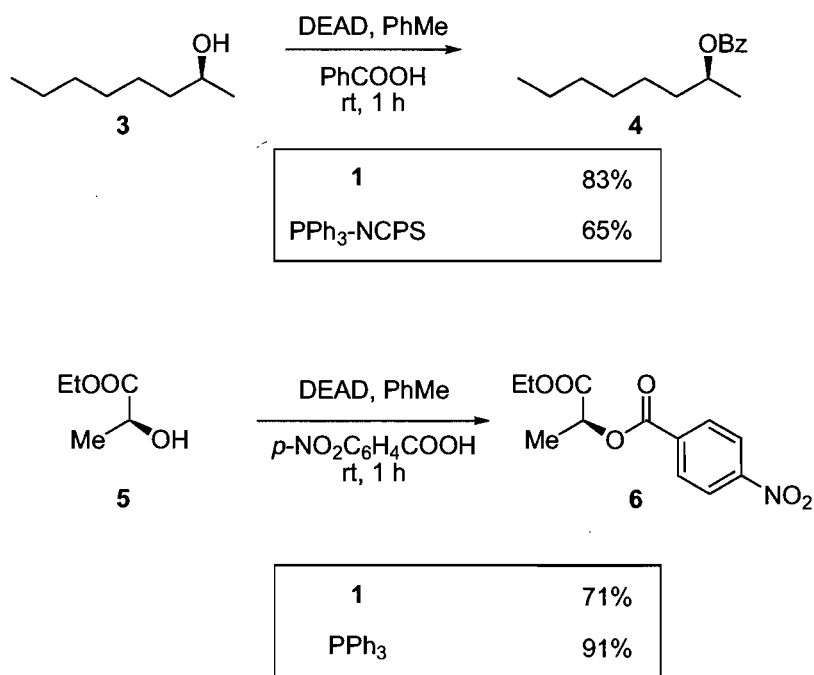
Figure 2-2. Comparison between NCPS-PPh$_3$ and other phosphines.

We next turned our attention on a reaction that could take advantage of the additional steric hindrance imparted by the polymeric backbone of phosphine **1**. We have previously developed a method that provides access to E-trisubstituted alkenes from Baylis-Hillman adducts.[12] This process occurs via a highly regioselective S_N2' (γ-attack) Mitsunobu reaction. Since it is reasonable to assume that nucleophilic attack at the γ position should be more favored with bulkier phosphines, one may anticipate that better regioisomeric ratios will be observed if the soluble phosphine polymer is used in these reactions.

$\gamma : \alpha$ 20:1 to >50:1

R = Et, *i*-Pr
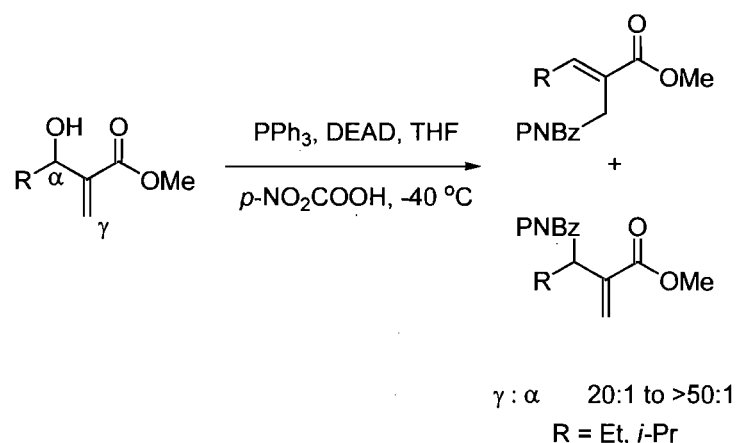
Équation 2-1

The results obtained for the Mitsunobu reaction on the Baylis-Hillman adduct **7** are summarized in **Table 2-2**. A direct comparison between triphenylphosphine and polymer **1** is also provided. Two conclusions can be drawn from the data, the first being that the nucleophilic substitution reaction mediated by polymer **1** leads to a significantly more regioselective transformation.

---

[12] (a) Charette, A. B.; Côté, B.; Monroc, S.; Prescott, S. *J. Org. Chem.* **1995**, *60*, 6888; (b) Charette, A. B.; Côté, B. *Tetrahedron Lett.* **1993**, *34*, 6833.

Table 2-2. Mitsunobu Reaction on Baylis-Hillman Adduct 7.

$\gamma : \alpha$ 20:1 to >50:1

R = Et, i-Pr
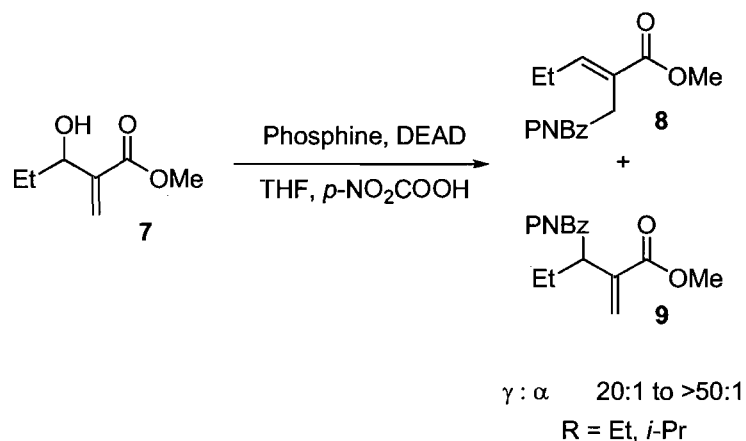
entry	temp (°C)	ratio (9:8)^a	phosphine	yield (%)^b
1	rt	1:6	PPh$_3$	90
2	rt	1:20	1	88
3	0	1:10	PPh$_3$	86
4	0	1:>90	1	81
5	-40	1:25	PPh$_3$	85
6	-40	1:>90	1	65

^{a} The ratios were determined by ^{1}H NMR of the crude reaction mixture. ^{b} Isolated yield of 8 + 9. ^{c} In this case, the remaining was the starting alcohol 7.

For example, when the reaction was done at room temperature, a 20:1 regioisomeric ratio of 8 and 9 (entry 2) was obtained when 1 was used compared to the 6:1 ratio observed with triphenylphosphine (entry 1). This trend was also observed at lower temperature. Another important feature of the reaction using the polymeric phosphine reagent is that higher selectivities are also observed at 0 °C. For example, the minor regioisomer could not be detected when the reaction was carried out at 0 °C. This contrasts with the 10:1 regioisomeric ratio obtained when the analogous reaction using triphenylphosphine was

carried out at 0 °C or the 25:1 ratio at -40 °C. To our surprise, the polymer **1** was still soluble at -40 °C although the reaction mixture was quite viscous, and it still showed reactivity in the nucleophilic substitution reaction.

2.2. Experimental Section[13]

Typical Procedure for the Mitsunobu Reaction Using Polymer 1. (1S,2S,5R)-1-(4-Nitrobenzoyl)-2-(1-methylethyl)- 5-methylcyclohexan-1-ol (2). To a solution of polymer **1** (333 mg, 0.32 mmol of phosphine) in PhMe (6 mL) were added p-nitrobenzoic acid (51 mg, 0.31 mmol) and menthol (40 mg, 0.26 mmol). To this clear solution was added DEAD (48 μL, 0.31 mmol) over 2 min. The reaction was then stirred at room temperature for 15 h. Volatiles were removed under reduced pressure, and the residue was suspended in MeOH (50 mL). The flask was equipped with a reflux condenser, and the suspension was heated under reflux for 4 h. The suspension was then filtered, and the polymer was redissolved in CHCl₃. The suspension/ filtration cycle was repeated three times. The combined methanolic solutions were concentrated under reduced pressure, and the residue was purified by flash chromatography (10% EtOAc/hexane) to afford the pure nitrobenzoate ester as a white crystalline solid (79 mg, 67%): $[\alpha]^{25}_D$ +18° (c 1, CHCl3); lit. $[\alpha]^{25}_D$ +18° (c 1, CHCl3).[15] The phosphine oxide was then quantitatively recovered and submitted to reducing conditions (N,N-dimethylaniline and trichlorosilane in p-dioxane at 100 °C) for its recycling according to our previously described procedure.[7]

(R)-1-Methylheptyl Benzoate (4). The title compound was obtained as a white solid on a 0.63 mmol scale (83%) according to the typical procedure: $[\alpha]^{25}_D$ -38° (c 2, EtOH).[14]

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[13] For the general experimental procedure, see ref 7.
[14] The characterization data (¹H, ¹³C NMR, IR, MS, $[\alpha]_D$) are identical to those reported: (a) Kunieda, N.; Suzuki, A.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1143; (b) Richard,

2-9

Ethyl (R)-2-((4-Nitrobenzoyl)oxy)propionate (6). The title compound was obtained as a white solid on a 1.05 mmol scale (71%) according to the typical procedure described above: $[\alpha]^{25}_D$ -13.1° (c 1, EtOH).[15]

Typical Procedure for the Mitsunobu Reaction on Baylis-Hillman Adducts. Methyl (E)-2-[[(4-Nitrobenzoyl)- oxy]methyl]-2-pentenoate (8). To a solution of polymer 1 (900 mg, 0.86 mmol of phosphine) in THF (34 mL) at 0 °C (bath temperature) were added p-nitrobenzoic acid (138 mg, 0.83 mmol) and the Baylis-Hillman adduct 7 (100 mg, 0.69 mmol). To this clear solution was added DEAD (130 μL, 0.83 mmol) over 2 min. The reaction was then stirred at 0 °C for 15 h. Volatiles were removed under reduced pressure, and the residue was suspended in Et$_2$O (50 mL). The flask was equipped with a reflux condenser, and the suspension was heated under reflux for 4 h. The suspension was then filtered, and the polymer was redissolved in Et$_2$O. The suspension/filtration cycle was repeated three times. The combined ether solutions were concentrated under reduced pressure, and the residue was purified by flash chromatography (10% EtOAc/hexane) to afford the nitrobenzoate ester 8 as a slightly yellow solid (164 mg, 81%). The characterization data were identical to those reported in the literature.[13a]

A. A.; Emblidge, R. W.; Havens, N. *J. Org. Chem.* **1983**, *48*, 3598; (c) Short, A. G.; Read, J. H. *J. Chem. Soc.* **1939**, 1306; (d) Dodge, J. A.; Trujillo, J. I.; Presnell, M. *J. Org. Chem.* **1994**, *59*, 234.

[15] The characterization data (^{1}H, ^{13}C NMR, IR, MS, $[\alpha]_D$) are identical to those reported: Overman, L. E.; Bell, K. L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *106*, 4192.

2.3. Acknowledgment.

Chapitre 3 : Cyclopropanation catalytique énantiosélective d'alcènes (introduction)

3.1. Introduction

Ce chapitre décrit initialement des exemples de molécules importantes possédant une sous-unité cyclopropyle. Plusieurs d'entre elles ont fait l'objet de synthèse en laboratoire. Les principales méthodes de cyclopropanation stéréosélective seront décrites et mises en relation avec les travaux du chapitre suivant. Devant l'ampleur du sujet, quelques exemples représentatifs de chaque classe de réactions de cyclopropanation intermoléculaires d'alcènes seront exposés avec une attention particulière portant sur les méthodes énantiosélectives efficaces.

3.1.1. Produits naturels ou d'importance pharmaceutique contenant des cyclopropanes

Le cyclopropane (**Figure 3-1**) est le plus petit des cycloalcanes; toutefois, cela ne l'empêche pas d'attirer une attention particulière. Une des premières raisons de l'intérêt porté à cette unité vient du fait que le cyclopropane possède une tension de cycle significative qui lui confère une réactivité distincte par rapport à la majorité des alkanes ou des autres cycloalcanes. En effet, la géométrie plane du cyclopropane implique que les angles entre ses liens C-C soient très faibles pour des carbones sp^3 ce qui explique que son énergie de tension, récemment révisée à la hausse, est de l'ordre de 28,6 kcal/mol.[1] Malgré tout, la plupart des composés possédant une unité de type cyclopropane sont assez stables

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[1] Bach, R. D.; Dmitrenko, O. *J. Am. Chem. Soc.* **2006**, *128*, 4598.

pour être entreposés et c'est une unité que l'on retrouve dans plusieurs molécules naturelles et non-naturelles.[2]
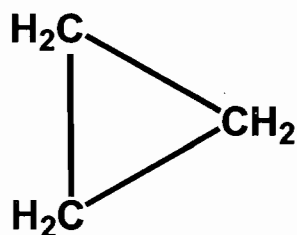
Figure 3-1. Cyclopropane.

La curacine A isolée de la cyanobactérie *Lygnbya majuscula*,[3] la cilastatine (MK-0791) des laboratoires Merck,[4] le dictyopterenes produit par des algues brunes du Pacifique,[5] l'anthroplalone et la noranthroplone produit par l'Okinawan actinia *Anthopleura pacifica*,[6] les dérivés polycyclopropanés FR-900848[7] et U-106305[8] isolés respectivement du *Streptoverticillium fervens* et du *Streptomyces sp. U-11136* sont des exemples choisis qui

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[2] (a) Djerassi, C.; Doss, G. A. *New J. Chem.* **1990**, *14*, 713; (b) Salaün, J. *Curr. Med. Chem.* **1995**, *2*, 511; (c) Salaün, J. *Top. Curr. Chem.* **2000**, *207*, 1; (d) Faust, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2251; (e) Donaldson, W. A., Tetrahedron **2001**, *57*, 8589; (f) Wessjohann, L.A.; Brandt, W. *Chem. Rev.* **2003**, *103*, 1625.

[3] Isolation: Gerwick, W. H.; Proteau, P. J.; Nagle, D. G.; Hamel, E.; Blokhin, A.; Slate, D. L. *J. Org. Chem.* **1994**, *59*, 1243. Synthèse: Ito, H.; Imai, N.; Tanikawa, S.; Kobayashi, S. *Tetrahedron Lett.* **1996**, *37*, 1795.

[4] Graham, D. W.; Ashton, W. T.; Barash, L.; Brown, J. E.; Brown, R. D.; Canning, L. F.; Chen, A.; Springer, J. P.; Rogers, E. F. *J. Med. Chem.* **1987**, 1074.

[5] (a) Moore, R. E. *Acc. Chem. Res.* **1977**, *10*, 40; (b) Jaenicke, L.; Boland, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 643.

[6] (a) Zheng, G.-C.; Hatano, M.; Ishitsuka, M. O.; Kusumi, T.; Kakisawa, H. *Tetrahedron Lett.* **1990**, *31*, 2617; (b) Zheng, G.-C.; Ichikawa, A.; Ishitsuka, M. O.; Kusumi, T.; Yamamoto, H.; Kakisawa, H. *J. Org. Chem.* **1987**, *52*, 4885.

[7] Yoshida, M.; Ezaki, M.; Hashimoto, M.; Yamashita, M.; Sigematsu, N.; Okuhara, M.; Kohsaka, M.; Horikoshi, K. *J. Antibiot.* **1990**, *43*, 748.

illustrent l'omniprésence des unités cyclopropane dans plusieurs produits naturels. Par ailleurs, les composés de la **Figure 3-2** ont tous également été synthétisés en laboratoire.[9]
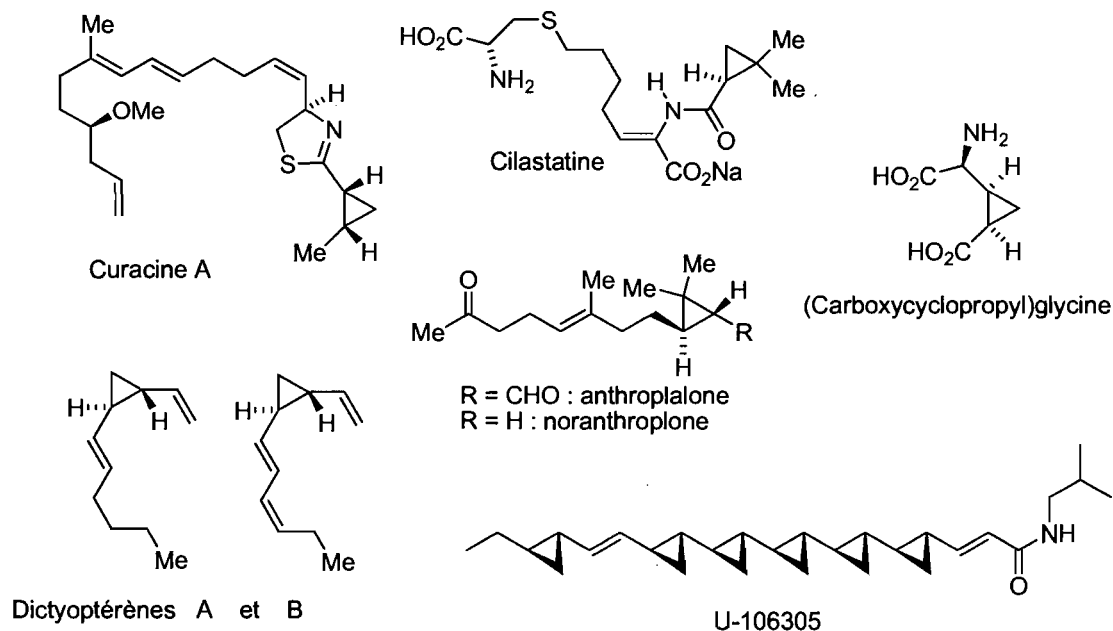
Figure 3-2. Composés importants contenant des unités cyclopropane.

Le cyclopropane est une unité structurale souvent utilisée afin de rigidifier certaines molécules, de modifier les agencements spatiaux de polypeptides ou d'en réduire la vitesse d'hydrolyse enzymatique.[10] De manière moins importante, le cyclopropane est aussi utilisé

[8] Kao, M. S.; Zielinski, R. J.; Cialdella, J. I.; Marschke, C. K.; Dupuis, M. J.; Li, G. P.; Kloosterman, D. A.; Spilman, C. H.; Marshall, V. P. *J. Am. Chem. Soc.* **1995**, *117*, 10629.

[9] Article de revue sur la synthèse de produits naturels contenant des cyclopropanes: Donaldson, W. A. *Tetrahedron* **2001**, *57*, 8589.

[10] (a) Cativiela, C.; Diaz-de-Villegas, M. D. *Tetrahedron: Asymmetry* **1998**, *9*, 3517; (b) Jimenez, A. I.; Cativiela, C.; Aubry, A.; Marraud, M. *J. Am. Chem. Soc.* **1998**, *120*, 9452; (c) Burgess, K.; Ke, C.-Y. *J. Org. Chem.* **1996**, *61*, 8627-8631. (d) Hillier, M. C.; Davidson, J. P.; Martin, S. F. *J. Org. Chem.* **2001**, *66*, 1657; (e) Reichelt, A.; Martin, S. F. *Acc. Chem. Res.* **2006**, *39*, 433.

comme produit de départ à partir duquel il est possible d'élaborer diverses structures moléculaires plus complexes.[11]

3.1.2. Cyclopropanes disubstitués d'intérêt

L'incorporation d'unités cyclopropyles lors de la conception de nouveaux inhibiteurs d'enzymes est une stratégie couramment employée dans le milieu pharmaceutique et agrochimique. Le cyclopropane-1,1-diacide carboxylique (CDA) et le *trans*-2-phénylcyclopropane-1-acide carboxylique (PCCA) sont des composés possédant des structures analogues au 1-aminocyclopropane-1-acide carboxylique (ACC). Ces composés ont la particularité d'inhiber la production d'éthylène due à la dégradation de l'ACC par l'ACC oxydase. La formation d'éthylène contribue au murissement rapide de certains fruits. Cette réaction de formation d'éthylène est également induite prématurément lorsque la surface de certains fruits est endommagée.[12] Le DCA et le PCCA et sont considérés comme des « inhibiteurs d'éthylène » non gazeux et non dommageables pour l'environnement. Ils peuvent être utilisés pour conserver les fleurs coupées ou pour le traitement post-cueillette des fruits, afin de ralentir leur décomposition ou leur murissement prématuré.[13]

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[11] Pour des revues sur les réarrangements de divinylcyclopropanes, voir: (a) Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203; (b) Mann, J. *Tetrahedron* **1986**, *42*, 4611; (c) Piers, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, p 971; (d) Hudlicky, T.; Fan, R.; Reed, J.; Gadamasetti, K. G. *Org. React.* **1992**, *41*, 1. Pour des revues sur les réarrangements de vinylcyclopropanes, voir: (e) Hudlicky, T.; Reed, J. W. Dans: *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, p 899; (f) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229; (g) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247. Pour des revues sur les ouvertures de cyclopropanes, voir: (h) Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, 347; (i) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73; (j) Salaün, J. R. Y. *Top. Curr. Chem.* **1988**, *144*, 1; (k) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; (l) Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165.

[12] Dourtoglou, V.; Kouississi, E. *Phytochemistry* **2000**, *55*, 203.

[13] Dourtoglou, V., Koussissi, E., Petritis, K., **1999**. Evaluation of novel inhibitors of ACC oxidase possessing cyclopropyl moiety. In: Kanellis, A.K., Chang, C., Klee, H., Bleecker, A.B., Pech, J.C., Grierson, D. (Eds.), Biology and Biotechnology of the Plant Hormone Ethylene II. Kluwer Academic, Dordrecht, pp. 13-20.
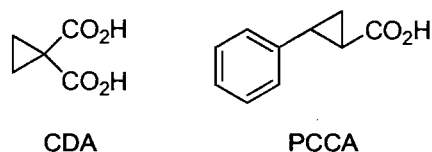
Figure 3-3. Analogues de l'ACC.

Les aminocyclopropanes, qui peuvent être synthétisés à partir des acides cyclopropylcinnamiques correspondants (**Figure 3-3**), forment une classe de composés présentant des activités biologiques d'intérêt thérapeutique. Un exemple précis est la tranylcipromine qui est préparée à partir d'une réaction de Curtius (**Équation 3-1**).[14]
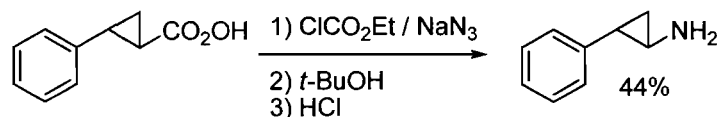
Équation 3-1

La tranylcipromine (connue commercialement sous le nom de: Parnat® ainsi que Jatrosom®) est un médicament administré oralement sous forme racémique dans le but de traiter les patients en dépression grave qui ne répondent pas aux autres traitements usuels. Un des énantiomères est cinq fois plus actif que l'autre dans l'inhibition de l'enzyme mono amine oxydase (MAO). La résolution du mélange racémique est la méthode la plus utilisée pour obtenir sélectivement un ou l'autre des énantiomères pour ce type de composé.

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[14] (a) Aggarwal, V. K.; de Vincente, J.; Bonnert, R. V. *Org. Lett.* **2001**, *3*, 2785; (b) Armstrong, A.; Scutt, J. N. *Org. Lett.* **2003**, *5*, 2331; (c) Kazuta, Y.; Hirano, K.; Natsume, K.; Yamada, S.; Kimura, R.; Matsumoto, S.; Furuichi, K.; Matsuda, A.; Shuto, S. *J. Med. Chem.* **2003**, *46*, 1980.

Tranylcipromine
Inhibiteur de MAO

Analogue de la dopamine

Effect pharmacologique semblable au LSD ou à la
Mescaline selon les variations de structure
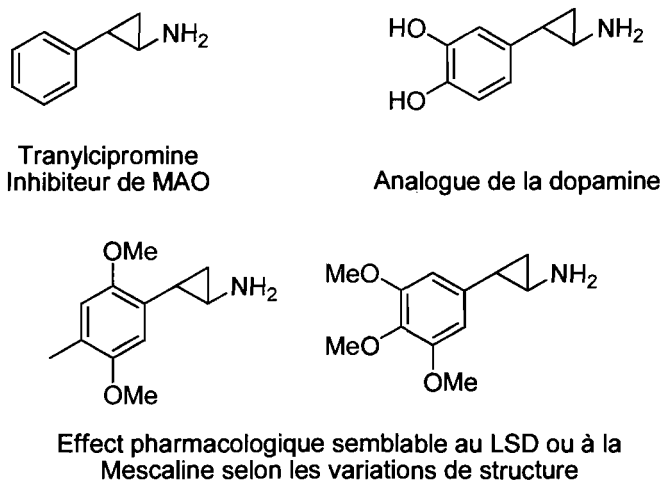
Figure 3-4. Tranylcipromine et analogues ayant des activités biologiques définies.

3.1.3. Principales méthodes de cyclopropanation intermoléculaires d'alcènes

Devant la place importante qu'occupent les cyclopropanes en chimie organique, il n'est pas étonnant que plusieurs procédés aient été développés pour la synthèse de ce cycloalcane. Les plus importantes méthodes de cyclopropanation intermoléculaire[15] à partir d'alcènes sont illustrées à la **Figure 3-5** (A: l'utilisation de carbène métallique, B: l'utilisation de carbénoïdes, C: la décomposition ou la cycloaddition suivie d'extrusion d'azote de composés diazoïques, D: la génération d'un anion géminal à un groupe partant, E: l'addition d'un nucléophile sur un substrat pour lequel une cyclisation intramoléculaire subséquente est possible, F: l'utilisation d'un carbène libre).
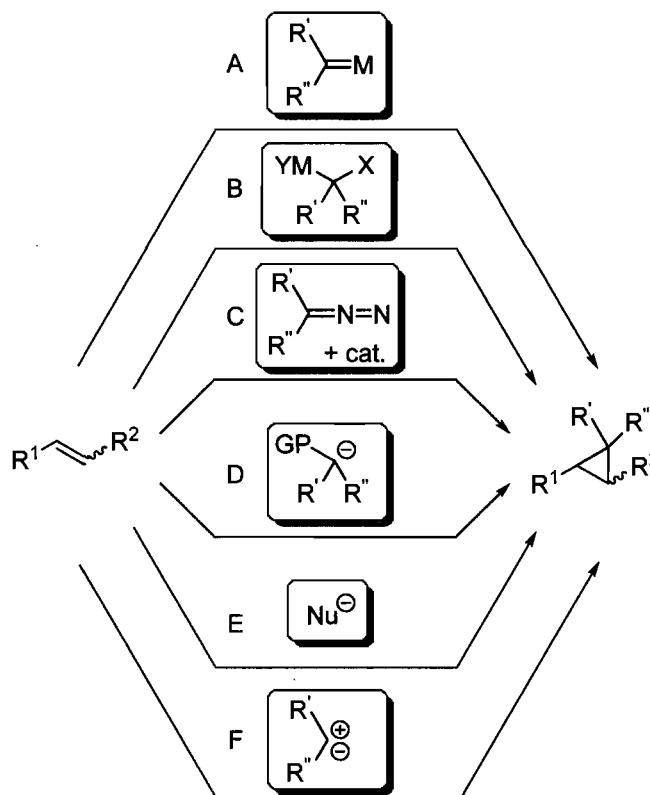
Figure 3-5. Espèces pouvant mener à la cyclopropanation intermoléculaire d'alcènes.

Toutes ces méthodes de cyclopropanation sont applicables à la synthèse de cyclopropanes achiraux ou racémiques. De manière traditionnelle, les méthodes de génération de carbènes métalliques ou de carbénoïdes peuvent être adaptées pour la formation stéréosélective de cyclopropanes de même que l'utilisation d'ylures. Dans certains cas, les autres méthodes peuvent aussi être adaptées pour devenir stéréosélectives.

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[15] Les stratégies de cyclopropanation intramoléculaire ne seront par décrites dans cette thèse par soucis de concision (voir: M. P. Doyle, *Modern Catalytic Methods for Organic*

3.1.4.   Cyclopropanation stéréosélective

La première réaction catalytique asymétrique homogène répertoriée a été la cyclopropanation impliquant un complexe de cuivre par Hitosi Nozaki en 1966 (**Figure 3-12**).[16] Malgré cette découverte, les travaux initiaux illustrant des cyclopropanations stéréosélectives les plus utiles synthétiquement ont d'abord porté sur le contrôle diastéréosélectif puis éventuellement sur le contrôle énantiosélectif lors du processus de cyclopropanation.[17]

3.2. Cyclopropanations stéréosélectives utilisant la réaction de Simmons-Smith

3.2.1.   Diastéréosélectivité

La réaction de Simmons-Smith, impliquant les carbénoïdes de zinc, est l'une des principales méthodes de cyclopropanation stéréosélective. Emschwiller[18], en 1929, observe que le diiodométhane peut réagir avec le zinc pour former des espèces d'iodométhylzinc. Cependant, ce n'est que 30 ans plus tard que Simmons et Smith[19] réalisent le potentiel synthétique de cette observation. Le carbénoïde de zinc formé a la capacité de transférer le groupe méthylène à un alcène de manière stéréospécifique et de produire ainsi un cyclopropane (**Figure 3-6**).

Synthesis with Diazo Compounds, Wiley, New, York, **1998**).

[16] (a) Meng, Q.; Li, M. *J. Mol. Struct.: THEOCHEM* **2006**, *765*, 13; (b) Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1966**, *43*, 5239.

[17] Pour une revue incontournable à propos de la synthèse stéréosélective de cyclopropanes voir: Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977.

[18] Emschwiller, G. *Compt. Rend.* **1929**, *188*, 1555.

[19] (a) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323. (b) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.
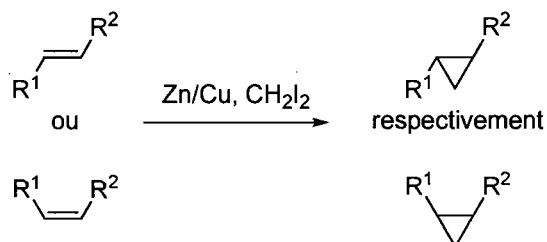
Figure 3-6. Cyclopropanation de Simmons et Smith.

La cyclopropanation diastéréosélective utilisant les carbénoïdes de zinc a été explorée utilisant des substrats chiraux cycliques et acycliques. Elle présente l'avantage d'avoir une bonne tolérance vis-à-vis plusieurs groupes fonctionnels et il est possible d'observer une bonne chimiosélectivité lorsque différents alcènes sont présents. Lorsque la cyclopropanation s'effectue sur des alcools allyliques chiraux, une diastéréosélectivité très élevée est généralement atteinte. Le groupe directeur le plus commun est l'hydroxyméthyle mais il n'est pas toujours nécessaire pour obtenir de bonnes sélectivités (**Figure 3-7**).
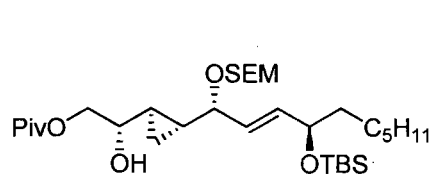
Synthèse de l'Halicolactone
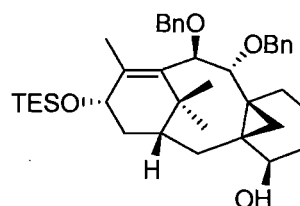
Synthèse de la Taxusine
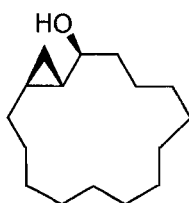
Synthèse de la Muscone
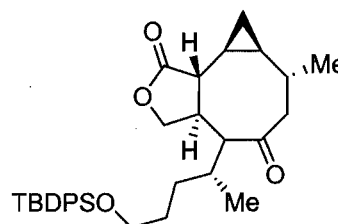
Synthèse de l'Acétoxycrénulide

Figure 3-7. Synthèse de produits intermédiaires comportant un cyclopropane *via* une réaction de cyclopropanation diastéréosélective.

La cyclopropanation à l'aide d'un carbénoïde de zinc est l'étape diastéréosélective clé lors la synthèse de plusieurs produits naturels et mène généralement à la formation d'un seul isomère (**Figure 3-7**).[20] Des méthodologies utilisant des auxiliaires chiraux principalement dérivés de sucres, d'acides aminées, de l'acide tartrique ou de camphre ont aussi été utilisées.[17]

3.2.2.   Énantiosélectivité

3.2.2.1.   Les alcools allyliques

Il a été relativement difficile de concevoir un système catalytique énantiosélectif pour la réaction de Simmons-Smith. En effet, alors que la plupart des ligands chiraux sont des bases de Lewis, le carbénoïde de zinc formé lors des réactions de Simmons-Smith est de nature électrophile. Ainsi, on peut s'attendre à ce que l'ajout de ligands chiraux diminue les vitesses de réaction (plutôt que de les augmenter), rendant alors le développement d'un cycle catalytique impliquant le ligand peu probable. Malgré cet obstacle, des méthodes efficaces qui permettent la synthèse énantiosélective des cyclopropanes ont pu être développées (**Figure 3-8**).

---

[20] (a) Halicolactone: Takemoto, Y.; Baba, Y.; Saha, G.; Nakao, S.; Iwata, C.; Tanaka. T.; Ibuka. T. *Tetrahedron Lett.* **2000**, *41*, 3653; Baba, Y.; Saha, G.; Nakao, S.; Iwata, C.; Tanaka, T.; Ibuka, T.; Ohishi, H.; Takemoto, Y. *J. Org. Chem.* **2001**, *66*, 81; (b) Taxusin: Hara, R.; Furukawa, T.; Horiguchi, Y.; Kuwajima, I. *J. Am. Chem. Soc.* **1996**, *118*, 9186; (c) Muscone: Oppolzer, W.; Radinov, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1593; (d) Acetoxycrenulide: Wang, T.-Z.; Pinard, E.; Paquette, L. A. *J. Am. Chem. Soc.* **1996**, *118*, 1309.
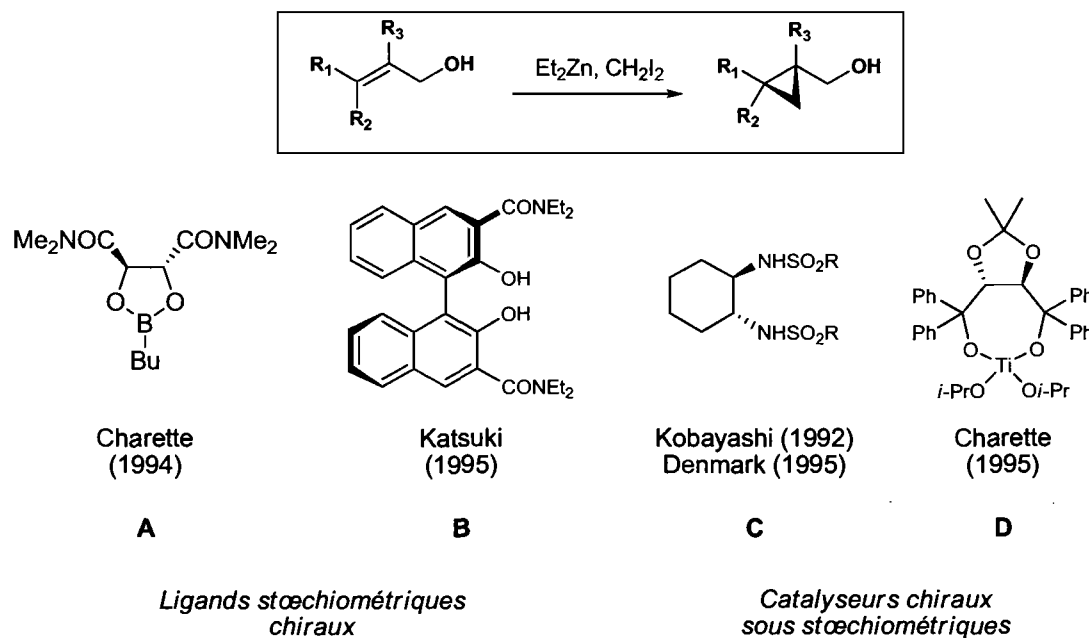
Figure 3-8. Simmons-Smith en version énantiosélective.

Les alcools allyliques ont été des substrats de choix pour la synthèse de cyclopropanes énantioenrichis. La méthode de Charette (**Figure 3-8**, méthode A), d'une grande utilité synthétique, permet, par l'utilisation d'un ligand stœchiométrique chiral dérivé de l'acide tartrique, la cyclopropanation énantiosélective d'alcools allyliques.[21] Des alcools allyliques *E* et *Z* ont été utilisés avec succès et des rendements supérieurs à 85% sont obtenus ainsi que des excès énantiomères variant de 88% à 94%. Katsuki a développé un ligand stœchiométrique dérivé du BINOL pour la cyclopropanation énantiosélective des alcools allyliques substitués-(*E*) seulement (**Figure 3-8**, méthode B). Cette dernière comporte le désavantage principal de nécessiter un grand excès de réactifs tout en ayant des rendements moyens de 60% pour des excès énantiomères d'environ 89%.[22] Kobayashi, de son côté, a

[21] (a) Charette, A. B.; Juteau, H. *J. Am. Chem. Soc.* **1994**, *116*, 2651. (b) Charette, A. B.; Prescott, S.; Brochu, C. *J. Org. Chem.* **1995**, *60*, 1081. (c) Charette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.* **1998**, *120*, 11943.

[22] Kitajima, H.; Aoki, Y.; Ito, K.; Katsuki, T. *Chem. Lett.* **1995**, 1113.

développé la première réaction de Simmons-Smith catalytique asymétrique efficace[23] et cette réaction a plus tard été étudiée et modifiée par Denmark (**Figure 3-8**, méthode C).[24] Les énantiosélectivités de cette dernière sont très variables en fonction de la substitution de l'alcool allylique de départ (moyenne de 70% ee) de même que les rendements (moyenne de 83%). Un protocole que Charette a développé utilise de manière catalytique (sous stœchiométrique à 0,25 équiv. de catalyseur par rapport à l'alcène) un taddolate de titane en tant qu'acide de Lewis lors de la cyclopropanation d'alcools allyliques substitués (**Figure 3-8**, méthode D).[25]

3.2.2.2.   Autres alcènes

Une méthode développée plus récemment par Shi utilise un dipeptide protégé en tant que ligand stœchiométrique chiral pour la cyclopropanation de styrènes substitués.[26] Les excès énantiomères de cette réaction atteignent 92%. Cette méthode constitue le premier exemple de cyclopropanation énantiosélective d'alcènes « non fonctionnalisés » de type styrène. Il est aussi possible, à l'aide d'un additif non chiral, d'utiliser 0,25 équivalent du dipeptide de Shi (par rapport au substrat) et d'obtenir jusqu'à 89% ee. Cependant, on observe généralement que les rendements et excès énantiomères chutent dans la plupart des cas par rapport à l'utilisation stœchiométrique de son dipeptide (**Équation 3-2**).[27]

---

[23] (a) Takahashi, H.; Yoshioka, M.; Ohno, M.; Kobayashi, S. *Tetrahedron Lett.* **1992**, *33*, 2575; (b) Takahashi, H.; Yoshioka, M.; Shibasaki, M.; Ohno, M.; Imai, N.; Kobayashi, S. *Tetrahedron* **1995**, *51*, 12013.

[24] (a) Denmark, S. E.; Christenson, B. L.; Coe, D. M.; O'Connor, S. P. *Tetrahedron Lett.* **1995**, *36*, 2215; (b) Denmark, S. E.; Christenson, B. L.; O'Connor, S. P. *Tetrahedron Lett.* **1995**, *36*, 2219; (c) Denmark, S. E.; Christenson, B. L.; O'Connor, S. P.; Noriaki, M. *Pure Appl. Chem.* **1996**, *68*, 23; (d) Denmark, S. E.; O'Connor, S. P.; Wilson, S. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1149; (e) Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* **1997**, *62*, 584. (f) Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* **1997**, *62*, 3390.

[25] (a) Charette, A. B.; Brochu, C. *J. Am. Chem. Soc.* **1995**, *117*, 11367; (b) Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168; (c) Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12160.

[26] Long, J.; Shi, Y. *J. Am. Chem. Soc.* **2003**, *125*, 13632.

Peut être utilisé en tant que
ligand stœchiométrique (2003)
ou comme catalyseur chiral (2005)

Shi
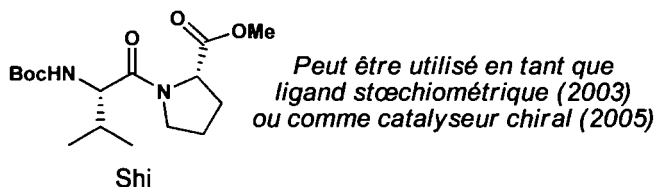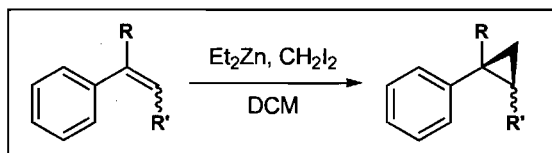
Équation 3-2

Charette a récemment publié une méthode de cyclopropanation d'alcènes ne portant pas obligatoirement de groupes basiques proximaux et impliquant l'utilisation d'une quantité stœchiométrique ou sous-stœchiométrique d'un ligand chiral (**Équation 3-3**).[28]

Ligand stœchiométrique
ou catalyseur chiral (2005)
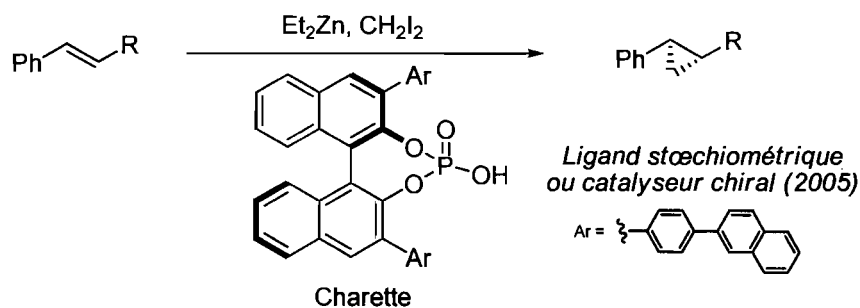
Charette

Équation 3-3

Malgré tous les efforts déployés pour développer une version asymétrique et catalytique de la réaction de Simmons et Smith, l'utilisation du dioxaborolane chiral en quantités stœchiométriques, développé par Charette, reste la méthode de choix pour le chimiste en synthèse.

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[27] Long, J.; Du, H.; Li, K.; Shi, Y. *Tetrahedron Lett.* **2005**, *46*, 2737.

3.3. Cyclopropanation intermoléculaire stéréosélective utilisant les composés diazoïques substitués

3.3.1. Introduction

Un grand nombre de complexes dérivés de métaux de transition réagissent avec les composés diazoïques et en induisent la décomposition. Selon les études dans ce domaine, cette décomposition mènerait à la formation d'un carbène métallique qui serait transféré à un alcène, formant ainsi un cyclopropane.[29]
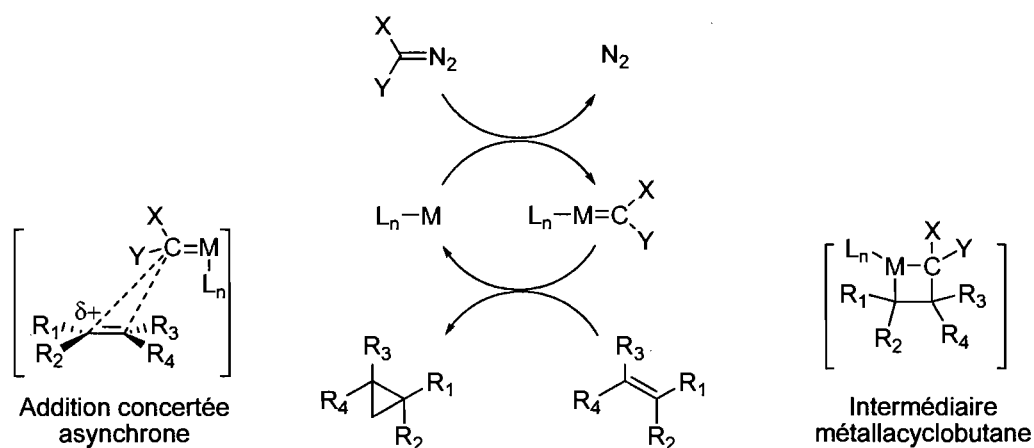
Figure 3-9. Deux voies possibles pour la cyclopropanation par carbènes métalliques.

[28] Lacasse, M.-C,; Poulard, C.; Charette, A. B. *J. Am. Chem. Soc.* **1995**, *127*, 12440.

[29] (a) Park, S.-B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303; (b) Pfaltz, A. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; Vol. II, p 513; (c) Nishiyama, H.; Aoki, K.; Itoh, H.; Iwamura, T.; Sakata, N.; Kurihara, O.; Motoyama, Y. *Chem. Lett.* **1996**, 1071; (d) Che, C.-M.; Huang, J.-S.; Lee, F.-W.; Li, Y.; Lai, T.-S.; Kwong, H.-L.; Teng, P.-F.; Lee, W.-S.; Lo, W.-C.; Peng, S.-M.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 4119; (e) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4843. Pour des indices impliquant le cuivre: (f) Straub, B. F.; Hofmann, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1288;

Une quantité indénombrable de variantes de cette réaction ont été étudiées. Un modèle d'état de transition est proposé pour l'étape de cyclopropanation qui impliquerait l'addition concertée mais asynchrone du carbène métallique sur l'alcène. Lors de ce processus, un développement de charge positive sur l'alcène est postulé.[30] La cyclopropanation viendrait à la suite de la formation d'un carbène métallique et de l'étape déterminante de la réaction, soit l'élimination d'une molécule d'azote (N_2). Ce modèle est préféré à celui où un métallacyclobutane est formé comme intermédiaire réactionnel (**Figure 3-9**). Principalement, les métaux utilisés pour cette transformation sont le cuivre, le rhodium, le ruthénium, le cobalt, le fer, l'osmium, le palladium, la platine et le chrome.

3.3.2.   Cyclopropanation diastéréosélective – auxiliaires chiraux

Les composés diazocarbonylés liés à des auxiliaires chiraux n'ont pas connu un grand succès dans les cyclopropanations intermoléculaires diastéréosélectives d'alcènes. Par exemple, les cyclopropanations du styrène en présence de catalyseurs non chiraux de rhodium ont conduit aux composés de la **Figure 3-10** dans lesquels les isomères *trans* sont majoritaires mais avec de très faibles diastéréosélectivités (entre 57:43 et 84:16).[31]

un modèle postulé précédemment: Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553.

[30] (a) Fraile, J. M.; Garcia, J. I.; Martinez-Merino, V.; Mayoral, J. A.; Salvatella, L. *J. Am. Chem. Soc.* **2001**, *123*, 7616; (b) Rasmussen, T.; Jensen, J. F.; Østergaard, N.; Tanner, D.; Ziegler, T.; Norrby, P. O. *Chem. Eur. J.* **2002**, *8*, 177.

[31] (a) Doyle, M. P.; Protopopova, M. N.; Brandes, B. D.; Davies, H. M. L.; Huby, N. J. S.; Whitesell, J. K. *Synlett* **1993**, *151*; (b) Doyle, M. P.; Dorow, R. L.; Terpstra, J. W.; Rodenhouse, R. A. *J. Org. Chem.* **1985**, *50*, 1663; (c) Haddad, N.; Galili, N. *Tetrahedron: Asymmetry* **1997**, *8*, 3367; (d) Gross, Z.; Galili, N.; Simkhovich, L. *Tetrahedron Lett.* **1999**, *40*, 1571; (e) Gross, Z.; Simkhovich, L.; Galili, N. *J. Chem. Soc., Chem. Commun.* **1999**, 599.
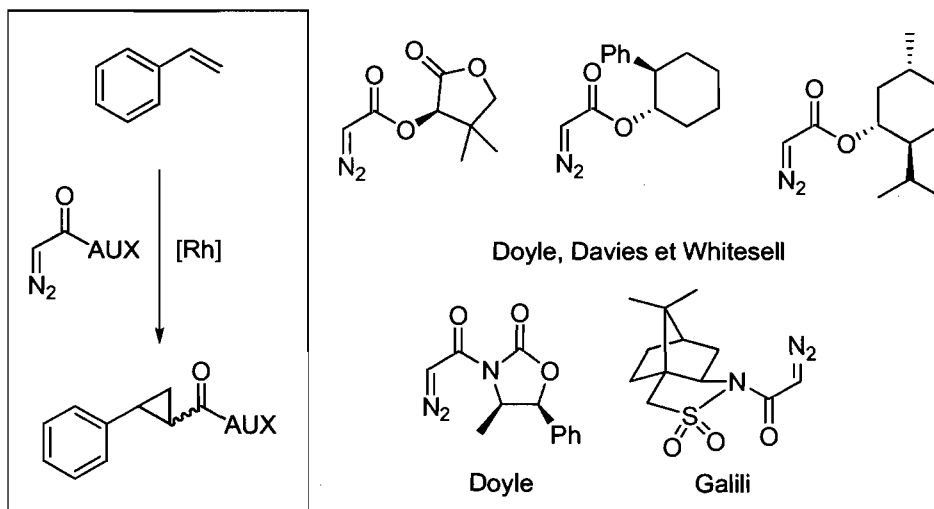
Figure 3-10. Auxiliaires chiraux pour la cyclopropanation du styrène.

3.3.3. Cyclopropanation énantiosélective intermoléculaire – les métaux à succès (Cu, Rh, Ru, Co)

Les systèmes efficaces de cyclopropanations énantiosélectives impliquent des composés diazoalkanes substitués par un ou deux groupes fonctionnels. La classe qui a eu le plus de succès et qui se démarque du lot est celle des α-diazoesters (**Figure 3-11**).[17, 32]

Le diazoacétate d'éthyle (composé A, **Figure 3-11**) est disponible commercialement mais bien que plusieurs catalyseurs permettent de le convertir en composés cyclopropanés, les diastéréosélectivités des réactions sont généralement modestes. Dans le but d'améliorer les diastéréo- et énantiosélectivités lors des réactions de cyclopropanation, des esters plus volumineux ont été synthétisés. Le diazoacétate de *tert*-butyle, le diazoacétate de menthyle et le diazoacétate de BHT (respectivement composé B, C, et D, **Figure 3-11**) ne sont pas disponibles commercialement mais ont conduit à des réactions de cyclopropanation

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[32] (a) Davies, H. M. L.; Antoulinakis, E. *Org. React.* **2001**, *57*, 1; (b) Rovis, T.; Evans, D. A. *Prog. Inorg. Chem.* **2001**, *50*, 1; (c) Nishiyama, H. *Enantiomer* **1999**, *4*, 569; (d) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911; (e) Singh, V. K.; DattaGupta, A.; (f) Sekar, G. *Synthesis* **1997**, 137; (g) Calter, M. A. *Curr. Org. Chem.* **1997**, *1*, 37.

beaucoup plus efficaces. Le diazoacétate de menthyle est utilisé dans la plupart des réactions énantiosélectives. Malgré le fait que ce réactif comporte un ester chiral, l'énantiosélectivité des cyclopropanations qu'il donne, une fois l'ester clivé, est très modeste en absence d'un catalyseur chiral. Pour un catalyseur chiral unique, cette réaction est presqu'aussi efficace avec un antipode de l'ester menthyle que l'autre.[17] Le diazoacétate de BHT utilisé par Evans[33] et subséquemment par Fu[34] respectivement avec des complexes de cuivre dérivés de bis(oxazolines) et des ferrocényles C2 symétriques sont parmi les systèmes les plus efficaces. Le clivage du groupe BHT du produit réactionnel requiert une réduction au LAH. Malgré ce désavantage, cette méthode est d'une efficacité redoutable menant à des énantiosélectivités quasi parfaites et un excellent contrôle de la diastéréosélectivité. Par contre, la diversité d'alcènes pouvant être utilisés est modeste.
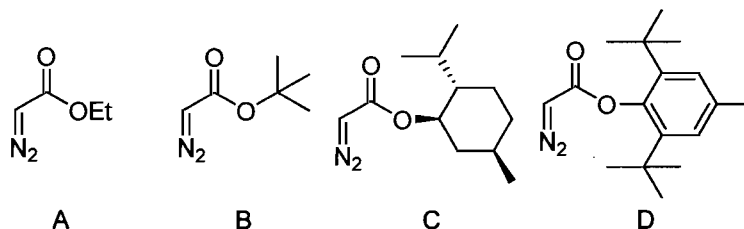
Figure 3-11. α-Diazoesters utilisés en catalyse asymétrique.

Tel que mentionné précédemment, Hitosi Nozaki a été l'instigateur du domaine de la catalyse énantiosélective homogène avec une réaction de cyclopropanation du styrène par le diazoacétate d'éthyle mais de très modestes énantiosélectivitées furent observées.[16b] Aratani a su exploiter ce type de ligand, optimiser le catalyseur et l'utiliser dans la synthèse d'esters chrysantémiques et de la chaine latérale de la cilastatine (**Figure 3-12**).[35]

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[33] (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726; (b) Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed.* **1992**, *31*, 430.

[34] (a) Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270; (b) Rios, R.; Liang, J.; Lo, M. M. C.; Fu, G. C. *J. Chem. Soc., Chem. Commun.* **2000**, 377.

[35] (a) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1977**, *18*, 2599; (b) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839.
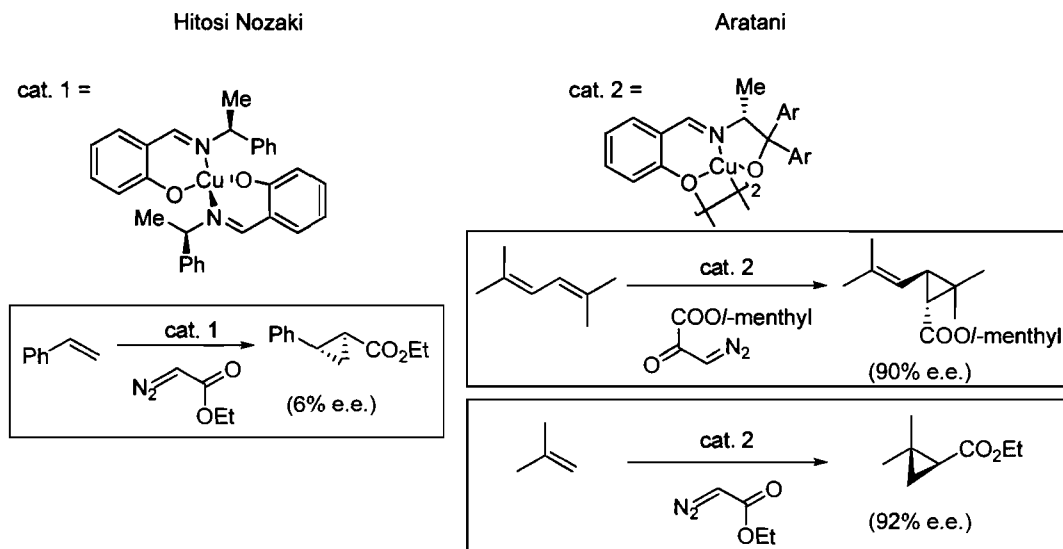
Figure 3-12. Évolution de la cyclopropanation énantiosélective de Hitosi Nozaki.

Des complexes représentatifs de chaque classe de catalyseurs sont représentés à la **Figure 3-13**. Des exemples de résultats relatifs au catalyseur d'Aratani ont déjà été exposés plus haut (**Figure 3-12**). Les autres catalyseurs sont comparés selon leur capacité à contrôler la cyclopropanation du styrène. La semicorrine de Pfaltz permet l'obtention du cyclopropane attendu avec d'excellentes énantiosélectivités et un contrôle encourageant de la diastéréosélectivité. Evans a développé ce qui est encore considéré aujourd'hui comme le système de référence en utilisant un ligand bis(oxazoline). Doyle su exploiter le rhodium et démontrer son efficacité en catalyse asymétrique dans une multitude de systèmes de cyclopropanations intramoléculaires ou à partir de composés diazoïques polysubstitués. Ce système est moins efficace pour la cyclopropanation intermoléculaire utilisant des composés diazoïques mono substitués. Nishiyama a su contrôler la réactivité du ruthénium en faveur de la cyclopropanation plutôt que la métathèse. Katsuki, quant à lui, a développé un catalyseur impliquant le cobalt qui donne accès aux cyclopropanes *cis* avec un degré élevé d'énantiosélectivité. L'ensemble de ces catalyseurs ainsi que plusieurs autres ont récemment fait l'objet d'un article de revue[17] et ne seront donc pas tous énumérés.

L'important, dans le cadre de cette thèse, est de remarquer les classes de composés diazoïques qui ont été utilisées efficacement en catalyse asymétrique.

Aratani

Pfaltz

Evans

R' = Et

92% e.e.

R=Ph
R'=menthyl
Ratio *trans:cis* 82:18
(97%e.e.; 95% e.e.)

R'=BHT
Ratio *trans:cis* 94:6
(99%e.e. maj.)

Katsuki

Doyle

Nishiyama

R=menthyl
Ratio *trans:cis* 57:43
(27%e.e.; 91% e.e.)

R=menthyl
Ratio *trans:cis* 97:3
(94%e.e.; 64% e.e.)

R=*t*-Bu
Ratio *trans:cis* 2:98
(98%e.e. maj.)
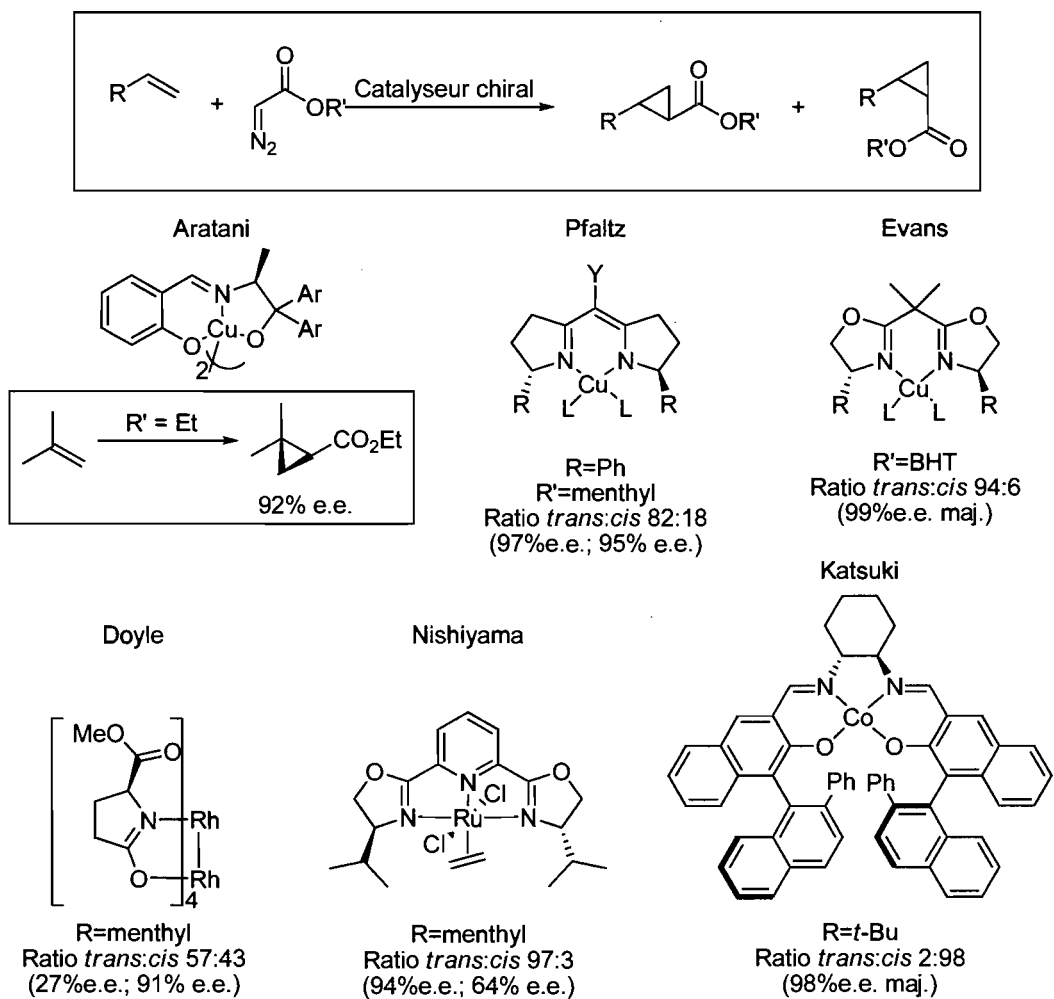
Figure 3-13. Quelques exemples de catalyseurs chiraux pour la cyclopropanation utilisant les α-diazoesters.

La **Figure 3-14** illustre les composés diazoïques comportant un substituant électroattracteur. Lorsque le composé diazoïque comporte deux groupes électroattracteurs, il devient moins réactif face aux métaux de transition.
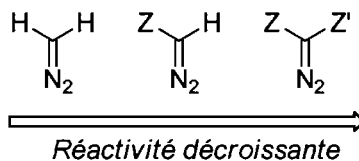
Figure 3-14. Réactivité des composés diazo envers les métaux de transition.

3.4. Cyclopropanation par l'utilisation du diazométhane

3.4.1. Le diazométhane

Le plus simple des composés diazoïques est le diazométhane. Il est facile de le générer à partir de composés disponibles commercialement.[36] De plus, il est possible de l'entreposer en solution dans différents solvants.
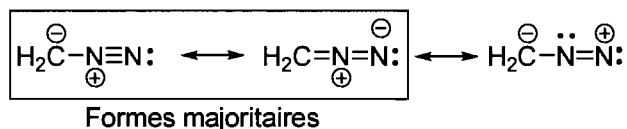
Figure 3-15. Formes de résonance du diazométhane.

Le diazométhane est un réactif extrêmement utile dans une vaste gamme de réactions. Il sert à générer des esters à partir d'acides carboxyliques et peut aussi former des éthers

[36] Black, T. W. *Aldrichim. Acta* **1983**, *16*, 3.

méthyliques à partir de groupes hydroxyles acides tels les phénols. Il peut effectuer des cycloadditions 1,3-dipolaires (réaction de Huisgen)[37] impliquant des alcènes pour la formation d'hétérocycles (potentiellement décomposables en cyclopropanes avec la génération d'azote comme seul sous produit). Le diazométhane peut réagir avec des chlorures d'acide ou des anhydrides pour former des liens carbone-carbone par une réaction de type Arndt-Eistert.[38] Les cycloalkanones, traitées avec le diazométhane, peuvent subir une expansion de cycle par la réaction de Tiffenau-Demjanov.[39]

Étant donné que le diazométhane réagit dans des conditions généralement neutres et génère de l'azote (N_2) comme sous-produit, on répertorie une multitude d'exemples de son utilisation. Il est utile lorsque des conditions réactionnelles douces sont requises. D'utilisation très courante en laboratoire de recherche et de développement qui effectuent des réactions sur petite échelle, son utilisation est plutôt restreinte une fois à l'échelle de la production. Par contre, des méthodes telles l'utilisation de réacteurs à flot continu et d'usines dédiées à l'utilisation de diazométhane ont permis son emploi à grande échelle de manière sécuritaire.

Le diazométhane est typiquement synthétisé à partir de dérivés « nitroso », plus spécifiquement par l'action d'une base sur le N-methyl-N-nitrosourée, le N-méthyl-N-nitroso-N-1-nitroguanidine (MNNG) ou le N-méthyl-N-nitroso-p-toluènesulfonamide (Diazald®) (**Figure 3-16**). Il est possible de distiller des solutions de diazométhane dans l'éther ou le dichlorométhane mais il faut noter que la plupart des explosions sont survenues pendant sa distillation, lors de la formation de cristaux ou à l'agitation.[40]

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[37] Huisgen, R.; Grashey, R.; Sauer, J. in: Chemistry of Alkenes, Interscience, New York, 1964, p.p. 806-877.

[38] Arndt, F.; Eistert, B. *Ber.* **1935**, *68*, 200.

[39] Demjanov, J.; Luschnikov, M. *J. Russ. Phys.-Chem. Soc.*, **1901**, *33*, 279; (b) Smith, P. A. S.; Baer, D. R. *Org. React.* **1960**, *11*, 157.

[40] Moore, J. A.; Reed, D. E. *Org. Synth.* **1973**, *5*, 351.
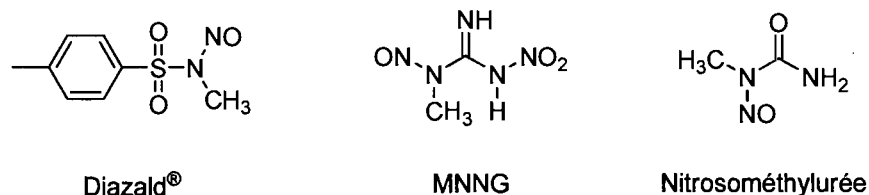
Figure 3-16. Précurseurs du diazométhane.

3.4.2. Cyclopropanations stéréosélectives par cycloaddition et élimination d'azote

Le diazométhane peut, en présence d'alcènes, effectuer une réaction de cycloaddition 1,3-dipolaire et former des pyrazolines. Ces pyrazolines peuvent éliminer une molécule d'azote, sous l'action de la chaleur ou de radiations, et former ainsi un cyclopropane. Ce processus est illustré à la **Figure 3-17**. On retrouve également dans cette figure des exemples d'alcènes chiraux à partir desquels il est généralement possible d'effectuer cette transformation de manière diastéréospécifique (>95:5 de ratio diastéréomère).[41]

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[41] (a) Hanessian, S.; Murray, P. J. *J. Org. Chem.* **1987**, *52*, 1170; (b) Hanafi, N.; Ortuno, R. M. *Tetrahedron: Asymmetry* **1994**, *5*, 1657; (c) Martin-Vila, M.; Hanafi, N.; Jimenez, J. M.; Alvarez-Larena, A.; Piniella, J. F.; Branchadell, V.; Oliva, A.; Ortuno, R. M. *J. Org. Chem.* **1998**, *63*, 3581; (d) Rife, J.; Ortuno, R. M. *Tetrahedron: Asymmetry* **1999**, *10*, 4245; (e) Muray, E.; Alvarez-Larena, A.; (f) Bartels, A.; Jones, P. G.; Liebscher, J. *Synthesis* **1998**, 1645; (g) Alcaraz, C.; Fernandez, M. D.; de Frutos, M. P.; Marco, J. L.; Bernabe, M.; Foces-Foces, C.; Cano, F. H. *Tetrahedron* **1994**, *50*, 12443; (h) Alcaraz, C.; Herrero, A.; Marco, J. L.; Fernandez-Alvarez, E.; Bernabe, M. *Tetrahedron Lett.* **1992**, *33*, 5605; (i) Sato, M.; Hisamichi, H.; Kaneko, C.; Suzaki, N.; Furuya, T.; Inukai, N. *Tetrahedron Lett.* **1989**, *30*, 5281; (j) Alami, A.; Calmes, M.; Daunis, J.; Escale, F.; Jacquier, R.; Roumestant, M.-L.; Viallefont, P. *Tetrahedron: Asymmetry* **1991**, *2*, 175; (k) Piniella, J. F.; Branchadell, V.; Ortuno, R. M. *J. Org. Chem.* **2000**, *65*, 388; (l) Jimenez, J. M.; Rife, J.; Ortuno, R. M. *Tetrahedron: Asymmetry* **1996**, 7, 537.
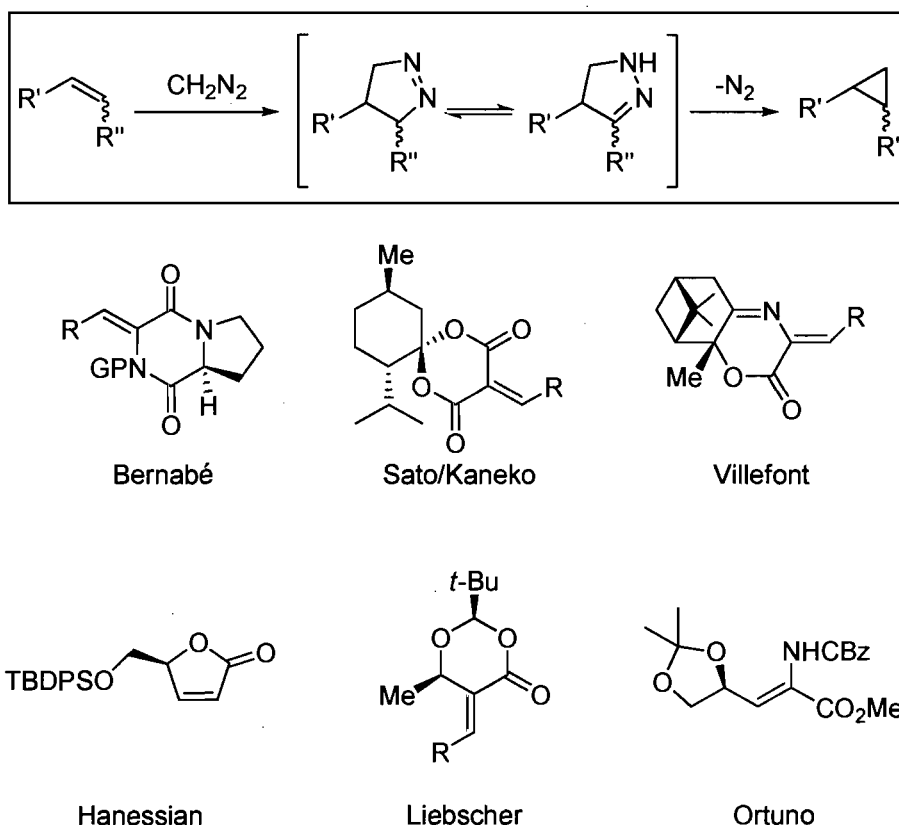
Figure 3-17. Substrats pour la cycloadition 1,3-dipolaire diastéréosélective.

3.4.3. Cyclopropanation non stéréosélective – catalyseurs

Selon les conditions, le diazométhane peut être considéré comme une base ou un acide, comme un électrophile ou un nucléophile, comme un dipôle-1,3 ou une source de carbène.[47] Dans le cadre du développement d'une méthode de cyclopropanation catalytique, ce dernier point est particulièrement intéressant. Les principales méthodes pour décomposer ou faire réagir le diazométhane utilisent soit la chaleur, les radiations ou des catalyseurs. La chaleur ou les radiations sont souvent incompatibles avec les substrats, ou encore avec l'échelle sur laquelle une transformation désirée doit être effectuée. Dans ce contexte, les méthodes catalytiques sont attrayantes d'autant plus que les réactions peuvent être modulées par le choix du catalyseur. Bien que la plupart des métaux du tableau

périodique puissent réagir avec le diazométhane, le cuivre et le palladium se sont démarqués par leur efficacité. L'état d'oxydation initial du catalyseur n'a pas vraiment d'importance tel que démontré par une multitude d'exemples de catalyseurs de cuivre (I) et (II) ainsi que de palladium (0) ou (II).

3.4.4.   Cyclopropanation diastéréosélective – dirigée par le substrat

La cyclopropanation diastéréosélective, sans avoir recourt à la cycloaddition du diazométhane puis à l'extrusion d'azote, est connue. En effet, lorsqu'un alcène chiral est traité au diazométhane en présence d'un sel de palladium, la cyclopropanation s'effectue généralement avec des rendements très élevés. La diastéréosélectivité de cette transformation est très variable et dépend surtout de la classe de substrats. Les alcènes rigides cycliques[42] réagissent généralement avec un degré élevé de diastéréosélectivité malgré quelques exemples de bonnes sélectivités pour certains alcènes acycliques (**Figure 3-18**).[43]

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[42] (a) Shimamoto, K.; Ishida, M.; Shinozaki, H.; Ohfune, Y. *J. Org. Chem.* **1991**, *56*, 4167; (b) Shimamoto, K.; Ohfune, Y. *Tetrahedron Lett.* **1989**, *30*, 3802; (c) Dzhemilev, U. M.; Dokichev, V. A.; Sultanov, S. Z.; Shul'ts, E. E.; Tomilov, Y. V.; Nefedov, O. M.; Tolstikov, G. A.; in *Primenenie Metallokompleksnogo Kataliza v Organicheskom Sinteze (Tezisy Dokladov)* [Application of Metal Complex Catalysis in Organic Synthesis (Abstracts of Reports)] (Ufa: **1989**), p.82.

[43] (a) Davletbakova, A. M.; Maidanova, I. O.; Baibulatova, N. Z.; Dokichev, V. A.; Tomilov, Y. V.; Yunusov, M. S.; Nefedov, O. M. *Russ. J. Org. Chem.* **2001**, *37*, 608; (b) Raduchel, B.; Mende, U.; Cleve, G.; Hoyer, G.-A.; Vorbruggen, H. *Tetrahedron Lett.* **1975**, *16*, 633.

Ohfune   Ohfune   Tomilov

Vorbruggen   Tomilov
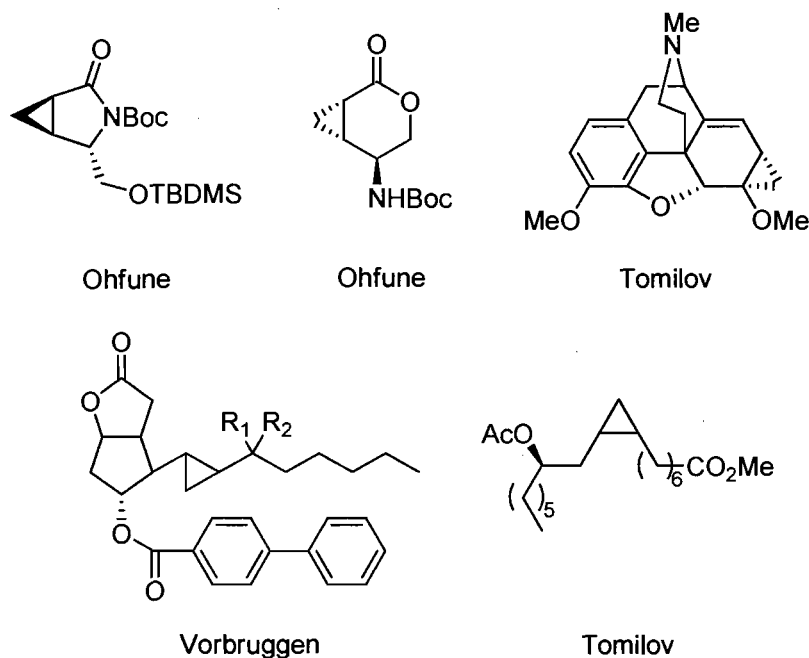
Figure 3-18. Cyclopropanation dont la diastéréosélectivité est dirigée par le substrat.

La capacité des sels de palladium à catalyser cette réaction est remarquable et en a fait des catalyseurs de choix. L'acétate ainsi que le bis(acétylacétonate) de palladium ont été utilisés dans les exemples présentés ci-dessus (**Figure 3-18**).

3.4.5. Cyclopropanation diastéréosélective – auxiliaires chiraux

Peu d'exemples de l'utilisation d'auxiliaires chiraux ont été répertoriés pour la cyclopropanation diastéréosélective impliquant le diazométhane (**Figure 3-19**). Carrié a utilisé le diazométhane pour la cyclopropanation d'un dérivé chiral issu de la condensation d'un aminoalcool et du cinnamaldéhyde. Un rendement quantitatif a été obtenu et un ratio

diastéréomére de plus de 95:5 a été observé pour cette transformation.[44] Un auxiliaire chiral dérivé de l'acide camphorsulphonique utilisé en cyclopropanation par Vallgarda permait l'obtention de produits dont les ratios diastéréoméres variaient entre 81:19 et 96:4.[45] Pietrusza a observé des ratios diastéréomères de 70:30 à 95:5 lors de l'utilisation d'un auxiliaire chiral dérivé de l'acide tartrique.[46]
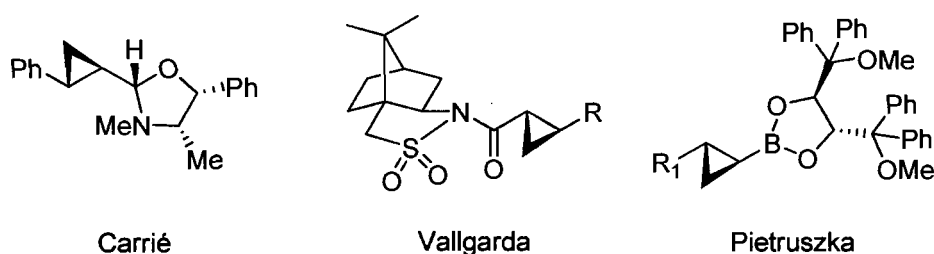
Figure 3-19. Cyclopropanes formés utilisant des auxiliaires chiraux.

3.4.6. Cyclopropanation énantiosélective utilisant le diazométhane – les efforts

Une grande diversité d'alcènes peut être convertie en cyclopropanes à l'aide du diazométhane et d'un catalyseur métallique approprié.[47] Il n'existe, par contre, aucune

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[44] (a) Abadallah, H.; Grée, R.; Carrié, R. *Tetrahedron Lett.* **1982**, *23*, 503. (b) Carrié, R. *Heterocycles* **1980**, *14*, 1529.

[45] (a) Vallgarda, J.; Appelberg, U.; Csoregh, I.; Hacksell, U. *J. Chem. Soc., Perkin Trans. 1* **1994**, 461. (b) Vallgarda, J.; Hacksell, U. *Tetrahedron Lett.* **1991**, *32*, 5625; (c) for an application of this methodology, see: Vangveravong, S.; Nichols, D. E. *J. Org. Chem.* **1995**, *60*, 3409.

[46] (a) Pietruszka, J.; Widenmeyer, M. *Synlett* **1997**, 977; (b) Luithle, J. E. A.; Pietruszka, J. Liebigs *Ann./Recl.* **1997**, 2297; (c) Luithle, J. E. A.; Pietruszka, J.; Witt, A. *J. Chem. Soc., Chem. Commun.* **1998**, 2651; (d) Luithle, J. E. A.; Pietruszka, J. *J. Org. Chem.* **1999**, *64*, 8287; (e) Pietruszka, J.; Witt, A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4293; (f) Luithle, J. E. A.; Pietruszka, J. *J. Org. Chem.* **2000**, *65*, 9194; (g) Luithle, J. E. A.; Pietruszka, J. *Eur. J. Org. Chem.* **2000**, 2557.

[47] Tomilov, Y. V.; Dokichev, V. A.; Dzhemilev, U. M.; Nefedov, O. M. *Russ. Chem. Rev. (Engl. Transl.)* **1993**, *62*, 799.

version énantiosélective efficace de cette réaction. Le cuivre et le palladium semblent avoir été les métaux qui ont fait l'objet d'une attention particulière pour le développement d'un catalyseur énantiosélectif pour la cyclopropanation qui implique le diazométhane. Vers la fin des années soixante, Hitosi Nozaki a développé un ligand dérivé de l'(α-méthyl)-benzylamine complexé au cuivre (**Figure 3-20**) dans une réaction de cyclopropanation utilisant le diazométhane. Il a observé un excès énantiomére d'environ 8% ee dans le cas du β-méthylstyrène. D'autres exemples se retrouvent dans cette communication mais la mesure de l'énantiosélectivité ne semblait pas avoir été concluante. Il s'appuyait sur des valeurs de pouvoirs rotatoires non nulles pour démontrer qu'une induction asymétrique avait eu lieu.[48]
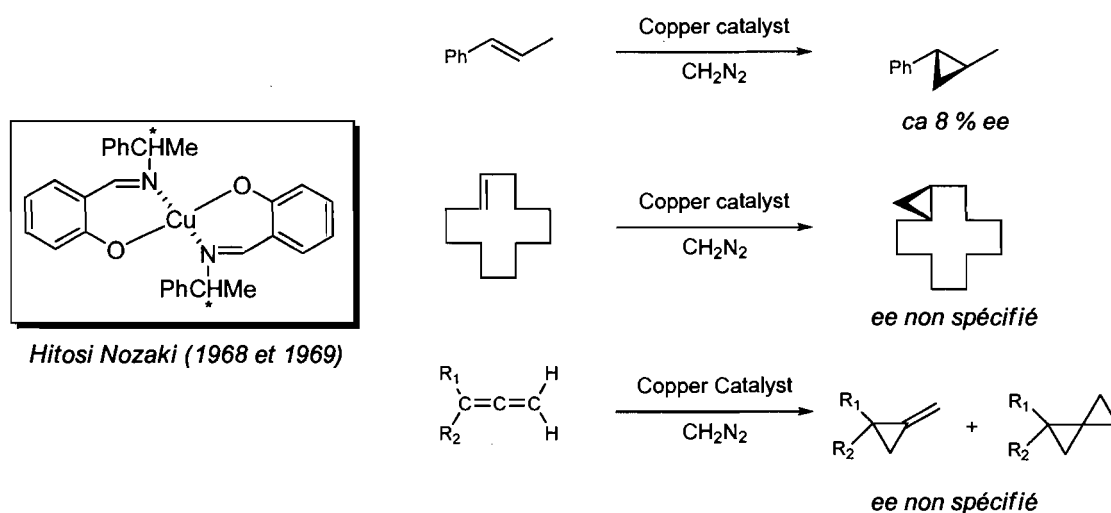
Figure 3-20. Première cyclopropanation énantiosélective utilisant le diazométhane par Hitosi Nozaki.

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[48] (a) Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron* **1968**, *24*, 3655; (b) Noyori, R.; Takaya, H.; Nakanisi, Y.; Nozaki, H. *Can. J. Chem.* **1969**, *47*, 1242.

Pfaltz, quant à lui, a élaboré une version énantiosélective de cyclopropanation comprenant le diazométhane comme source de méthylène. Aucun détail expérimental n'a été formellement dévoilé et les résultats sont mentionnés dans le cadre d'articles de revues.[49] Selon ces sources, Pfaltz aurait utilisé un catalyseur impliquant une semicorrine liée au cuivre (I), et aurait réussi de cette façon à cyclopropaner le β-méthylstyrène avec un rendement de 46% et un excès énantiomère de 75%. Le cinnamate de méthyle a pu être converti en cyclopropane à l'aide de la même méthode. Un rendement de 25% fut obtenu et un excès énantiomère de 70% a été observé (**Figure 3-21**).
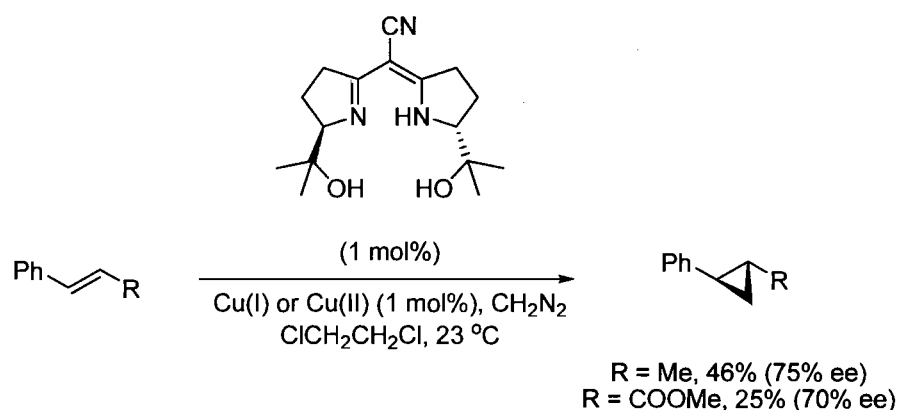
Figure 3-21. Cyclopropanation énantiosélective de Pfaltz utilisant le diazométhane.

Denmark a testé plusieurs catalyseurs chiraux ayant comme centre actif un atome de palladium pour tenter d'effectuer une cyclopropanation énantiosélective impliquant le diazométhane (**Figure 3-22**).[50] Bien que très efficace du point de vue de la réactivité, il n'a pas réussi à obtenir une réaction énantiosélective (les sélectivités furent décrites comme étant « ≤ 2% ee » dans tous les cas étudiés).

[49] (a) Pfaltz, A. dans: *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds. Cyclopropanation and C-H insertion with Cu; Springer: Berlin, 1999; Vol. II, pp. 513-603; (b) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339.

[50] Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375.

Il explique ces résultats à l'aide d'observations par RMN qui sous-entendent qu'il y aurait une dissociation totale ou partielle entre le ligand chiral et le palladium. De plus, il postule qu'il y aurait formation possible d'un carbène libre qui serait une source potentielle de réaction de cyclopropanation conduisant au produit racémique, même en présence du ligand chiral. Lors des mêmes travaux, Denmark a pu récupérer le catalyseur utilisé dans la réaction mais non quantitativement. Il existerait donc une possibilité où une petite fraction du catalyseur se dégraderait en palladium libre et pourrait être une cause potentielle de cyclopropanation racémique.
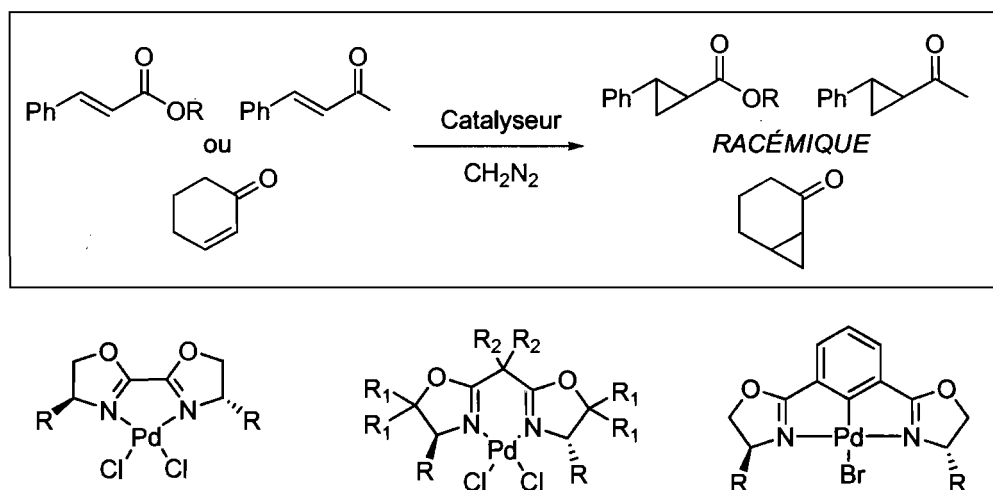
Figure 3-22. Tentatives échouées de cyclopropanation énantiosélective par Denmark.

Le peu d'exemples de cyclopropanations énantiosélectives impliquant le diazométhane est quand même surprenant compte tenu du nombre de publications relatant la réaction analogue avec le diazoacétate d'éthyle. Il reste naturellement beaucoup de place au développement et l'absence de méthodes efficaces nous porte à croire que des obstacles importants devront être contournés par les chercheurs qui s'aventureront dans ce domaine.

3.5. Autres méthodes de synthèse stéréosélective de cyclopropanes

Voici deux autres exemples de cyclopropanation ne tombant pas dans les catégories discutées jusqu'ici. Un premier exemple de cyclopropanation organo-catalytique asymétrique récent réalisé par MacMillan est illustré à la **Figure 3-23**.[51]

67%; 72:1 dr; 92% ee
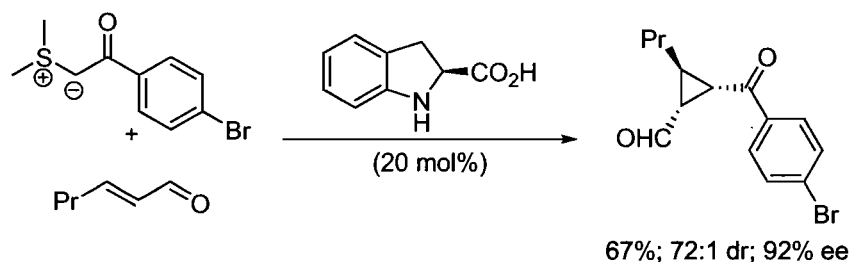
Figure 3-23. Exemple représentatif de la cyclopropanation organocatalytique.

Par ailleurs, Madalengoitia avait conçu auparavant une méthode de cyclopropanation énantiosélective qui utilise de manière stœchiométrique un acide de Lewis chiral. La gamme de substrats compatibles avec cette réaction est relativement restreinte et l'alcène doit posséder deux sites de coordination basiques (**Figure 3-24**).[52] Toutes ses tentatives de réduire la quantité d'acide de Lewis ont échoué tel que démontré par l'érosion importante de l'énantiosélectivité en présence d'une quantité sous-stœchiométrique du ligand chiral.

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[51] Kunz, R. K.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 3240.

[52] Mamai, A.; Madalengoitia, J. S. *Tetrahedron Lett.* **2000**, *41*, 9009.
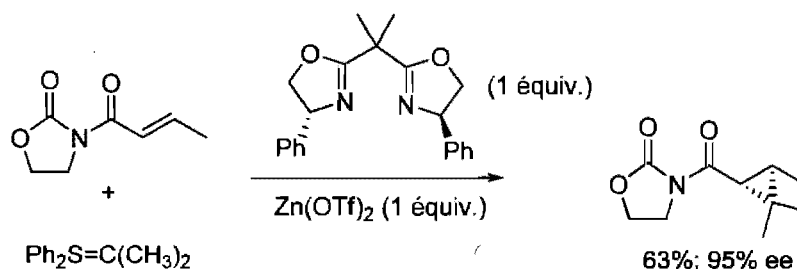
Figure 3-24. Utilisation stœchiométrique d'un acide de Lewis chiral par Madalengoitia.

3.6. Mise en perspective des travaux de recherche proposés

La réaction de Simmons-Smith, par sa nature, requiert l'utilisation d'excès de réactifs organométalliques pyrophoriques et les méthodes les plus efficaces sont limitées à des classes de substrats restreintes. L'utilisation d'une quantité stœchiométrique d'un composé chiral demeure la méthode de choix pour la synthèse de cyclopropanes impliquant cette méthode.

Bien que les méthodes de cyclopropanation d'alcènes à partir de composés diazo sont nombreuses et permettent la synthèse de cyclopropanes avec un contrôle quasi parfait de l'énantiosélectivité, ces transformations ne sont pas quantitatives et le contrôle de la diastéréosélectivité demeure, dans bien des cas, imparfait. L'ajout d'un substituant géminal électroattracteur à la structure diazométhane en réduit généralement la réactivité tandis que l'ajout de deux de ces groupes géminaux rend la discrimination nécessaire à l'énantiosélectivité plus difficile. Les produits formés comportent souvent des esters encombrés qui sont difficiles à hydrolyser. Le recours à des moyens extrêmes comme la réduction au LAH est souvent requise pour pouvoir élaborer une structure moléculaire plus complexe à partir de cette fonction.

Selon nous, il n'existe pas de méthode efficace de cyclopropanation énantiosélective d'alcènes utilisant le diazométhane. Historiquement des travaux furent publiés impliquant des catalyseurs de cuivre mais avec des niveaux d'induction très bas pour la cyclopropanation. Plus tard, des mentions dans des articles de revues sur le sujet indiquèrent que des exemples d'énantiosélectivités moyennes furent observés pour la conversion d'alcènes en cyclopropanes, à l'aide du cuivre mais sans détail expérimental ou publication formelle. Un article fait état de l'impossibilité de convertir énantiosélectivement des alcènes en cyclopropanes utilisant le palladium en tant que catalyseur. Dans ce domaine, il reste beaucoup de place pour le développement de nouvelles méthodes. Nous proposons de développer une méthode énantiosélective de cyclopropanation d'alcènes utilisant le diazométhane. Cette méthode devra être sous-stœchiométrique en chiralité et en métal en plus d'utiliser des conditions réactionnelles compatibles avec un grand nombre de fonctions chimiques.

Chapitre 4 : Stereoselective cyclopropanation using diazomethane

4.1. Bisoxazoline·copper(I)-catalyzed enantioselective cyclopropanation of cinnamate esters with diazomethane (published article)

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4.1.1. Abstract

Chiral bisoxazoline–copper(I) complexes were found to be effective catalysts for the enantioselective cyclopropanation reaction of *trans*-cinnamate esters exploiting an argon flow mediated diazomethane addition method. After optimization of the catalyst structure, good yields and enantiomeric excesses were obtained with electron-poor methyl cinnamate derivatives. Sterically demanding esters gave lower yields and enantioselectivities. The

correlation between the product enantiopurities and the σ^+ values of the aromatic *para*-substituents was shown to be linear in a Hammet-type plot.

4.1.2.   Introduction

The addition of a metal carbene or carbenoid complex to an alkene is one of the most widely used methods for the synthesis of cyclopropane units.[1] Our research group has been interested for some time in the catalytic enantioselective cyclopropanation of allylic alcohols using zinc carbenoids.[2] Kobayashi and Denmark have also made important contributions to this field.[3] In contrast to zinc carbenoids, the catalytic enantioselective cyclopropanation of alkenes via decomposition of diazo compounds is not limited to substrates bearing oxygen directing groups.[1] However, up to now, efficient and highly enantioselective intermolecular cyclopropanations have only been observed with diazo ester compounds.[1a,b,c] Diazoalkanes are known to react with transition metal complexes[4] and diazomethane (the simplest diazoalkane) has been used extensively for the racemic or diastereoselective cyclopropanation of alkenes.[5] Interestingly, the cyclopropanation of *E* or

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[1] (a) Doyle, M. P. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed. Asymmetric Addition and Insertion Reactions of Catalytically-Generated Metal Carbenes; Wiley-VCH: New York, 2000; pp. 191–228; (b) Lydon, K. M.; McKervey, M. A. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds. Cyclopropanation and C–H insertion with Rh; Springer: Berlin, 1999; Vol. II, pp. 540–580; (c) Pfaltz, A. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds. Cyclopropanation and C–H insertion with Cu; Springer: Berlin, 1999; Vol. II, pp.513–538; (d) Charette, A. B.; Lebel, H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds. Cyclopropanation and C–H insertion with Metals other than Cu and Rh; Springer: Berlin, 1999; Vol. II, pp. 581–603.

[2] Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168.

[3] (a) Denmark, S. E.; O'Connor, S. P.;Wilson, S. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1149; (b) Shibasaki, M.; Ohno, M.; Imai, N.; Kobayashi, S. *Tetrahedron* **1995**, *51*, 12013 and references cited therein.

[4] Putala, M.; Lemenovskii, D. A. *Russ. Chem. Rev.* **1994**, *63*, 197.

Z alkenes employing diazomethane leads to *trans* or *cis* cyclopropanes, respectively.[5] Extensive efforts have been directed towards the development of a catalytic enantioselective cyclopropanation reaction using diazomethane and transition metal complexes.[6] Pfaltz has shown that a chiral semicorrin–copper complex (**Equation 4-1**)[1c,6a] catalyzed the cyclopropanation of β-methyl styrene (46% yield, 75% ee) and methyl *trans*-cinnamate (25% yield, 70% ee) with modest yields using the Gaspar–Roth[7] method (an inert gas flow mediated addition of diazomethane).[8] In contrast, chiral bisoxazoline–palladium catalysts were reported by Denmark to produce only racemic cyclopropane products.[6b]

$$\text{(1 mol\%)}$$
$$\overline{\text{Cu(I) or Cu(II) (1 mol\%), CH}_2\text{N}_2}$$
$$\text{ClCH}_2\text{CH}_2\text{Cl, 23 °C}$$

R = Me, 46% (75% ee)
R = COOMe, 25% (70% ee)
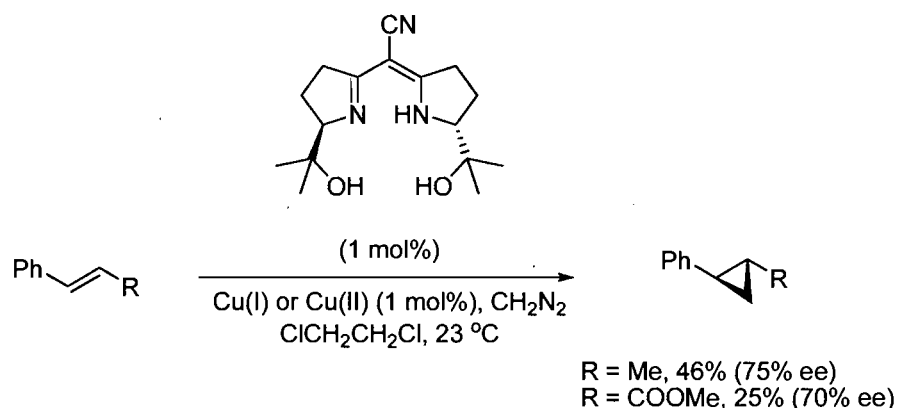
Equation 4-1

[5] (a) Tomilov, Y. V.; Dokichev, V. A.; Dzhemilev, U. M.; Nefedov, O. M. *Russ. Chem. Rev. (Engl. Transl.)* **1993**, *62*, 799; (b) A copper carbene formed by diazomethane decomposition has never been isolated but for an example of an isolated carbene from the decomposition of a diazocarbonyl compound, see: Straub, B. F.; Hofmann, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1288.

[6] (a) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339; (b) Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375; (c) Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron* **1968**, *24*, 3655; (d) Noyori, R.; Takaya, H.; Nakanisi, Y.; Nozaki, H. *Can. J. Chem.* **1969**, *47*, 1242.

[7] Doering, W. V. E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715.

[8] Complete experimental details were not reported.

Our interest in developing new stereoselective methods using diazomethane for the cyclopropanation of alkenes led us to survey a wide range of catalytic systems. In light of previously reported unsuccessful attempts using various chiral palladium catalysts, we focused our efforts on copper salts as catalysts. It is well precedented that chiral ligands such as salicylaldimines, diketones, phosphites, phosphoramidites, bis(oxazolines), semicorrins, bipyridines, diamines and diimines derivatives bind copper salts leading to complexes that can efficiently catalyze enantioselective reactions.[9] Herein, we report our findings on the screening of bisoxazoline ligands for the enantioselective cyclopropanation of alkenes involving chiral copper(I)triflate complexes and diazomethane.

4.1.3. Results and discussion

4.1.3.1. Technical considerations for the addition of diazomethane

Low yields (less than 24%, 75% ee) of the cyclopropanated product $3a$[10] are observed (**Figure 4-2**).[11] when 10 mol% of a 2:1 or 1:1 bisoxazoline **1c**-copper(I)triflate complex

[9] Rovis, T.; Evans, D. A. In *Progress In Inorganic Chemistry*; Karlin, K. D., Ed. Structural and Mechanistic Investigations in Asymmetric Copper(I) and Copper(II) Catalyzed Reactions; John Wiley and Sons: New York, 2001; pp. 1–150.

[10] Properties or references for compounds **3a–h**: (1R,2R)-**3a** $[\alpha]_D^{20}$ = −238.1 (c 1.24, CHCl$_3$); literature value for enantiopure (1S,2S)-**3a**: $[\alpha]_D^{20}$ = 324.7 (c 1.24, CHCl$_3$); Krieger, P. E.; Landgrebe, J. A. *J. Org. Chem.* **1978**, *43*, 4447; (1R,2R)-**3b**: $[\alpha]_D^{20}$ = −227.5 (c 2.7, CHCl$_3$); literature value for enantiopure (1S,2S)-**3b**: $[\alpha]_D^{20}$ = 311.7 (c 2.7, CHCl$_3$); Scholl, B.; Hansen, H.-J. *Helv. Chim. Acta* **1986**, *69*, 1936; **3c**: $[\alpha]_D^{20}$ = −146.5 (c 1.14, CHCl$_3$); IR (neat) υ 3064, 3032, 2954, 1722, 1605, 1497, 1456, 1406, 1324, 1264, 1166, 753, 697 cm–1; ^{1}H NMR (400 MHz, CDCl3) δ 7.39–7.25 (m, 7H), 7.23–7.19 (m, 1H), 7.13–7.07 (m, 2H), 5.17 (d, 1.7 Hz, 2H), 2.61–2.53 (m, 1H), 2.02–1.94 (m, 1H), 1.69–1.61 (m, 1H), 1.39–1.31 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 173.7, 140.3, 136.3, 129.0, 128.9, 128.7, 128.6, 126.9, 126.6, 67.0, 26.8, 24.5, 17.7. Anal. calcd for C$_{17}$H$_{16}$O$_2$: C, 80.93; H, 6.39. Found: C, 80.72; H, 6.78%; **3d**: $[\alpha]_D^{20}$ = −240.0 (c 0.74, CHCl$_3$); IR (neat) υ 3062, 3030, 1742, 1592, 1493, 1457, 1400, 1339, 1196, 1161, 1137, 934, 751, 696 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44–7.09 (m, 10H), 2.75–2.66 (m, 1H), 2.21–2.13 (m, 1H), 1.82–1.73 (m, 1H), 1.53–1.45 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 172.4, 151.2, 140.1,

was treated with a solution of diazomethane in dichloromethane (caution: appropriate precautions must be taken when using diazomethane)[12,13] in the presence of methyl *trans*-cinnamate **2a** at 0 °C.

$$Ph\diagup\diagdown\diagup\!\!\underset{O}{\overset{}{\diagdown}}\!\!OMe$$

2a

(1c, 10 mol%)

CuOTf-PhCH₃ (5 mol%)
CH₂N₂ / CH₂Cl₂ or Et₂O
CH₂Cl₂, 0 °C

3a

< 24% conversion (75% ee)
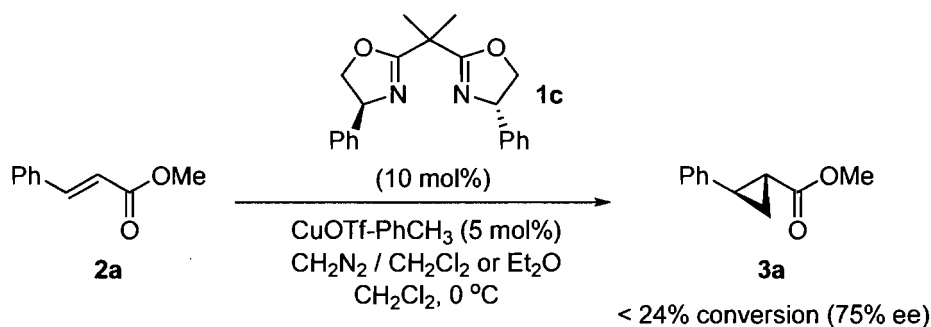
Équation 4-1

We postulated that a slow addition of diazomethane would reduce carbene dimerization, polymerization or diazomethane attack on the metal carbene, thus leading to the desired

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129.8, 129.0, 127.1, 126.7, 126.2, 121.9, 27.5, 24.5, 18.2; HRMS (MAB) calcd for $C_{16}H_{14}O_2$ [M]⁺: 238.0994, found 238.1006; **3e**: $[\alpha]_D^{20}$ = –175.1 (*c* 1.32, CHCl₃); IR (neat) υ 2980, 2938, 1720, 1606, 1458, 1407, 1321, 1269, 1189, 1108, 755, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.26 (m, 2H), 7.24–7.18 (m, 1H), 7.14–7.08 (m, 2H), 5.06 (h, *J*=6.27 Hz, 1H), 2.55–2.48 (m, 1H), 1.93–1.86 (m, 1H), 1.65–1.56 (m, 1H), 1.34–1.29 (m, 1H), 1.29–1.24 (m, 6H); ¹³C NMR (100 MHz, CDCl3) δ 173.3, 140.7, 128.9, 126.8, 126.53, 126.52, 68.4, 26.4, 24.9, 22.3, 17.6; HRMS (MAB) calcd for $C_{13}H_{16}O_2$ [M]⁺: 204.1150, found 204.1151; **3f** and **3g**: Beres, J. A.; Crouch, R. D., Jr. *Org. Prep. Proced. Int.* **1988**, 187; **3h**: Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695.

[11] Charette, A. B.; McCoy, C., unpublished results.

[12] Black, T. W. *Aldrichim. Acta* **1983**, *16*, 3.

[13] Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: from Cyclopropanes to Ylides*; John Wiley and Sons: New York, 1998; p. 94.

cyclopropane with greater efficiency.[14] Since the slow addition of diazomethane is technically challenging due to its low boiling point (−23 °C), an alternative delivery system is required. The Gaspar–Roth method is an attractive way to control the rate of diazomethane addition into reaction mixtures.[7] In addition, this method prevents the dilution of the reaction mixture, even if a large excess of diazomethane is required.
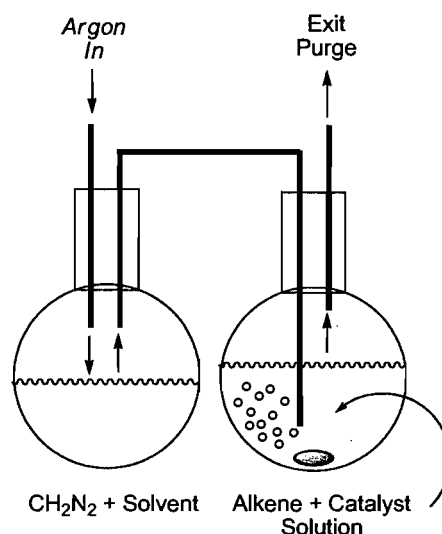
Figure 4-1. Scheme of experimental apparatus.

Our adaptation of the Gaspar–Roth method involved passing a flow of argon over a cooled (0°C) diazomethane solution (**Figure 4-1**). This flow was then directed into the reaction *via* cannula. When 5 mol% of a 1:1 ratio of bisoxazoline **1c**–copper(I)triflate complex was treated with a dichloromethane solution of diazomethane in the presence of methyl *trans*-cinnamate in dichloromethane at −40 °C, the cyclopropanated product was isolated in 80% yield and 72% ee (**Équation 4-2**). When the reaction was carried out at 0 °C, the yield

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[14] Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: from Cyclopropanes to Ylides*; John Wiley and Sons: New York, 1998; Vol. 94, pp. 61–111.

dropped slightly to 74% (72% ee) but the temperature variation had no effect on the enantioselectivity.[15]
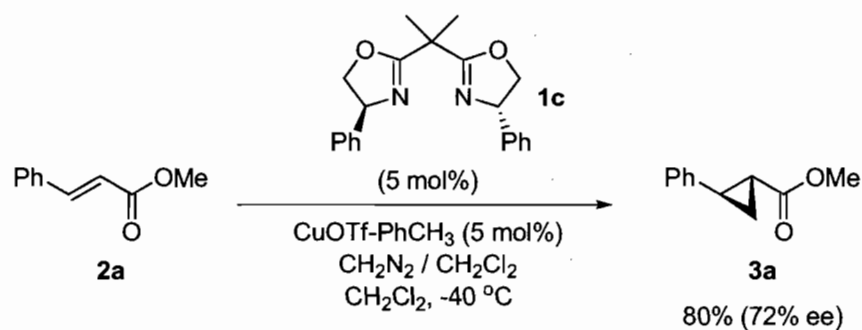
Équation 4-2

4.1.3.2. Variations of the chiral ligand
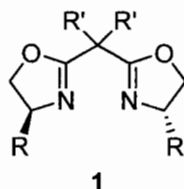
Figure 4-2. Chiral bisoxazoline ligand scaffold.

We then investigated various chiral complexes in the cyclopropanation reaction. Among those tested, chiral bisoxazoline ligands (**Figure 4-2**) proved to be the most promising candidates exhibiting good levels of reactivity and enantioselectivity. Chiral bisoxazoline

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[15] Dichloromethane was found to be the optimal solvent among those tested including: Et₂O, THF, PhMe, PhH, DME, (ClCH₂)₂ and MeCN.

1a–g[16] ligands were reacted with CuOTf·0.5PhCH₃ to form bisoxazoline–copper complexes that were used directly as catalysts for the cyclopropanation of cinnamate esters. Methyl *trans*-cinnamate was used as a test substrate for this study because it exhibited good reactivity under our reaction conditions. The ligand optimization involving the modification of R and R' groups is summarized in **Tableau 4-1**.

Tableau 4-1. Ligand structure effect on the reactivity and enantioselectivity of the cyclopropanation of methyl *trans*-cinnamate.

$$\text{Ph}\diagdown\diagup\text{OMe} \quad \xrightarrow[\substack{CH_2Cl_2,\ -40\ °C}]{\substack{\text{Ligand } \mathbf{1a\text{-}g}\ (5\ mol\%) \\ \text{CuOTf-0.5PhCH}_3\ (5\ mol\%) \\ \hline CH_2N_2\ /\ CH_2Cl_2}} \quad \text{Ph}\diagdown\diagup\text{OMe}$$
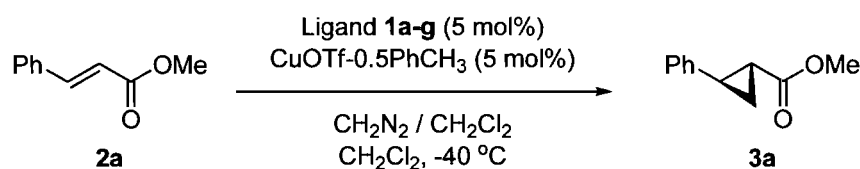
Entry	Ligand	R	R'	Yield (%)[a]	Ee (%)[b]
1	1a	Me	Me	40	50
2	1b	Bn	Me	20	53
3	1c	Ph	Me	80	72
4	1d	*i*-Pr	Me	35	48
5	1e	*t*-Bu	Me	30	24
6	1f	Ph	-CH₂CH₂-	71	77
7	1g	Ph	Bn	49	60

[a] Isolated yield. [b] Determined by SFC or GC using a chiral stationary phase.

[16] **1a**: Sibi, M. P.; Venkatramaman, L.; Liu, M.; Jasperse, C. P. *J. Am. Chem. Soc.* **2001**, *123*, 8444; **1d**: Woerpel, K. A.; Ph.D. Thesis, 1992, Harvard University; **1f**: $[\alpha]_D^{20} = -50.2$ (*c* 0.62, CHCl3); IR (neat) υ 3062, 3029, 2902, 1661, 1368, 1167, 1105 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.40–7.22 (m, 10H), 5.22 (dd, *J*=10.3, 7.93 Hz, 2H), 4.69 (dd, *J*=10.1, 8.4 Hz, 2H), 4.17 (t, 8.0 Hz, 2H), 1.59 (s, 4H); ¹³C NMR (75 MHz, CDCl3) δ 166.8, 42.2, 128.5, 127.4, 126.5, 75.3, 69.3, 18.3, 15.7; LRMS (APCI, Pos) calcd for C₂₁H₂₀N₂O₂: 332.15, found 333.2; **1g**: Burgette, M. I.; Fraile, J. M.; Garcia, J. I.; Garcia-Verdugo, E.; Herrerias, C. I.; Luis, S. V.; Mayoral, J. A. *J. Org. Chem.* **2001**, *66*, 8893. **1b**, **1c** and **1e** are commercially available.

For the ligand optimization study, 5 mol% of a 1:1 ratio of bisoxazoline–copper(I) triflate complex was treated with a dichloromethane solution of diazomethane via a flow of argon in the presence of methyl *trans*-cinnamate in dichloromethane at −40 °C. The reaction mixture was filtered through a short pad of silica gel using dichloromethane and directly treated with ozone at −78 °C and then with methyl sulfide prior to column chromatography to remove the unreacted alkene. The optimal R group was found to be phenyl (entry 3), whereas a methyl group or an ethylene bridge were the optimal R' groups (entries 3 and 6, respectively).[17] The reactivities and the enantioselectivities were lower when the R substituents were either alkyl (entries 1, 4 and 5) or benzyl groups (entry 2).[18]

Although we used CuOTf, we observed that Cu(OTf)$_2$ was equally effective. It is well known that the active catalyst in the cyclopropanation reaction with diazo compounds is a copper(I) species and that copper(II) species can be reduced to copper(I) during the course of the reaction by the diazo reagent.[19,20]

4.1.3.3.   Substrate variations

In a second set of experiments, the nature of the ester moiety was modified. Using the previously described reaction conditions with catalyst **1c**, we studied the cyclopropanation

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[17] Since catalysts **1c** and **1f** exhibited similar reactivity and enantioselectivity, **1c** was chosen as the optimal catalyst because it is commercially available.

[18] Chiral 1-aminoindan-2-ol derived bis(oxazolines) were also tested and exhibited very low reactivity.

[19] (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889; (b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300.

[20] Other copper salts were tested and found to be inactive under our reaction conditions: CuSO$_4$, Cu(BF$_4$)$_2$·xH$_2$O, Cu(OAc)$_2$, CuCl$_2$, CuF$_2$, CuCN, CuI and CuBr.

of alkenes **2a–e**.[21] The results are summarized in **Tableau 4-2** and indicate that non-sterically encumbered alkyl esters gave similar results (entries 1 and 2) as the benzyl ester (entry 3). The phenyl ester is surprisingly less reactive than the alkyl esters, providing the desired cyclopropane in only 49% yield with similar enantioselectivity (74% ee) (entry 4). In addition, the more sterically hindered isopropyl ester led to a further decrease in reactivity and enantioselectivity (43% yield, 69% ee, entry 5).

Tableau 4-2. Alkene structure effect on the reactivity and the enantioselectivity of the cyclopropanation reaction.

Ligand **1c** (5 mol%)
CuOTf-0.5PhCH$_3$ (5 mol%)

Ph OR
O
2a-e

$\longrightarrow$

CH$_2$N$_2$ / CH$_2$Cl$_2$
CH$_2$Cl$_2$, -40 °C

Ph OR
O
3a-e
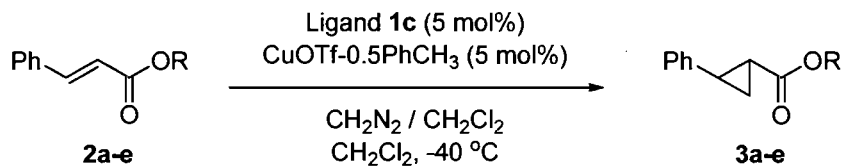
Entry	Alkene	R	Yield (%)[a]	Ee (%)[b]
1	2a	Me	80	72
2	2b	Et	80	73
3	2c	Bn	79	75
4	2d	Ph	49	74
5	2e	i-Pr	43	69

[a] Isolated yield. [b] Determined by SFC or GC using a chiral stationary phase.

We also examined the effect of changing the *para*-substituent on the phenyl ring of methyl *trans*-cinnamate with regards to the enantioselectivity and reactivity of the

[21] **2d**: IR (neat) υ 3060, 1723, 1635, 1484, 1305, 1140, 971, 761, 679 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) δ 7.90 (d, J=16.0 Hz, 1H), 7.66–7.58 (m, 2H), 7.49–7.39 (m, 5H), 7.32–7.25 (m, 1H), 7.23–7.17 (m, 2H), 6.67 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 165.8, 151.2, 147.0, 134.6, 131.1, 129.9, 129.4, 128.7, 126.2, 122.1, 117.7. Anal. calcd for C$_{15}$H$_{12}$O$_2$: C, 80.34; H, 5.39. Found: C, 80.63; H, 5.57%; **2a**, **2b**, **2c** and **2e** are commercially available.

cyclopropanation.[22] Using the previously described reaction conditions, alkenes **2a, f–h**[23] were submitted to the cyclopropanation conditions and the alkene:cyclopropane ratio determined by ^{1}H NMR after a standardized reaction time of 5 h. The cyclopropanation with substrates containing electron donating *para*-groups such as methoxy or methyl was faster but the product was obtained in lower enantiomeric excess (entries 1 and 2) than the parent alkene where R=H (entry 3). In contrast, when the *para*-substituent of the aromatic moiety of the substrate was an electron-withdrawing group, the cyclopropanation reaction was slower while the enantioselectivity increased to 80% (entry 4).

[22] For an example of electronic effects in catalytic asymmetric reactions, see: Palucki, M.; Finney, N. S.; Pospisil, P. J.; Güler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948.

[23] **2f** is commercially available; **2g**: IR (neat) υ 3060, 3027, 2919, 2840, 1703, 1631, 1605, 1434, 1316, 1190, 1167, 998, 815 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) δ 7.68 (d, *J*=16.0 Hz, 1H), 7.43 (d, *J*=8.1 Hz, 2H), 7.20 (d, *J*=8.1 Hz, 2H), 6.41 (d, *J*=16.0 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 168.1, 145.3, 141.1, 132.0, 130.0, 128.5, 117.1, 52.1, 21.9. Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.36; H, 7.27%; **2h**: IR (neat) υ 3036, 3002, 2951, 2835, 1703, 1633, 1590, 1566, 1489, 1431, 1313, 1191, 1167, 1003, 830, 818 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, *J*=16.0 Hz, 1H), 7.49–7.43 (m, 2H), 7.39–7.33 (m, 2H), 6.42 (d, *J*=16.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.0, 143.2, 136.0, 132.7, 129.1, 129.0, 118.2, 51.6; Anal. calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.91; H, 4.33; N, 6.59%.

Tableau 4-3. Aromatic ring *para*-substituent effect on the reactivity and the enantioselectivity of the cyclopropanation reaction.

R⟨benzene ring⟩CH=CH–C(=O)OMe → Ligand **1c** (5 mol%) / CuOTf-0.5PhCH₃ (5 mol%) / CH₂N₂ / CH₂Cl₂ / CH₂Cl₂, -40 °C → R⟨benzene ring⟩–cyclopropane–C(=O)OMe

2a, f-h → **3a, f-h**
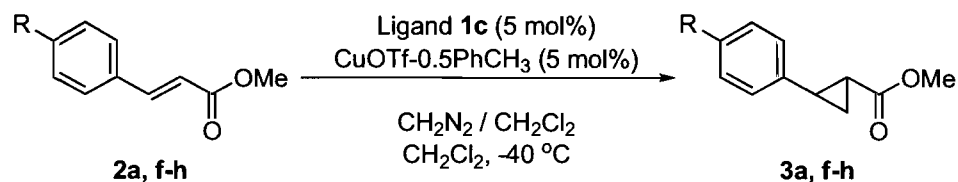
Entry	Alkene	R	Ratio (2n:3n)[a]	Yield (%)[b]	Ee (%)[c]
1	2f	MeO	7:93	81	55
2	2g	Me	7:93	79	60
3	2a	H	9:91	80	72
4	2h	NO₂	23:77	62	80

[a] Determined by 1H NMR analysis of the crude product. [b] Isolated yield. [c] Determined by SFC or GC using a chiral stationary phase.

A Hammett-type plot (**Figure 4-3**) shows a linear correlation between the enantioselectivity and the σ^+ value of the *para*-substituent, indicating that the variation in enantioselectivity is due to the electronic character of the alkene.[24] It seems unlikely that the steric perturbation imposed by the variation of the *para*-substituent on the alkene aromatic ring plays a significant role.

[24] The best correlation is obtained when the σ^+ set of values is used (over σ^- and σ^p) since the reaction center is electron rich and directly conjugated with the *para*-substituent imparting the electronic characteristics of the alkene.
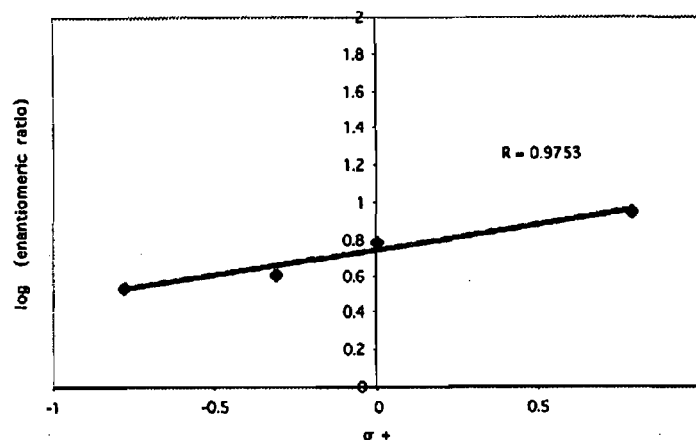
Figure 4-3. Hammett-type plot correlating the enantioselectivity of the cyclopropanation with the σ^+ values.

It was suggested that the reaction between copper salts and diazomethane leads to the formation of a metal carbene intermediate.[5,25] A possible explanation to account for the observed results could be that the carbene is electrophilic and that electron-rich alkenes react faster through an early transition state which displays less enantiocontrol. According to the Hammond postulate, a later transition state is more product-like which generally implies a greater difference in energy between diastereomeric transition states in an enantioselective system. Therefore, an electron-poor alkene would be less reactive and exhibit higher enantioselectivity. For example, alkene **2h** bearing a *para*-nitro substituent on the aromatic ring gave the highest enantioselectivity yet (**Tableau 4-3**, entry 4) and showed reduced reactivity (as evidenced by the lower yields), whereas alkene **2f** (entry 1)

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[25] Other possible mechanistic pathways include: diazomethane attack onto the complexed alkene or [2+2] cycloaddition of copper carbene and the alkene. The diastereoselective [3+2] cycloaddition of diazomethane to alkenes is also known, forming pyrazolines which can be decomposed to cyclopropanes with heat or irradiation. For recent examples, see: (a) Rife, J.; Ortuno, R. M. *Tetrahedron: Asymmetry* **1999**, *10*, 4245; (b) Muray, E.; Alvarez-Larena, A.; Piniella, J. F.; Branchadell, V.; Ortuno, R. M. *J. Org. Chem.* **2000**, *65*, 388. Under our reaction conditions, without catalyst, formation of pyrazolines does not occur and the starting alkene is recovered quantitatively. Formation of the pyrazoline and

showed increased reactivity but gave lower enantioselectivities in agreement with the above postulate.

4.1.4.   Conclusion

In conclusion, a methodology has been developed for the catalytic enantioselective cyclopropanation of *trans*-cinnamate esters using an argon flow mediated diazomethane addition method.[26] Our preliminary studies indicate that 5 mol% of a 1:1 ratio of bisoxazoline–Cu(I) complex is sufficient for good reactivity. Good yields and enantioselectivities were observed for unhindered cinnamate esters, with electron-poor alkenes giving the highest enantioselectivities. The above described methodology induces

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subsequent cyclopropane under lewis acidic conditions cannot be excluded as mechanistic possibilities although no enantioselective examples have been reported.

[26] Under a dry argon atmosphere, CuOTf·0.5PhCH₃ (14 mg, 0.055 mmol) and ligand **1c** (19 mg, 0.056 mmol) are weighed in the reaction flask which was then fitted with a septum. Dichloromethane (5 mL) was added forming a brown suspension that was magnetically stirred at room temperature for 60 min at which point the reaction mixture was a clear green solution. Alkene **2a** (178 mg, 1.098 mmol) was then added as a solution in dichloromethane (5 mL) and the solution was cooled to −40 °C (bath temp.). An argon flow was then passed over a cooled (0 °C, bath temp.) diazomethane (CAUTION)[12] solution in dichloromethane ($\approx$ 0.4 M) and directed into the reaction mixture via a Teflon canula (if the yellow coloration of the diazomethane solution subdues, more should be added). After 5–15 min, the reaction mixture became clear pale yellow and diazomethane bubbling was continued for 5 h. The reaction mixture was filtered through a pad of silica gel that was subsequently rinsed with ethyl acetate (50 mL) and volatiles were removed under reduced pressure. The crude product was dissolved in dichloromethane (30 mL) and cooled to −78 °C (bath temp.) upon which it is treated with ozone until the solution was blue. Oxygen was then bubbled into the solution until the blue color had subdued (5 min) then methyl sulfide (1 mL) was added at −78 °C (bath temp.) and left to warm to room temperature. Volatiles were removed under reduced pressure and the residue was purified by column chromatography using silica gel and 10% ethyl acetate/hexanes as eluent. Compound **3a** was obtained (155 mg) as a clear oil (80% yield, 72% ee). Ees were determined using GC (cyclodex G, H₂ 26 psi, 120 °C isotherm, enantiomers: 14.20 and 14.43 min); $[\alpha]_D^{20} = -238.1$ (*c* 1.24, CHCl₃).

the highest reported level of enantioselectivity ever obtained for a cyclopropanation using diazomethane (80% ee) with good yields (up to 80%). Further studies are currently in progress to develop a more effective catalyst and expand the scope of the reaction.

4.1.5. Acknowledgements

4.2. Optimization and scope of the bisoxazoline•copper(I)-catalyzed enantioselective cyclopropanation

Our previously described work led us to survey a wide variety of catalysts for the enantioselective cyclopropanation of cinnamates. We had previously determined that a mixture of the phenyl bisoxazoline (chapter 4, compound **1c**) and copper(I) triflate, afforded the highest enantioselectivities and yields for the catalytic asymmetric cyclopropanation of cinnamates using diazomethane (see section 4.1). Slow addition of diazomethane using an inert gaseous carrier was found to be critical for the reaction to proceed. Although academically these were important discoveries, the reaction afforded products in modest enantiomeric excesses (80% ee for cinnamate substrates). This section will describe our unpublished work aimed at finding classes of substrates or catalysts that would provide synthetically useful level of enantioselectivities.

4.2.1. Solvent

Diazomethane is traditionally generated and stored as a diethyl ether solution. More recently, it was shown to be stable when generated and stored as a dichloromethane solution.[24e] To maximize the enantioselectivities, we have screened a variety of solvents that could be compatible with diazomethane. Reactions were performed in a parallel synthesis fashion using a multi-reaction setup (**Figure 4-4**).[27] Results from the solvent study are detailed in **Tableau 4-4**.

[27] The procedure was based on the previously published one described in this chapter with the following modifications: diazomethane addition was done over a 5-hour period, at 0 °C with a 2:1 ligand to copper ratio at a 10 mol% catalyst loading. At the end of the reaction time, volatiles were removed and the crude reaction mixtures were purified by flash
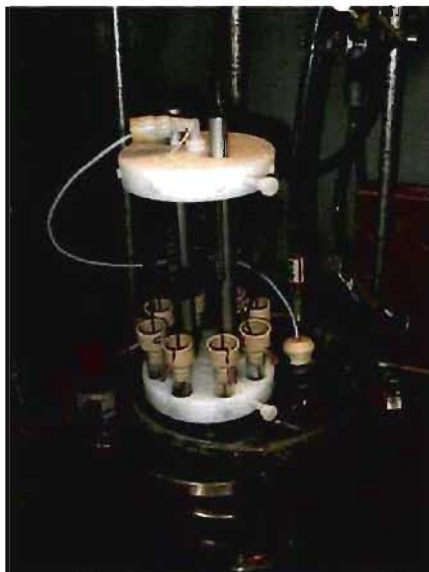
Figure 4-4. Experimental setup for parallel reactions.

Although ethereal solvents gave slightly higher enantiomeric excesses, the conversions were lower than those observed with chlorinated solvents (entries 1-2 vs 7-8). Similar enantioselectivities were observed in toluene (entry 3) and benzene (entry 4) but the conversions were not optimal. This is probably due to lack of solubility of the catalyst in these aromatic solvents. Furthermore, the addition of hexane to a solution of the catalyst in dichloromethane led to the partial precipitation of the catalyst. Not surprisingly, this solvent mixture led to lower conversions. Acetonitrile was found to be incompatible with the cyclopropanation reaction (entry 6). It appears that the Lewis basicity of acetonitrile substantially decreased the catalyst activity and the reaction between diazomethane and the alkene proceeded exclusively via a [3+2] cycloaddition pathway leading to pyrazines.

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chromatography using 5% to 10% of AcOEt/Hexanes as eluent. This method allowed the isolation of an unseparable mixture of unreacted starting material and the desired cyclopropane product, from which the conversion and the enantiomeric excess were determined.

Dichloromethane and 1,2-dichloroethane were the best choices in terms of reactivity and enantioselectivity although the ee's were slightly lower using the later.

Tableau 4-4. Solvent effect on the enantioselectivity and reactivity.
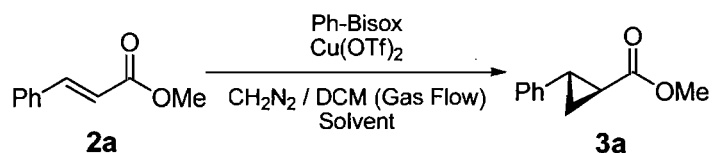
Entry	Solvent	Isolated ratio (2a:3a)	Mass recovery (%)	ee (%)
1	THF	65:35	87	76
2	Et$_2$O	78:22	94	80
3	PhMe	48:52	87	78
4	PhH	27:73	53	79
5	DCM / Hex	43:57	59	67
6	MeCN	90:10	3	--
7	DCE	23:77	66	68
8	DCM	23:77	71	77

4.2.2. Ligand

The use of a ligand in the copper-catalyzed cyclopropanation of *trans*-methylcinnamate **2a** was not necessary for conversion to occur. Indeed, treatment of *trans*-methylcinnamate with diazomethane in the presence of CuOTf or Cu(OTf)$_2$ led to the formation of racemic cyclopropane **3a** in *ca.* 50% yield (**Figure 4-5**, I). In the presence of a chiral ligand, this background reaction may be a competitive process leading to racemic cyclopropane.

However, the addition of a ligand to the copper salt suspension in CH_2Cl_2 afforded a homogeneous solution within less than 30 minutes so it was assumed that the copper complexation of the copper with the chiral ligand was quantitative.

In the initial exploratory studies involving the copper-catalyzed cyclopropanation reaction, we had surveyed different classes of ligands. BINAP•Cu complex (**Figure 4-5**, A) was found to be a poor catalyst both in terms of turnover number as well as enantioselectivity. The copper complexes derived from cyclohexanediamine type ligands (**Figure 4-5**, B and C) bearing pyridine or phenol groups were also found to be ineffective. The phosphoramidite•Cu complex (**Figure 4-5**, E) did not catalyze the diazomethane decomposition whereas the complex derived from Tomioka type ligand (**Figure 4-5**, F) led to low conversions and racemic cyclopropanes. The copper catalysts derived from bisoxazoline ligands lacking the bridging isopropylidene (**Figure 4-5**, D) resulted in low conversions and low enantiocontrol. Finally, the cyclopropanation with PYBOX•Cu catalysts (**Figure 4-5**, G and H) possessing two oxazoline moieties proceeded smoothly but without any level of enantiocontrol. Bis(oxazolines)•Cu catalysts similar to those described in our publication (section 4.1) provided the best enantiocontrol and remain the catalysts of choice (**Figure 4-5**, J, K and L).

A

70:30 (**2a:3a**)
79% (mass recovery)
3% e.e.; 0 °C

B

64:36 (**2a:3a**)
67% (mass recovery)
5% e.e.; 0 °C

C

8:92 (**2a:3a**)
56% (mass recovery)
1% e.e.; 0 °C

D

23:77 (**2a:3a**)
63% (mass recovery)
12% e.e.; 0 °C

E

100:0 (**2a:3a**)
0 °C

F

79:21 (**2a:3a**)
55% (mass recovery)
0% e.e.; 0 °C

G

25:75 (**2a:3a**)
75% (mass recovery)
5% e.e.; 0 °C

H

83% yield (**3a**)
1% e.e.; 0 °C

I

No ligand

50% yield (**3a**)
0 °C

J

82:18 (**2a:3a**)
90% (mass recovery)
59% e.e.; -30 °C

K

85:15 (**2a:3a**)
94% (mass recovery)
80% e.e.; -30 °C

L

83:17 (**2a:3a**)
90% (mass recovery)
69% e.e.; -30 °C

Figure 4-5. Ligands used as catalyst's precursors.

Besides solubilizing the metal and affording an enantioselective reaction, the substituents of the ligands seem to play a pivotal role in the progression of the reaction. As stated in our previous communication, Ph-bisoxazoline **1c** was the optimal ligand and very few modification were tolerated.[28] Most modifications in the chirality projection area (**Figure 4-6**) led to a decrease in yields as well as in enantioselectivities. The bridge area substituents of the same ligand were more permissive of structural modifications since at least one modification led to good results.[29] Nevertheless, it is believed that modifications to the bridge area substituents will change the bite angle of the ligand which modulates its reactivity, as well as its enantioselectivity. We will therefore focus our discussion on the chirality projection area.
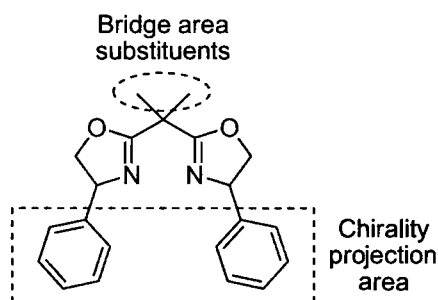
Figure 4-6. Green: modifications are tolerated; Red: modifications are not tolerated (based on ligand **1c**).

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[28] The ligand (L) to metal (M) ratio can be changed without extensively affecting the reaction outcome (evaluated with *trans*-methyl cinnamate). Essentially, excess metal (copper(I) or copper(II) triflate; [L] < [M]) is tolerated since uncomplexed metal is less reactive than the corresponding soluble bisoxazoline complex. If an excess of the ligand is used ([L] > [M]), enantioselectivities are slightly improved (increase of *ca* 3% ee). The use of equimolar amounts of alkenes, the bisoxazoline and the metal salt did not lead to cyclopropane formation (with gaseous delivery of diazomethane as well as solution delivery).

When the phenyl rings of ligand **1c** (**Figure 4-6**) were replaced by other groups, the cyclopropanation process did occur but in lower yield. To us, this was more surprising than the variations in enantioselectivities. We postulated that the role of the phenyl group was more than just structural to account for these observations. Smaller groups, such as a methyl, led to lower enantioselectivities probably because the chirality is not close enough to the reactive center of the catalyst (40% yield, 50% ee; **Tableau 4-1**). Furthermore, the diminished steric hindrance around the carbene might have facilitated the approach of the alkene and favor an earlier transition state leading to a less enantioselective reaction. The drop in yield associated with this modification was also quite important. It could be explained by the fact that the metallic carbene is more accessible leading to unproductive side reactions with diazomethane. However, such a steric argument could also have been used to explain a better reactivity between the carbene and the alkene leading to higher cyclopropane yields. The phenylalanine-derived bisoxazoline, had led to similar enantioselectivities and, surprisingly, even lower yields (20% yield, 53% ee; **Tableau 4-1**) compared to the benchmark ligand **1c** (80% yield, 72% ee ; **Tableau 4-1**). Bigger leucine and *tert*-leucine analog gave respectively 35% yield (48% ee) and 30% yield (24% ee) respectively (**Tableau 4-1**). Ligands showing subtle modifications to ligand **1c** in order to restrict the rotation of its phenyl groups were. However these slight modifications also led to a less active catalyst and lower conversions to the cyclopropane were observed (**Figure 4-5**; J, K, L).

Bisoxazoline copper complexes of Cu(II) species have been well characterized.[30] In these cases, the geometry around the metal atom seems to be dictated by the ligands and most complexes have intermediate geometries between square planar and tetrahedral (distorted

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[29] Ligand **1f** (**Figure 4-6**) gave a slightly higher enantioselectivity than ligand **1c** (**Tableau 4-6**) but since the later gave a better yield and is commercially available it was chosen as the optimal ligand.
[30] Cambridge database

square planar). It is difficult to predict geometry of Cu(I) carbene complexes which are the postulated active species in cyclopropanation reactions.[31] The methylene carbene formed from diazomethane is less sterically hindered than substituted carbenes. As a result, the orientation of the carbene is more difficult to predict and possibly has more mobility. Nonetheless, a working model explaining the enantioselectivity of the diazomethane cyclopropanation reaction has been postulated by Pfaltz.[32]
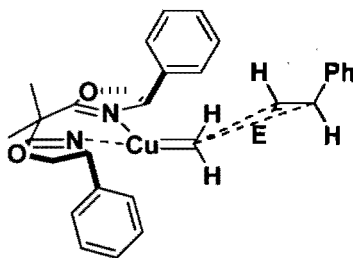
Figure 4-7. Adaptation of Pfaltz model.

An adaptation of Pfaltz's model for the chirality projection of the diazomethane cyclopropanation reaction is depicted in **Figure 4-7**. The enantiodiscriminating interactions probably occur between the group "E" and one phenyl rign of the ligand.
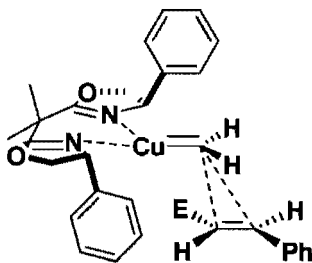
Figure 4-8. Proposed model leading to the formation of the minor enantiomer.

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[31] Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973,** *95,* 3300.

[32] Pfaltz, A. In Comprehensive Asymmetric Catalysis; Jacobsen, E. N., Pflatz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; Vol. II

If the proposal was correct, bisoxazolines bearing similarly sized groups other than phenyl should exhibit similar enantioselectivity, which was not observed. We thus postulated an interaction between the phenyl group of the ligand and the metallic carbene via pi interactions or a Wheyland type complex delocalizing a charge into the phenyl ring.[33]

4.2.3. Scope of the enantioselective cyclopropanation reaction

4.2.3.1. Cinnamates

The enantioselectivity of the reaction was strongly affected by the nucleophilic character of the alkene. Indeed, variations of the R substituent on the aryl group directly conjugated with the alkene (**Figure 4-9**) had a strong impact on the enantioselectivity of the reaction (**Tableau 4-3**). We had concluded that an electrophilic metallic carbene was probably generated during the reaction process.
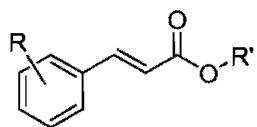
Figure 4-9. Areas of the substrate with tolerance for substitution.

In our efforts to further examine the scope of the reaction, we had previously modified the other substituent on the alkene (**Figure 4-9**) such as the R' of the ester group (**Tableau 4-2**). Variations in the nature of the substituents of the ester group had shown that large alkyl groups were not well tolerated and that less hindered groups gave better results. The later modifications had an impact mainly on the yields and not on the enantioselectivities.

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[33] Cyclopropanation of phenyl rings: Tomilov, Y. V.; Dokichev, V. A.; Dzhemilev, U. M.; Nefedov, O. M. *Russ. Chem. Rev. (Engl. Transl.)* **1993**, *62*, 799.

We then modified the R' group of the aryl ester ring of the β-arylcinnamates (**Figure 4-10**) to test the hypothesis that subtle electronic effects could give us some insights about this reaction. These new substrates were submitted to our typical reaction conditions[34] and the results are summarized in **Tableau 4-5**.
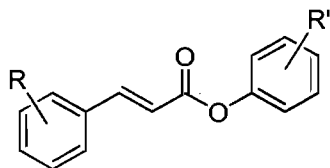
Figure 4-10. General scaffold of aryl ester substrates.

Modification of the *para*-substituents had little effect on the reaction outcome (**Tableau 4-5**, entries 2 to 4) except in the case of the nitro substituent. The presence of a nitro group at the *para* position of the arylester group (**Tableau 4-5**, entry 1) had a strong detrimental effect on the yield of the reaction. The substrate was consumed in the reaction but many by-products appeared. Positioning a nitro group at the *meta* position had essentially the same effect.

The observed results could be explained by the attack of diazomethane at the carbonyl group resulting in the cleavage of the nitro-phenol ester group (prior to or following the cyclopropanation reaction). Further activation by the reaction catalyst for the nucleophilic attack could explain the observed low yields. The reaction proceeded smoothly for other alkenes that were tested but the enantioselectivities were not better than those observed with the previously tested cinnamates.

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[34] Yields were determined by NMR using an internal standard. The crude product was dissolved in MeOH and potassium carbonate was added. Reaction mixture was stirred at room temperature for 2 hours. Volatiles were removed under reduced pressure and water was added. The aqueous mixture was extracted with dichloromethane (3x) and dried using sodium sulfate. The dichloromethane solution was filtered on short path of silica gel, and volatiles removed under reduced pressure. Enantiomeric excesses were determined on the derived methyl esters (same as for compound **3a**, Chapter 4).

alkenes that were tested but the enantioselectivities were not better than those observed with the previously tested cinnamates.

Tableau 4-5. Cyclopropanation of substituted aryl cinnamates.

Ph-BOX
CuOTf
$$Ph \diagdown \diagup C(=O)-O-Ar \quad \xrightarrow[\text{DCM, -35°C}]{CH_2N_2 / DCM} \quad Ph \diagdown \triangle C(=O)-O-Ar$$
2i-n   **3i-n**
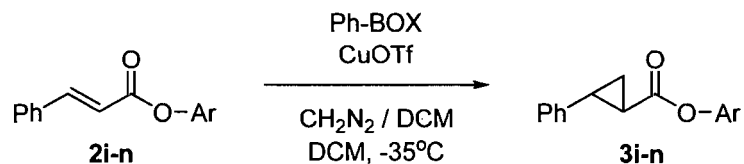
Entry	Ar	% ee	Yield
1	4-NO$_2$-Ph (**2i**)	24	10 (**3i**)
2	4-Br-Ph (**2j**)	73	83 (**3j**)
3	4-MeO-Ph (**2k**)	73	87 (**3k**)
4	4-t-Bu-Ph (**2l**)	74	80 (**3l**)
5	3-NO$_2$-Ph (**2m**)	26	10 (**3m**)
6	3-Cl (**2n**)	73	85 (**3n**)

4.2.3.2. Cinnamyls

From our previous work, we knew that electron rich substituted cinnamate derivatives could be converted to cyclopropanes in good yields under our reaction conditions but the enantioselectivities decreased as the nucleophilicity of the alkene increased. Cyclopropane (**3o**) (**Figure 4-11**) was obtained in good yield when the related β,γ-unsaturated ester (**2o**) was submitted to the optimal reaction conditions. However, low enantioselectivity was observed possibly due to poorer coordination of the substrate or a more reactive alkene.

78 % yield (3o)
15 % e.e.
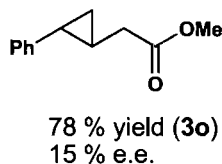
Figure 4-11. Insightful result.

We then turned our attention to substrates that exhibited good reactivity with the hope of optimizing the enantioselectivities.

Cinnamyl ethers (**Figure 4-12**) were chosen as the next candidates to be tested in the diazomethane cyclopropanation reaction. The resulting alkene should be significantly more nucleophilic than the corresponding cinnamate derivatives. Furthermore, one oxygen atom is still present for a possible coordination with the catalyst if preassociation between the various species is important.
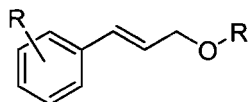
Figure 4-12. General scaffold of cinnamate substrates.

Tableau 4-6 summarizes our efforts along those lines. As hoped, benzylcinnamate (**Tableau 4-6**, entry 1) could be converted to the corresponding cyclopropane in good yield (82%). However the enantioselectivity (20% ee) was found to be dramatically lower than that observed with the corresponding cinnamate ester. Cinnamyl pivalate (Tableau 4-6, entry 2) gave a slightly better yield (89%) but the enantioselectivity was reduced (14% ee). The cinnamyl acetate (**Tableau 4-6**, entry 6) gave approximately the same result indicating that the additional bulk of the pivalate group was not detrimental to the reaction outcome. The TBDPS cinnamyl ether (**Tableau 4-6**, entry 7), when tested under our typical reaction

conditions, afforded the corresponding cyclopropane in good yield (82%) but with no enantiocontrol.

This last result indicates that there are probably some interactions between the oxygen atom of the substrate and the catalyst in the enantiodetermining step leading to the major enantiomer. We had experienced low yields using the *tert*-butyl bisoxazoline ligand in the cinnamate series. We hoped that a better match could occur between this ligand and the more reactive cinnamyl substrate with more reactive alkenes. Unfortunately, using cinnamyl pivalate (**Tableau 4-6**, entry 3) as a substrate and *tert*-butyl bisoxazoline as a ligand, a very low yield (<30%) of the corresponding cyclopropane was obtained. These last results contrast with those obtained by Masamune where an increase of more than 30% ee was observed when substituting a phenyl group for a *tert*-butyl bisoxazoline in the diazocarbonyl cyclopropanation of styrene.[35]

In past experiments, we had determined that cyclopropyl cinnamates were obtained in good yields when using PYBOX ligands (**Figure 4-5**, G and H). Unfortunately, as we found for most cases exhibiting good conversions, the enantioselectivity was dramatically reduced (in these cases to an average of 15% ee). Nonetheless, we tested two PYBOX ligands with cinnamyl ethers.[36] Ph-PYBOX (**Figure 4-5**, ligand G) exhibited lower reactivity (loss of 13% in yield) comparatively to the phenyl-bisoxazoline in the cyclopropanation of cinnamyl pivalate (**Tableau 4-6**, entry 4). The use of *iso*-butyl-PYBOX (**Figure 4-5**, ligand H) resulted in even lower conversions for the same substrate (**Tableau 4-6**, entry 5). In both cases, no enantioselectivities were observed thus ruling out PYBOX derivatives as good ligand candidates.

[35] (a) Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005; (b) Doyle, M. P. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed. Asymmetric Addition and Insertion Reactions of Catalytically-Generated Metal Carbenes; Wiley-VCH: New York, 2000.
[36] Compounds **2p-v** and **3p-v** were previously reported, see: Lacasse, M.-C., Thèse de doctorat, Université de Montréal, **2006**.
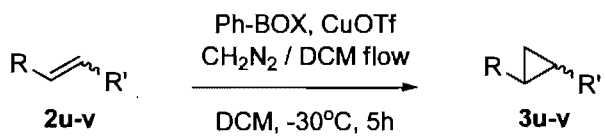
Tableau 4-6. Cyclopropanation of cinnamyl ethers.

Ligand, CuOTf
CH_2N_2 / DCM flow
→
DCM, -30°C, 5h

Ph⌒⌒OR   Ph△⌒OR
2p-t   **3p-t**
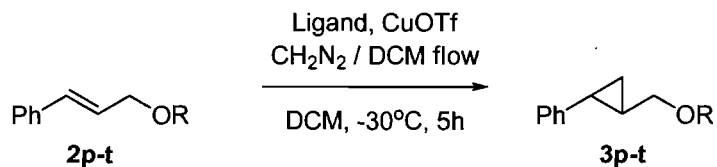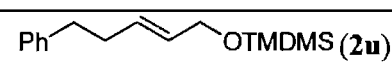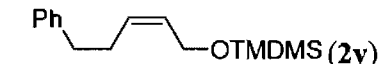
entry	Ligand	R	ee	yield
1	Ph-BOX	Bn	20	82 (**3p**)
2	Ph-BOX	Piv	14	89 (**3q**)
3	*t*-Bu-BOX	Piv	--	<30 (**3q**)
4	Ph-PYBOX	Piv	0	76 (**3q**)
5	*i*-Bu-PYBOX	Piv	0	36 (**3q**)
6	Ph-BOX	OAc	14	84 (**3r**)
7	Ph-BOX	TBDPS	0	82 (**3s**)
8	Ph-BOX	(CO)CH_2OAc	20	25 (**3t**)

4.2.3.3.   Cyclopropanation of unfunctionalized alkenes

Most reagents are not very effective for the cyclopropanation of unfunctionalized alkenes or alkenes that do not bear directing groups. In our typical reaction conditions, it was possible to form cyclopropanes from alkenes bearing alkyl groups and non coordinating heteroatoms in good yield (**Tableau 4-7**). For example, the TBDPS ether of *cis-* and *trans-*5-phenylpent-2-en-1-ol (**Tableau 4-7**, entries 1 and 2) were converted to their corresponding cyclopropanes in 89% and 80% yield respectively but with no detectable enantioselectivity.

Tableau 4-7. Cyclopropanation of unfunctionalized alkenes.

R ⤴ R'   Ph-BOX, CuOTf   R ▷ R'
            CH₂N₂ / DCM flow
2u-v   ⟶   **3u-v**
            DCM, -30°C, 5h

entry	Substrate	ee	yield
1	Ph ⌇⌇ OTMDMS (**2u**)	0	89 (**3u**)
2	Ph ⌇⌇ OTMDMS (**2v**)	0	80 (**3v**)

4.2.3.4. Attempts at increasing the scope of the reaction: alkenes that failed

Structurally different alkenes were submitted to the optimized reaction conditions in order to expand the scope of the reaction. **Tableau 4-8** provides a qualitative summary of the results. Unfortunately, in all the cases, either decomposition or no conversion to the desired product was observed. Substituted vinyl bromide and iodide did not react under optimized conditions (entries 1-2). Conversely, a α,β-unsaturated nitrile (entry 3), ketone (entry 4) and aldehyde (entry 5) led to decomposition products. In addition, α,β-unsaturated amides (entries 6 and 7) and thioester (entry 8) did not react presumably due to catalyst deactivation by complexation with the amides and thioester. Finally, product degradation was observed with ethyl crotonate and cyclohexenone (entry 9 and 10).

Tableau 4-8. Alkenes tested under optimized cyclopropanation conditions.

Entry	Alkene	Conclusion	
		No transformation of the alkene	Destruction of substrate and/or product
1	Ph⌒=⌒Br (2w)	√	
2	Ph⌒=⌒I (2x)	√	
3	Ph⌒=⌒CN (2y)		√
4	Ph⌒=⌒C(O)Ph (2z)		√
5	Ph⌒=⌒C(O)H (2aa)		√
6	Ph⌒=⌒C(O)N(CH₃)₂ (2ab)	√	
7	Ph⌒=⌒C(O)-piperidine (2ac)	√	
8	Ph⌒=⌒C(O)SEt (2ad)	√	
9	⌒=⌒C(O)OEt (2ae)		√
10	cyclohex-2-enone (2af)		√

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4.2.3.5.   Attempts at increasing the scope of the reaction: coumarin derivatives

Although most of the alkenes tested either did not react or led to decomposition products upon treatment with the copper•bisoxazoline complex and diazomethane, coumarin **2ag** was converted to the corresponding cyclopropane **3ag**[37] in satisfactory yield and with excellent enantioselectivity (**Tableau 4-9**, entry 1). Solvent optimization allowed us to improve the ee up to 90% by using chloroform as the reaction solvent however the yield

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[37] Under a dry argon atmosphere, CuOTf·0.5PhH (12 mg, 0.048 mmol) and ligand **1c** (16 mg, 0.048 mmol) were weighed in the reaction flask which was then fitted with a septum. Dichloromethane (4 mL) was added forming a brown suspension that was magnetically stirred at room temperature for 60 min at which point the reaction mixture was a clear green solution. Coumarin **2ag** (140 mg, 0.956 mmol) was then added as a solution in toluene (4 mL) and the solution was cooled to -30 °C (bath temp.). An argon flow was then passed over a cooled (-30 °C, bath temp.) diazomethane solution in dichloromethane (≈ 0.4 M) and directed into the reaction mixture via a Teflon canula (if the yellow coloration of the diazomethane solution subdues, more should be added). After 5–15 min, the reaction mixture became clear pale yellow and diazomethane bubbling was continued for 15 h. The reaction mixture was filtered through a pad of silica gel that was subsequently rinsed with ethyl acetate (50 mL) and volatiles were removed under reduced pressure. The crude product was dissolved in dichloromethane (30 mL) and cooled to -78 °C (bath temp.) upon which it is treated with ozone until the solution was blue. Oxygen was then bubbled into the solution until the blue color had subdued (5 min) then methyl sulfide (1 mL) was added at -78 °C (bath temp.) and left to warm to room temperature. Volatiles were removed under reduced pressure and the residue was purified by column chromatography using silica gel and 10% ethyl acetate/hexanes as eluent. Compound **3ag** was obtained (92 mg) as a white solid (60% yield, 88% ee). M.p. 79.0 °C uncorrected. Ees were determined using GC (cyclodex B, H_2 26 psi, 180 °C isotherm, enantiomers: 38.73 and 39.60 min); $[\alpha]_D^{20} =$ +165.0 (c 0.675, $CHCl_3$). RMN H[1] (400 MHz, CDCl3) $\square$ 7.36 (dd, $J = 7.53$, 1.64 Hz, 1 H Ar), 7.23-7.18 (m, 1 H Ar), 7.10 (td, $J = 7.48$, 1.23 Hz, 1 H Ar), 6.99 (dd, $J = 8.18$, 1.11 Hz, 1 H Ar), 2.61-2.56 (m, 1 H), 2.36-2.30 (m, 1 H), 1.78-1.72 (m, 1 H), 0.97 (dd, $J = 10.13$, 4.94 Hz, 1 H); RMN C[13] (100 MHz, CDCl3) $\square$ 167.5, 150.1, 128.0, 127.9, 124.5, 122.3, 117.5, 20.2, 17.9, 14.8; Anal. calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03; O, 19.98. Found: C, 74.77; H, 5.25; O, 20.17%.

dropped to 31%. As expected, replacement of the chlorinated solvent by complexing ethereal solvents decreased the catalyst's activity (**Tableau 4-9**).

Tableau 4-9. Cyclopropanation of coumarin in various solvents.
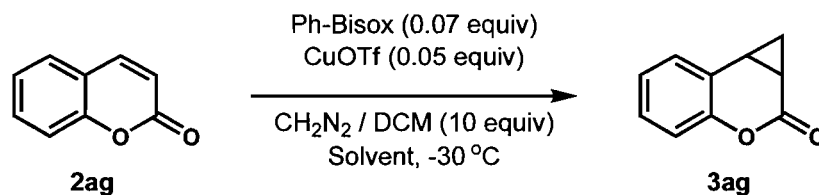
entry	Solvent	ee	yield
1	CH_2Cl_2	89	60^a
2	$(CH_2Cl)_2$	86	31
3	$CHCl_3$	90	31
4	CCl_4	86	14
5	PhCl	83	47
6	PhMe	--	$--^b$
7	AcOEt	85	32
8	THF	89	5
9	DME	89	14
10	t-BuOMe	82	27

^{a}Highest obtained isolated yield ^{b}Catalyst not soluble.

Further variations in the ligand structure, the catalyst loading, the reaction temperature and the reaction time led to no improvement of the yields and enantioselectivities. Examples of other coumarins that were tested are depicted in **Figure 4-13**.[38] Although the enantiomeric excesses of compounds **3ah** and **3ai** derived from coumarin **2ah** and **2ai** were good, we were unable to push the conversions above 18%. Since it is usually not feasible to separate

the starting material from the cyclopropane by chromatography, these conversions are not high enough for the process to be synthetically useful. Furthermore, no reaction was observed in the case of coumarin **2aj** that contains an additional substituent at the β-position.
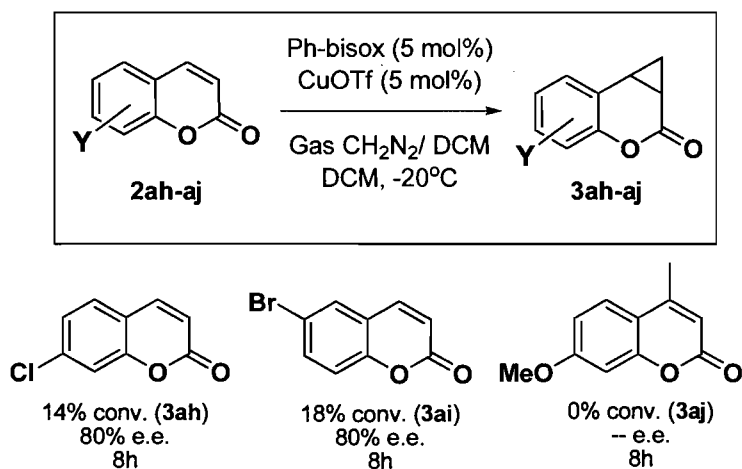
Figure 4-13. Enantioselective cyclopropanation of substituted coumarin derivatives.

4.2.4. Metal salt

Different metal salts were considered as substitutes for copper and palladium in the diazomethane cyclopropanation of alkenes. Zinc, iridium, gold, silver, scandium and ytterbium salt were tested for their catalytic activity in the metal catalyzed diazomethane cyclopropanation of both, an electron rich (benzyl protected cinnamyl alcohol) and electron poor (methyl cinnamate) alkene. All the salts tested were found to be inactive with both alkenes (**Equation 4-3** and **Equation 4-4**). Complexes of cobalt and ruthenium bearing chiral ligands were also found not to be active (**Equation 4-5**).

Tested unreactive salts:

$Zn(OTf)_2$	ZnI_2
$Zn(TFA)_2$	Crabtree
$Zn(OAc)_2$	

Ph-BOX (0.07 equiv)
Salt (0.05 equiv)

$Ph\diagup\diagdown\diagup OBn$
2p $\xrightarrow{\quad}$ $Ph\triangleleft\diagdown OBn$ **3p**

CH_2N_2 / DCM (10 equiv)
DCM, 0 °C

Tested control salts:

$Pd(OAc)_2$	100% yield (0%ee)
CuOTf-0.5PhMe	84% yield (20%ee)

Equation 4-3

Tested unreactive salts:

AuI	$Zn(OTf)_2$	$NiCl_2$
AuCl	ZnI_2	$Sc(OTf)_3$
$AuBr_3$	AgOTf	
$Au(OAc)_3$	$AgBF_4$	$Yb(OTf)_3$

Ph-BOX (0.07 equiv)
Salt (0.05 equiv)

$Ph\diagup\diagdown\diagup CO_2Me$
2a $\xrightarrow{\quad}$ $Ph\triangleleft\diagdown CO_2Me$ **3a**

CH_2N_2 / DCM (10 equiv)
DCM ou PhMe, -30 °C

Equation 4-4

Equation 4-5

4.2.5. Further discussion on the copper-catalyzed cyclopropanation of alkenes

As previously stated, fast addition of a solution of diazomethane is not compatible with the bisoxazoline•copper catalyzed cyclopropanation reaction. An inert gas flow addition method was required to achieve good conversions. Two main hypotheses had led us to test this later method of diazomethane delivery. Firstly, we hypothesized that some impurities contained in the diazomethane solution could inhibit the catalyst and shut down the reaction prematurely thus resulting in very low yields of the cyclopropane product. By adding diazomethane with the aid of a vector gas flow (nitrogen or argon), only volatiles

would be delivered to the reaction vessel. Any non-volatile impurities would not be transferred to the reaction mixture. However, this hypothesis was not unequivocally confirmed and NMR analysis of the diazomethane solution showed similar compositions, before and after a gas transfer. Secondly, the gas delivery method delivers the diazomethane over a longer period of time. It is reasonable to postulate that an excess of diazomethane would favor the formation of side products. For example, the metallic carbene ($L_nM=CR_2$, **Figure 4-14**) could be converted to a carbene dimer (ethylene), or into poly(methylene) by the pathways depicted in **Figure 4-14**. In this case, diazomethane is competing directly with the substrate (S) for reaction with the metal carbene. By lowering the concentration of diazomethane in the reaction media, the rates of the competing processes leading to destruction of the reagent are decreased.
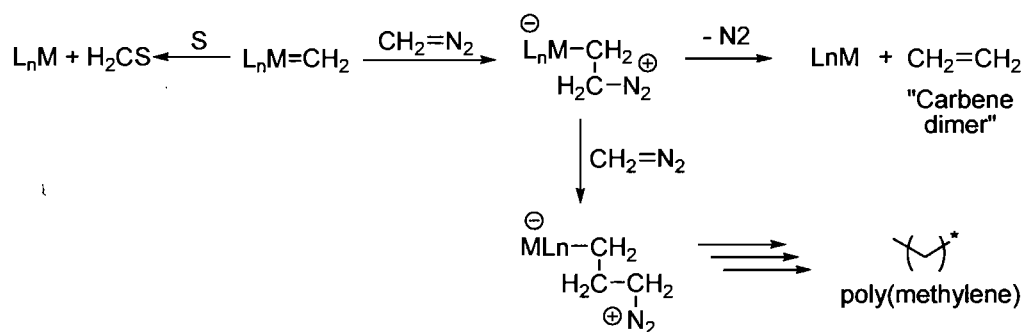
Figure 4-14

Cinnamate esters can also undergo 1,3-dipolar cycloaddition with diazomethane to form pyrazones (**Figure 4-15**). For example, we found that when diazomethane is added to methylcinnamate in dichloromethane at 0 °C the reaction is complete in less than one hour with quantitative yield. This reaction occurs without the presence of a catalyst. However, under the same reaction conditions when a metal salt is added as a catalyst, only traces of pyrazones ($\leq 10\%$) can be observed in the crude reaction mixture, the main product being the desired cyclopropane. By lowering the reaction temperature to between -40 °C and -20 °C, no pyrazone was observed in the crude cyclopropanation reaction mixture.

Furthermore, in a similar control experiment as described above (without the use of a catalyst), no cycloaddition product can be observed at temperatures below -20 °C. It is not known if the pyrazone products can inhibit the catalyst or if the presence of a catalyst further promotes the formation of pyrazones. In addition, when pyrazones were submitted to standard reaction conditions, the formation of the cyclopropane was not observed (**Figure 4-15**).
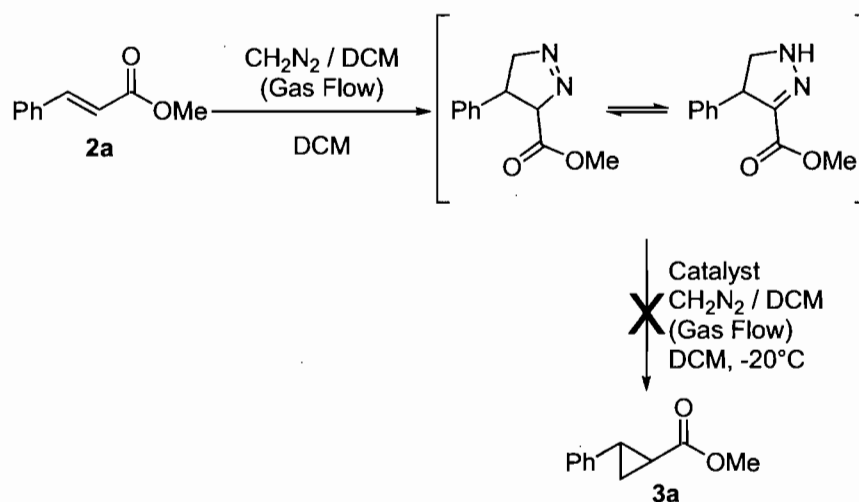
Figure 4-15. Diazomethane 1,3-dipolar cycloaddition.

At this time we cannot explain why the reaction does not proceed to complete conversion. The catalyst seems to become inactive during the reaction and a brown viscous oil forms within the reaction mixture. One possibility could be that the catalyst is trapped at the terminal position of a polymethylene chain (see Figure 4-14). Evidence for this is that residual copper species prevented NMR analysis of the oil.

4-39

Many different structural modifications were done to the bisoxazoline ligand in order to optimize the enantioselectivities of the cyclopropanation reaction. The structural components in green (**Figure 4-16**) have been modified to determine how they affect both, the yield and the enantioselectivity of the reaction. Areas in red have not been modified and could be the subject of a follow-up work.
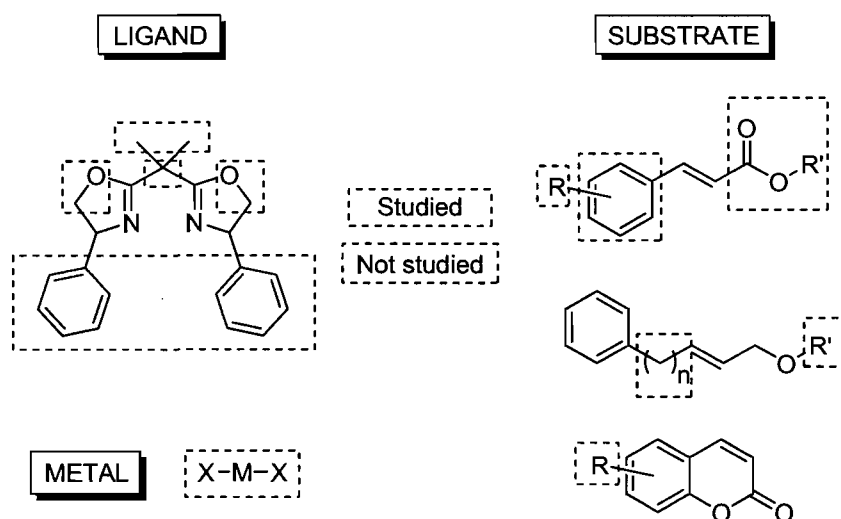
Figure 4-16. SAR type analysis of ligand and substrate.

This study provides ground-work for the development of a general catalytic enantioselective cyclopropanation of substituted as well as unsubstitututed alkenes. The main advantage of this method is the substoichiometric use of a metal complex and of an enantiopure chiral ligand. Most other methods that allow cyclopropanation of unfunctionalized alkenes, require the use of excess pyrophoric organometallic reagents and must rely on the use of stoichiometric (or close to stoichiometric) quantities of chiral material.

4.3. Palladium-catalyzed cyclopropanation of alkenes using diazomethane

4.3.1. Background

Palladium complexes are among the most efficient cyclopropanation catalysts for reactions involving diazomethane. However, even though numerous chiral palladium complexes have been tested in this cyclopropanation reaction, they always led to racemic cyclopropane derivatives.[39]

The mechanism for this reaction remains unclear but metal carbene or carbenoid species have been postulated as potential reactive intermediates for this reaction. Schechter favored the implication of a metal carbene since he observed the expected dimerization product resulting from that species.[40] This hypothesis was supported by Hubert who added that the alkene needed to be coordinated to the metal for the cyclopropanation to occur.[41] However, Doyle has shown that coordinated alkenes are not reactive and free alkenes react preferentially.[42]

McCrindle[43] demonstrated by crystallography that a palladium carbenoid was formed upon addition of diazomethane to a palladium halide salt. This carbenoid could not be transferred

[39] Denmark, S. E.; Stavenger R.; Faucher A. M. ; Edwards J. P. *J. Org. Chem.* **1997**, *62*, 3375; (b) Ph.D thesis, James P. Edwards, **1991**, University of Illinois.
[40] Schechter, H. ; Shankar, B. K. *Tetrehedron Lett.* **1982**, *23*, 2277.
[41] Anciaux, A. J. ; Hubert, A. J. ; Noels, A. F. ; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695.
[42] Doyle, M. P.; Wang, L.; Loh, K. L. *Tetrehedron Lett.* **1984**, *25*, 4087.
[43] McCrindle, R. ; Arsenault, G. J. ; Farwaha, R. ; McAlees, A. ; Sneddon, D. *J. Chem. Soc. Dalton Trans.*, **1989**, *62*, 761.

to an alkene but the addition of excess diazomethane to this complex formed an undefined species that did then readily transfer a methylene group to an alkene. Failed attempts by Denmark to develop an asymmetric palladium catalyzed cyclopropanation reaction were described in the introduction chapter concerning the cyclopropanation (**section 3.4.6**). In order to explain the absence of enantioselectivity in this reaction, he postulated that either a free carbene was responsible for the cyclopropanation reaction or that a ligand free palladium carbene was involved.

The use of a palladium complex as a catalyst is appealing because of its ability to convert alkenes into cyclopropanes very efficiently upon diazomethane decomposition. However the literature precedent suggests that this process may not be possible.

Examples of diastereoselective cyclopropanation reactions involving palladium and diazomethane are known and were briefly discussed in section **3.4.5**. For example, Vallgrada's use of a chiral auxiliary to control the selectivity of the cyclopropanation reaction is depicted in **Tableau 4-10**.[44] A variety of cinnamate amides were submitted to the reaction conditions and it was found that the β-substituent modulated the outcome of the reaction. In section 4.3.3 we describe our use of this reaction as a probe to gain insights about the nature of the catalytically active species involved in these reactions.

Chiral *N*-heterocyclic carbenes (NHC) have emerged as potential ligands for use in catalytic asymmetric processes. They are known to bind strongly to metal centers and to increase the stability of catalysts (see Chapter 5 for a more detailed introduction on this subject). **Figure 4-17** illustrates some chiral NHC precursors and NHC metal complexes.[45]

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[44] (a) Vallgarda, J.; Appelberg, U.; Csoregh, Il; Hacksell, U. *J. Chem. Soc., Perkin Trans 1* **1994**, *21*, 461; (b) Vallgarda, J.; Hacksell, U. *Tetrahedron Lett.* **1991**, *32*, 5625.

[45] For an excellent review see: (a) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951; or see: (b) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483; (c) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913; (d) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem.*

Tableau 4-10. Vallgarda's diastereoselective cyclopropanation.
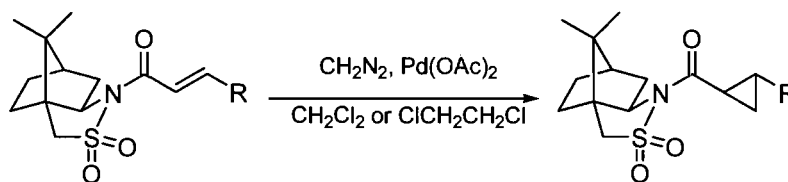
R	Yield (%)	de (%)
Ph	73	86
2-MeO-C$_6$H$_4$	73	92
3-MeO-C$_6$H$_4$	63	72
4-NC-C$_6$H$_4$	29	60

Enders   Rovis   Grubbs

Hoveyda   Hartwig   Burgess
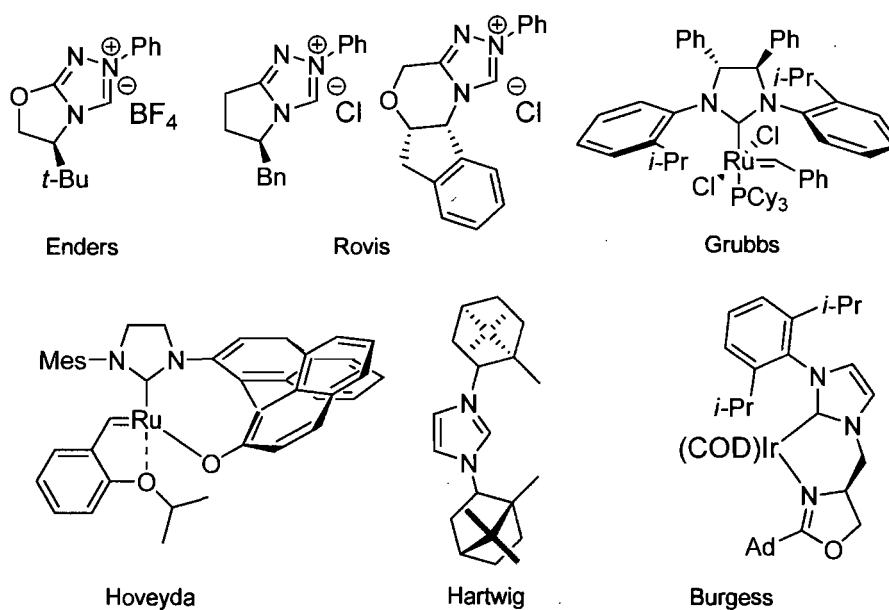
Figure 4-17. Chiral NHC ligands used in catalysis.

Soc. **2002**, *124*, 10298; (e) Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2005**, *127*, 6284; (f) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18; (g) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954; (h) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402; (i) Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878.

If ligand dissociation from palladium was the reason for poor stereoselectivity in the cyclopropanation reation, NHC's were envisioned as ligands that could potentially solve the problem due to their ability to bind strongly to metals. Lebel and Charette have been involved in the study of novel chiral NHC-Pd complexes toward the development of efficient chiral catalysts for the enantioselective cyclopropanation reaction. The first chiral catalyst that was prepared was highly reactive in the diazomethane cyclopropanation reaction but afforded racemic cyclopropanes. The structure of the catalyst was established by X-ray crystallographic analysis and shown to involve two bound chiral NHC (**Figure 4-18**).[46]
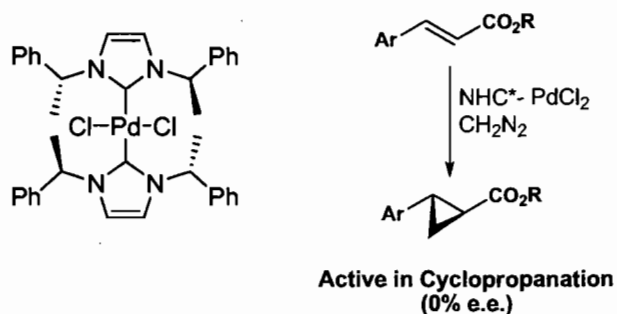
Figure 4-18. Enantioselective cyclopropanation using a chiral NHC•Pd complex.

4.3.2.   Further discussions on the metal catalyzed diazomethane cyclopropanation of alkenes

We felt that the mechanism of the palladium catalyzed cyclopropanation reaction involving diazomethane is not well understood and that it is only through its study that an enantioselective catalytic reaction will emerged.

[46] Lebel, H.; Salvatori, M. del R.; Bélanger-Gariepy, F. *Acta Cryst.* **2004**, *E60*, 755.

Preliminary work on the use of chiral NHC's by Lebel had not resolved the enantioselectivity "enigma" of this reaction. Nonetheless, more efforts on the use of these ligands are justified since the α-methylbenzylamine derived NHC does not efficiently project the chirality near the presumed reactive center (**Figure 4-18**). Additionally, if ligand dissociation is the problem, NHC could potentially solve this issue.

Before dedicating further efforts based on this premise, we were looking for indications that NHC based ligands could possibly lead to the formation of different reactive species than those involved in previous cyclopropanation reactions. We postulated that if the same ligand-free active species was generated regardless of the ligand used, then the same diastereoselectivities should be obtained in a diastereoselective reaction. However, if the ligand was involved in the transition structure leading to product, then it would be quite plausible that the diastereoselectivity of a reaction would be ligand dependant.

4.3.3. Diastereoselective cyclopropanation using various palladium complexes

Vallgarda's diastereoselective reaction was chosen as a probe to get further insights about the nature of the catalytically active species involved in the palladium catalyzed cyclopropanation reaction.

Two alkenes (**2ak** and **2al**) bearing a chiral camphorsulphonic acid derived auxiliary were submitted to cyclopropanation conditions with diazomethane using different catalysts.[47] The reaction using both palladium acetate and palladium dibenzylideneneacetone displayed similar diastereoselectivities as those reported for the formation of cyclopropanes from alkene **2ak** and **2al** (**Tableau 4-11**, entries 1, 2 and 5). The catalyst containing NHC ligands exhibited not only slightly lower diastereoselectivities for both substrates but also

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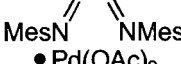
[47] **2ak**, **2al**, **3ak** and **3al**: See ref. 45 (chapter 3).

lower yields (**Tableau 4-11**, entries 3 and 6). Palladium acetate bearing a diimine ligand led to a similar diastereoselectivity as ligand free palladium acetate. These results hinted towards the fact that NHC ligands had an influence on the cyclopropanation reaction. However, it is not clear whether or not the ligand is involved in the transition structure leading to product. More rigourous experiments at various palladium concentrations are still needed since the slight difference in dr when various ligands are used may be a reflection of the concentration of "free palladium" in each reaction. In other words, strongly coordinating ligands liberate less catalytically active free palladium therefore, the overall concentration in catalytically active palladium is lower in the case of NHC•Pd complexes. This would also explain the lower yields observed with NHC•Pd when both alkenes were treated with diazomethane. Secondly, the diastereoselectivity may also depend upon the palladium concentration.

Tableau 4-11. Diastereoselective cyclopropanation reactions with various palladium complexes.
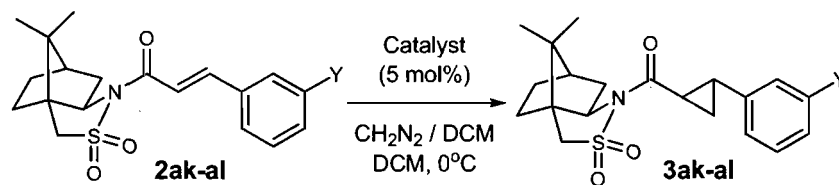
Entry	Y	CATALYST	YIELD (%)	d.r.
1	MeO	Pd(OAc)$_2$	71 (**3ak**)	8:1
2	MeO	Pd$_2$(dba)$_3$	70 (**3ak**)	8:1
3	MeO	Imes$_2$PdCl$_2$	65 (**3ak**)	6:1
4	H	MesN⏜NMes •Pd(OAc)$_2$	94 (**3al**)	10:1
5	H	Pd(OAc)$_2$	93 (**3al**)	9:1
6	H	Imes$_2$PdCl$_2$	65 (**3al**)	6:1
7	H	Silica gel	0 (**3al**)	–

4.3.4. Additional insights into the mechanism of the palladium catalyzed cyclopropanation

We had previously postulated that an electrophilic metal carbene was involved in the copper catalyzed cyclopropanation reaction. This followed the trend found in the literature with diazocarbonyl cyclopropanation chemistry.[1a] An experiment was designed to allow an insight into the electronic nature of the methylene transfer agent in the case of palladium catalysis (**Equation 4-6**). We mixed equimolar amounts of electronically different alkenes and submitted them to the cyclopropanation conditions using only one equivalent of diazomethane. We have found that an electron deficient alkene was converted into its corresponding cyclopropane in a greater proportion than the electron rich alkene. This is in contrast with the results obtained with copper complexes and led to the postulate that a nucleophilic metal carbene is involved with palladium catalysis. Of course, this is not definitive proof since Salomon and Kochi have shown that binding of the alkene to the metal center also plays a key role in chemoselective cyclopropanation.[48]
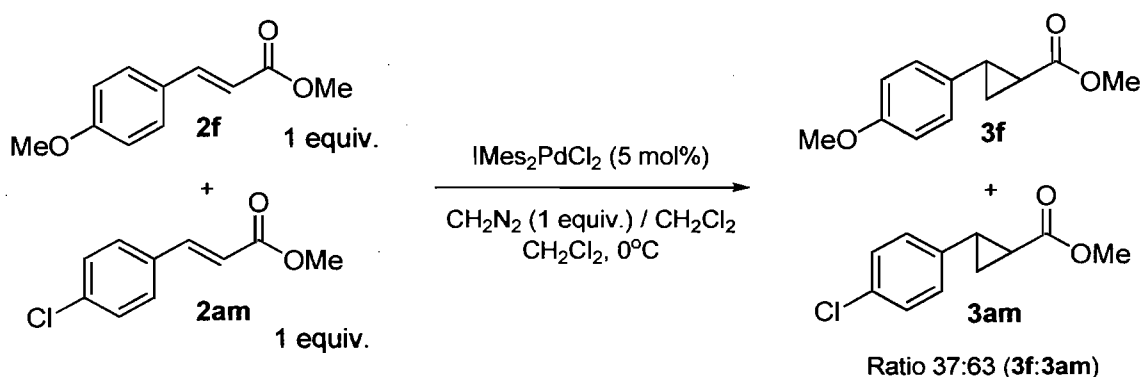
Equation 4-6

[48] Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300.

4.3.5.   Cyclopropanation using σ-donating ligands

Generally, strong σ-donating ability of a ligand is associated with a strong binding to a metal center. Denmark proposed that in the case of bisoxazoline ligands (**Figure 4-19**, A), dissociation leading to a ligand free metal carbene could possibly explain the lack of enantioselectivity when chiral palladium complexes were used as the cyclopropanation catalysts. Stoltz had successfully used a sparteine palladium complex in asymmetric oxidation.[49] We turned our attention to ligands known for their strong binding abilities to palladium such as sparteine and NHC's (**Figure 4-19**, B and C) to try to solve this problem. Unfortunately, as described in **Tableau 4-12**, although these complexes were very effective catalysts, they all led cleanly to racemic cyclopropane **3a** from alkene **2a**.

Bis(oxazoline)-PdX₂

A

(-)-Spart·PdCl₂

B

NHC-PdXₙLₙ

C
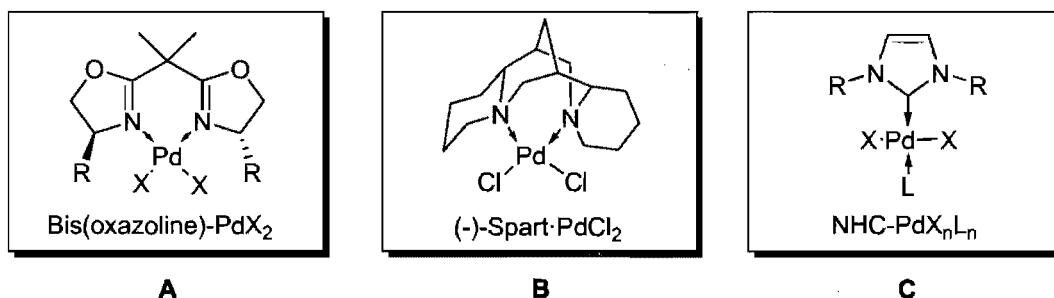
Figure 4-19. Various σ-donating ligands tested in the Pd-catalyzed cyclopropanation.

[49] Nielson, R. J.; Keith, J. M.; Stoltz, B. M.; Goddard, W. A. III. *J. Am. Chem. Soc.* **2004**, *126*, 7967.

Tableau 4-12. Cyclodpropanation reactions using various palladium complexes bearing σ-donating ligands.
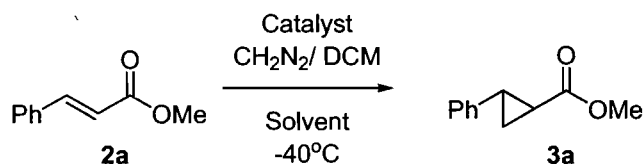
Entry	Solvent	Catalyst	Yield (%)	e.e. (%)
1	PhMe	Sparteine (20 mol%) Pd(OAc)₂ (5 mol%)	98	0
2	DCM	Sparteine (20 mol%) Pd(OAc)₂ (5 mol%)	96	0
3	DCM	Sparteine·PdCl₂ complex (1 mol%)	83	0
4	DCM	Ph-bisox·CuOTf (5 mol%) *	84	72

*control experiment

Equation 4-7 illustrates possible reaction pathways and reactive intermediates for the reaction of diazomethane with a palladium salt. Diazomethane can insert methylene into a palladium-halide bond via the elimination of nitrogen to generate a carbenoid intermediate. This step can be repeated to form a bis-carbenoid species. Reductive elimination could lead to a Pd(0) intermediate which could then lead to a ligand free metal carbene intermediate. The three intermediates in blue are all possibly active cyclopropanation species. Strategies to develop an enantioselective process must account for all possible mechanisms and will be different depending of the active species in play during the cyclopropanation step. Deuteration experiments have shown that some isolated palladium carbenoids were not

active methylene transfer agents.[43] It is not known how general these observations are and we cannot rule out a possible carbenoid mechanism for this reaction. Attempts to detect by-products that would result from a reductive elimination pathway were not successful.[50]
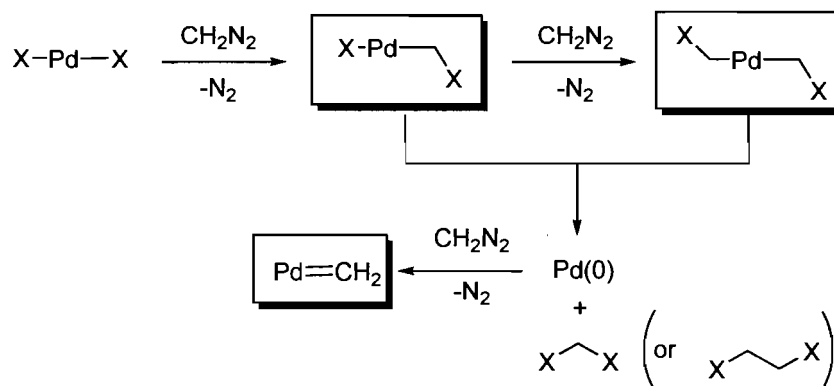
Equation 4-7

In order to develop the first palladium-catalyzed enantioselective diazomethane cyclopropanation reaction, we had to explore all possible avenues. If a carbenoid species was in play during the cyclopropanation process (**Equation 4-7**), the replacement of the X groups by chiral groups may lead to some enantioselectivities. We hypothesized that chiral palladium carboxylates would have a fair chance of success in this process if a carbenoid was indeed the active methylene transfer agent. Several chiral catalysts were generated by treating palladium acetate with chiral carboxylic acids. Removal of acetic acid followed by filtration on silica gel afforded catalysts that were active in the cyclopropanation using diazomethane. Unfortunately all the chiral palladium carboxylates led to racemic cyclopropane derivatives (**Equation 4-8**).

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[50] Lebel, H.; Sanchez-Salvatori, M., PDF report, *unpublished results*

49% conv. (R=Me **3a**)
0% e.e.

75% conv. (R=Me **3a**)
0% e.e.

76% conv. (R=Me **3a**)
0% e.e.

42% conv. (R=*i*-Pr **3e**)
0% e.e.
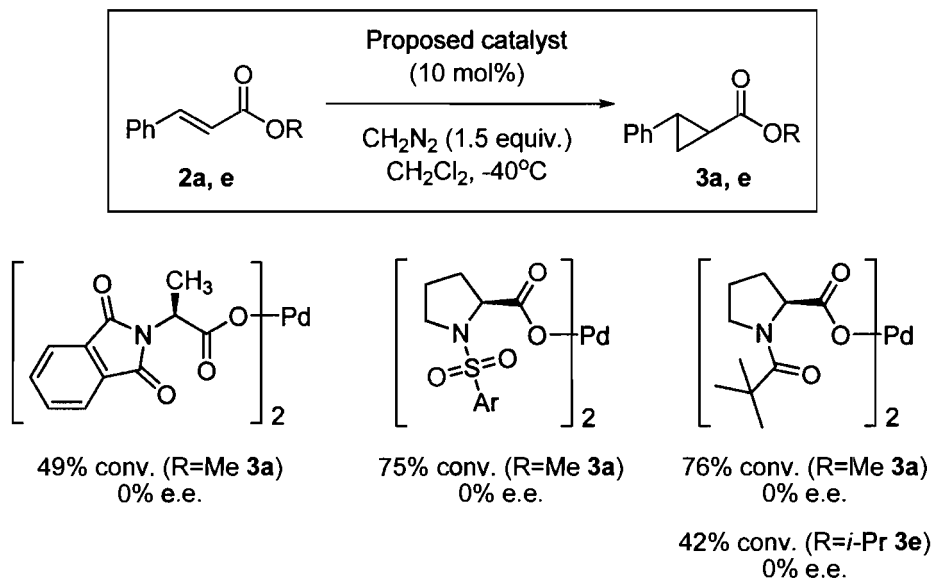
Equation 4-8

4.4. Conclusion

Since all our efforts to develop an enantioselective cyclopropanation reaction have failed, an alternative hypothesis must be formulated in order to explain these observations. Our main hypothesis is that very low concentration of a ligand free soluble palladium species is actually the active catalyst in this reaction that obviously leads to racemic cyclopropane.[51] If this hypothesis was not true, by comparison with the very similar copper reaction, enantioprojection of the ligand should have led to enantioenriched cyclopropane products.

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[51] (a) Alimardanov, A.; Schmieder-van de Vondervoort, L.; de Vries, A. H. M.; de Vries, J. G. *Adv. Synth. Catal.* **2004**, *346*, 1812; (b) de Vries, A. H. M.; Mulders, J. M. C. A.; Mommers, J. H. M. Henderickx, H. J. W.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 3285.

Chapitre 5 : Synthèse de complexes métalliques de carbènes *N*-hétérocycliques (CNH): Introduction

5.1. Formation de complexes métalliques normaux de carbènes *N*-hétérocycliques

Depuis les découvertes de Öfele[1] et Wanzlick[2], les complexes métalliques de carbènes *N*-hétérocycliques (CNH) ont modifié considérablement le domaine de la catalyse. La diversité des techniques qui ont été développées pour synthétiser ces complexes est illustrée dans ce chapitre à l'aide d'exemples et de notes historiques.

La découverte des carbènes *N*-hétérocycliques comme ligands pour des complexes métalliques, est le résultat de travaux concomitants de Öfele et de Wanzlick. Les travaux de Öfele ont principalement consisté à traiter un sel d'imidazolium avec un hydrure de chrome pour produire un complexe CNH-Cr alors que simultanément, ceux de Wanzlick utilisaient un sel de mercure pour produire un complexe (CNH)₂-Hg (**Figure 5-1**).

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[1] Öfele, K. *J. Organomet. Chem.* **1968**, *12*, 42.
[2] Wanzlick, H. W.; Schönherr, H. J. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141.
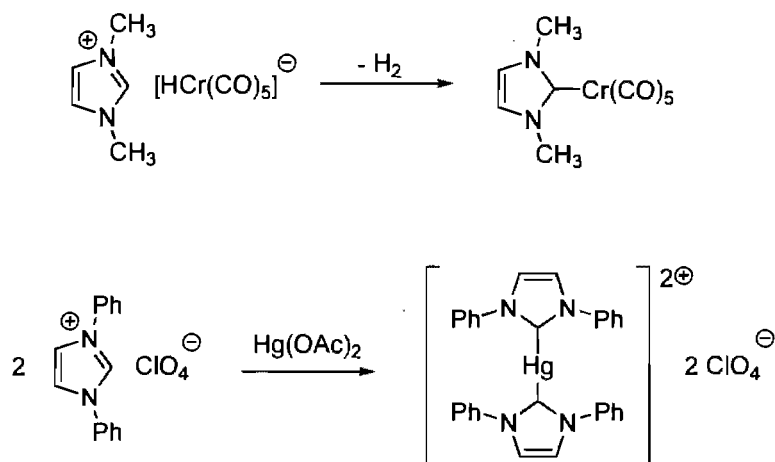
Figure 5-1. Les premiers complexes CNH-M de Öfele (Cr) et de Wanzlick (Hg).

L'intérêt que la communauté scientifique porte envers ce type de complexe est de plus en plus important. De nombreux complexes ont été synthétisés avec plusieurs métaux de transition et ensuite, ont été utilisés en tant que catalyseurs dans une multitude de réactions.[3] L'exemple le plus connu, dû à son succès en catalyse, a été la substitution d'une phosphine par un carbène *N*-hétérocyclique sur le catalyseur de métathèse d'alcènes[4] de Grubbs de première génération (**Figure 5-2**).[5] Dans un premier temps, un carbène insaturé (IMes) dérivé d'un imidazolium a pu remplacer (par déplacement) une des phosphines du catalyseur pour former un complexe plus actif que son précurseur.[6] Deuxièmement, lorsqu'un carbène saturé a été utilisé (SIMes), un catalyseur encore plus actif a été généré.

[3] Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.

[4] Revue à propos de la métathèse d'alcènes: Astruc, D. *New J. Chem.* **2005**, *29*, 42.

[5] Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18 et références citées.

[6] Pour la première isolation de CNH libre voir: (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361 et pour des revues à ce sujet: (b) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913; (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

La décomposition thermique d'un carbène masqué a été nécessaire dû à la difficulté d'isolement du carbène saturé libre lors de la synthèse du carbène de Grubbs de deuxième génération.[7,8]
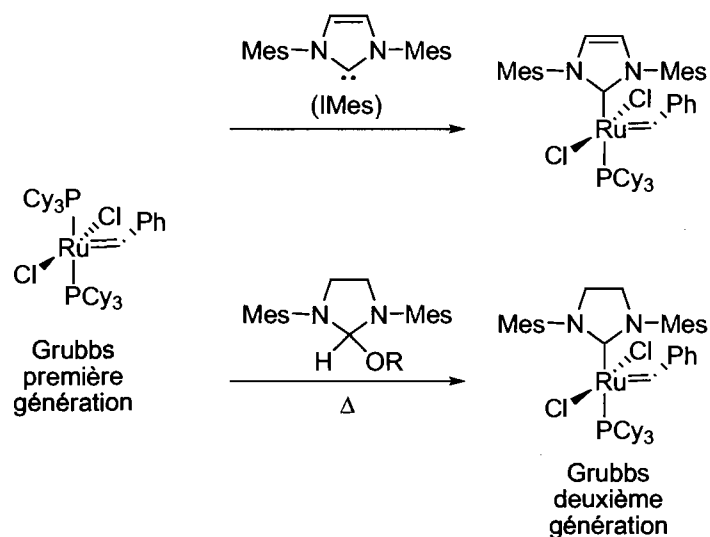
Figure 5-2. Déplacement d'une phosphine par un CNH sur le catalyseur de Grubbs et utilisation d'un CNH masqué dans la synthèse du catalyseur de deuxième génération.

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[7] Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

[8] De manière concomitante à Grubbs, Nolan et Herrmann ont aussi publié le catalyseur de Grubbs impliquant le carbène insaturé IMes: (a) Huang, J.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 2674; (b) Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362.

Le couplage au palladium est un autre domaine où le succès des complexes métalliques de carbènes *N*-hétérocycliques (CNH) a été important.[9] Le premier exemple de couplage impliquant des complexes du type CNH-Pd a été décrit par Herrmann en 1995 dans le cadre d'une réaction de Heck.[10] La synthèse du catalyseur a été effectuée à partir de la réaction d'un sel d'imidazolium avec de l'acétate de palladium (**Figure 5-3**). Il a été ensuite utilisé pour générer des complexes impliquant deux carbènes par métal ayant une géométrie *cis*. Une autre version de la réaction avec deux imidazoliums pontés est aussi possible.

En reaction de
Suzuki: TON > 200
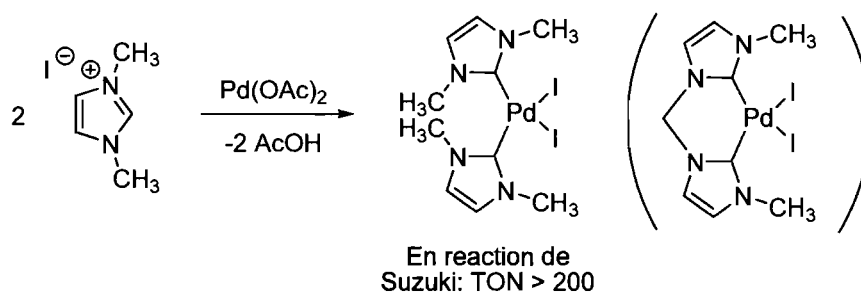
Figure 5-3. Premier catalyseur de couplage au palladium impliquant des CNH.

Plusieurs de ces complexes sont des catalyseurs efficaces qui ont des « turnover number » (TON) de plus d'un million (**Figure 5-4**).[11,12]

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[9] (a) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889; (b) Fürstner, A.; Leitner, A. *Synlett* **2001**, 290; (c) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C. P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617*, 616; (d) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1077; (e) Viciu, M. S.; Grasa, G. A.; Nolan, S. P. *Organometallics* **2001**, *20*, 3607; (f) Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C. M.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866; (g) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C. L.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69; (h) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470; (i) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166; (j) Eckhardt, M.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 13642; (k) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 3690.

[10] Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371.

[11] McGuinness, D. S.; Cavell, K. J. *Organometallics*, **2000**, *19*, 741.

TON = 1 700 000   TON = 2 700 000
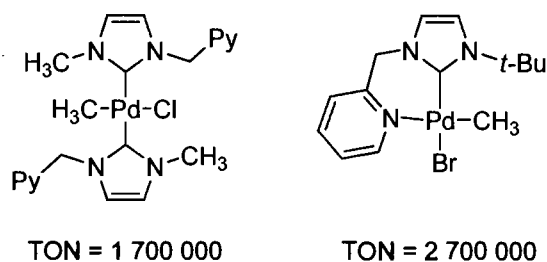
Figure 5-4. Catalyseurs pour la réaction de Suzuki ayant un TON dépassant le million.

Par la suite, de nombreux travaux ont été réalisés pour développer l'utilisation de CNH pour des couplages au palladium, notamment par Nolan, qui a synthétisé plusieurs catalyseurs structurellement définis **(Figure 5-5)**[13] et d'autres qui furent générés *in situ* à partir de précurseurs de carbènes **(Figure 5-6)**.[14] Il faut aussi noter que Fu, Hartwig et Jutan ont également grandement contribué à ce domaine.[15]

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[12] Tulloch, A. A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenza, S.; Hursthouse, M. B. *Chem. Commun.* **2000**, 1247.

[13] (a) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470; (b) Viciu, M. S.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 2229; (c) Viciu, M. S.; Kelly, R. A., III; Stevens, E. D.; Naud, F.; Studer, M.; Nolan, S. P. *Org. Lett.* **2003**, *5*, 1479.

[14] Mini-revue sur le sujet: Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.

[15] (a) Eckhardt, M.; Fu. G. C. *J. Am. Chem. Soc.* **2003**, *125*, 13642; (b) Stauffer, S. R.; Lee, S. W.; Stambuli, J. P.; Heuck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423; (c) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.

Suzuki
Amination
Couplage d'énolates

Amination

Amination
Couplage d'énolates

Ar = 2,6-*i*-Pr-Ph

Ar' = Mes, 2,6-*i*-Pr-Ph ou Ad
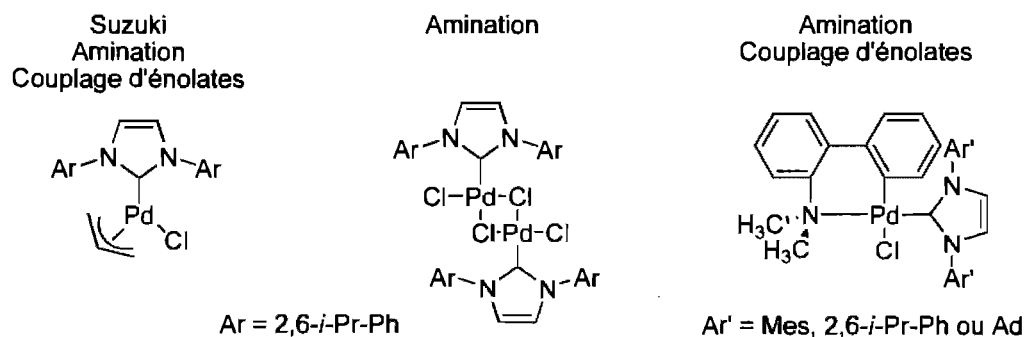
Figure 5-5. Catalyseurs pour des couplages au palladium structurellement définis de Nolan.

Heck

Heck
Sonogashira
Suzuki
Stille
Amination

Ar' = Mes, 2,6-*i*-Pr-Ph ou Ad
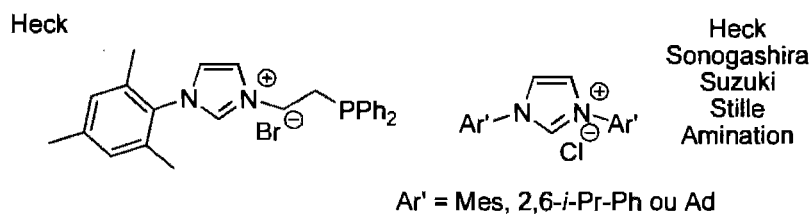
Figure 5-6. Précurseurs de carbènes pour la génération *in situ* de catalyseurs au palladium pour les réactions de couplages.

Dans le contexte de cette thèse, il est important de souligner les travaux de Rajanbabu bien qu'à ce jour, il n'y ait pas encore d'exemples d'utilisation de ce type de complexes en catalyse. Ce dernier a fait réagir des sels d'imidazolium avec des sels de palladium sans ajouter de base pour la synthèse de complexes de palladium (**Figure 5-7**).[16] Ce type de réactions a aussi déjà été décrit préalablement par Herrmann.[8,9]

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[16] Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; Rajanbabu, T. V. *Org. Lett.* **2000**, *2*, 1125.
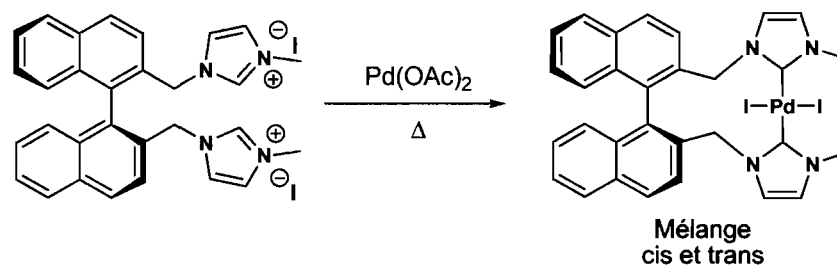
Figure 5-7. Synthèse d'un complexe de CNH et de palladium de Rajanbabu.

Plus récemment, Sigman[17] et Stoltz[18] ont travaillé sur la synthèse de catalyseurs utiles pour l'oxydation d'alcools primaires ou secondaires. Sigman a utilisé les CNH en tant que ligand pour le palladium.[19] Son nouveau catalyseur, qui comprend un CNH lié à l'acétate de palladium qui est aussi coordonné par une molécule d'eau, est actif dans la réaction de Wacker[20] et dans l'oxydation d'alcools.[21] Utilisé conjointement avec une base chirale énantiopure, il a pu effectuer des résolutions d'alcools chiraux racémiques. La synthèse a été accomplie à partir de sels d'imidazolium traités avec une base en présence de chlorodimères-π-allyle de palladium, suivie par l'ajout d'acide chlorhydrique. Le dimère intermédiaire $(CNH)_2Pd_2Cl_2$ a pu être isolé et traité avec de l'acétate d'argent pour donner le catalyseur de Sigman (**Figure 5-8**).[19]

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[17] Jensen, D. R.; Pugsley, J. S.; Sigman, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 7475.

[18] Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 7725.

[19] Jensen D. R.; Sigman, M. S. *Org. Lett.* **2003**, *5*, 63.

[20] Cornell, C. N.; Sigman, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2796.

[21] Jensen, D. R.; Schultz, M. J.; Mueller, J. A.; Sigman, M. S. *Angew. Chem. Int. Ed.* **2003**, *42*, 3810.
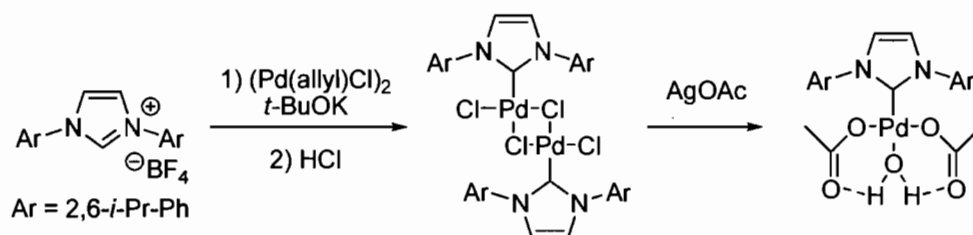
Figure 5-8. Synthèse d'un catalyseur d'oxydation de Sigman.

Un autre domaine où l'utilisation de diaminocarbènes cycliques a amélioré de manière significative l'efficacité des catalyseurs est l'hydrosilation. L'addition de l'unité Si-H à un alcène pour former un alkylsilane est d'une grande importance industrielle. Marko, en utilisant des CNH au lieu de phosphines pour coordonner le platine, a réussi à enrayer la formation de sous produits réactionnels nuisibles (**Figure 5-9**).[22] Le même catalyseur impliquant une phosphine au lieu du diaminocarbène n'avait pas réussi à diminuer la formation de sous-produits nuisibles à la réaction par rapport à l'utilisation du catalyseur de Karsted dans la même réaction.
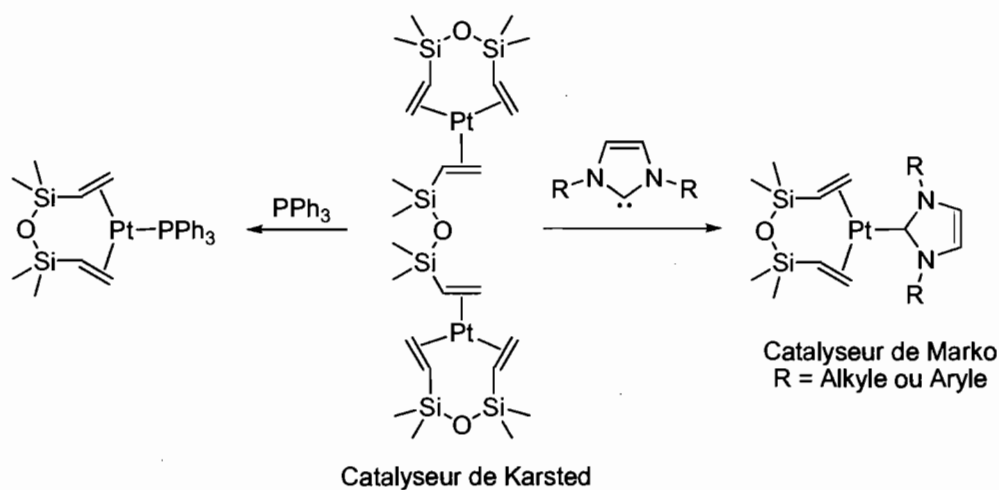
Figure 5-9. Catalyseur d'hydrosilation de Karsted amélioré par Marko à l'aide d'un CNH.

En résumé il existe plusieurs méthodes pour la synthèse de complexes métalliques impliquant des carbènes *N*-hétérocycliques (**Figure 5-10**). Toutes ces méthodes ont en commun le fait de générer un carbène libre qui est parfois isolable. Toutefois, son isolement n'est pas toujours nécessaire et il peut être piégé *in situ* par coordination à une espèce métallique. Les méthodes de synthèses sont: 1) déprotonation de sels d'imidazolium, 2) décomposition thermique de carbènes masqués, 3) insertion de métaux dans un dimère de Wanzlick (qui lui est postulé être en équilibre avec le carbène libre) et 4) désulfurisation de thio-urées. [23]
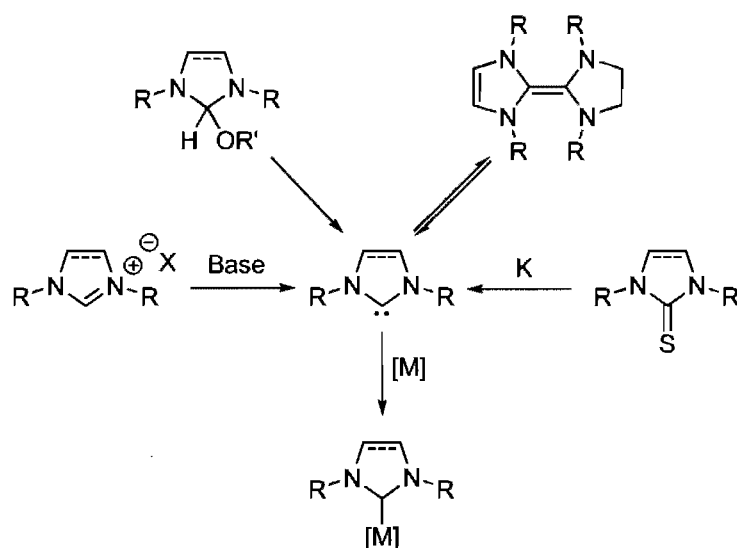
Figure 5-10. Les méthodes de synthèse des complexes CNH-M.

[22] Markó, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P. *Science* **2002**, *298*, 204.

[23] Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fürstner, A. *Chem. Eur. J.* **2005**, *11*, 1833.

Étant donné les nombreux champs d'applications pour ces catalyseurs métalliques, quantité d'efforts ont été déployés pour développer ce domaine d'étude. Pour contrôler et utiliser efficacement les capacités du palladium, des ligands tels les phosphines ont été utilisés. Depuis le succès retentissant des catalyseurs comprenant des phosphines et du palladium, une panoplie de mono- et bisphosphines ont été développées. Maintenant, les carbènes *N*-hétérocycliques sont de plus en plus utilisés en tant que ligands pour les métaux de transition et ils ont beaucoup contribué à améliorer les catalyseurs pour les couplages croisés et les métathèses d'alcènes. Initialement utilisés comme substituts aux phosphines, ils constituent maintenant une classe à part surpassant souvent les phosphines pour stabiliser les catalyseurs et augmenter leur pouvoir catalytique.

5.2. Formation de complexes anormaux entre des sels d'imidazolium et des métaux de transition

5.2.1. Réactivité générale des groupes C-H des carbènes ou précurseurs de carbènes.

Malgré les précédents de la littérature, des comportements inattendus surviennent parfois lors de réactions chimiques et il existe quelques exemples dans le domaine des carbènes *N*-hétérocycliques. En étudiant de manière plus approfondie les publications sur le sujet, nous pouvons trouver des indices qui auraient permis aux chimistes de pouvoir prédire certaines réactivités anormales.
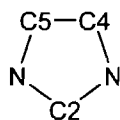
Figure 5-11. Squelette de type imidazole.

Le site réactionnel des CNH ou de leurs précurseurs ne se situe pas exclusivement à la position C2 sur le squelette de type imidazole (**Figure 5-11**). Les CNH libres peuvent subir une chlorination des positions C4 et/ou C5 (selon le cas) par traitement au tetrachlorure de carbone et leur stabilité est plus grande que leurs analogues non halogénés.[24] Ces mêmes positions peuvent être substituées par des atomes de deutérium lorsque les carbènes sont

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[24] Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742.

dissous dans le DMSO ou le méthanol deutéré.[25] La métallation par l'osmium de ces positions a également été observée.[26]

5.2.2.   Réactivité anormale de CNH ou de leurs précurseurs

Le dicarbène illustré à la **Figure 5-12** fut solubilisé en présence d'un sel de fer et une métallation anormale a été observée. Dans le complexe, un des carbènes se lie au fer de manière attendue tandis que l'autre carbène est converti en imidazolium et subit une métallation anormale de son squelette.[27] Le même ligand en présence de ruthénium mène exclusivement à la formation d'un complexe normal.[28] La métallation anormale par le fer, dans ce cas, serait due à l'encombrement stérique du ligand.

R = 2,6-*i*-Pr-Ph
ou
2,6-CH$_3$-4-*t*-Bu-Ph
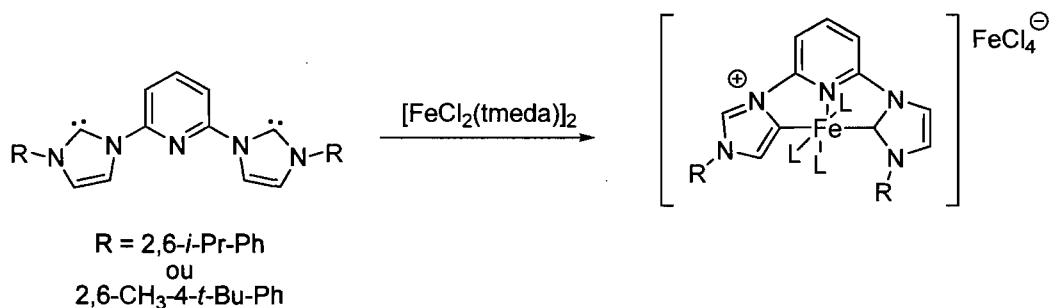
Figure 5-12. Complexe anormal de Danopoulos.

[25] Denk, M. K.; Rodezno, J. M.; Gupta, S.; Lough, A. J. *J. Organomet. Chem.* **2001**, *617*, 242.

[26] Herrmann, W. A.; Roesky, P. W.; Elison, M.; Artus, G.; Ofele, K. *Organometallics* **1995**, *14*, 1085.

[27] Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166.

En fait, l'iridium est connu pour ses capacités à effectuer des réactions d'insertion de type C-H. Crabtree, en 2001, publia une réaction inattendue entre un sel d'imidazolium et un hydrure d'iridium (**Figure 5-13**)[29] lors d'une réaction rappelant celle d'Oféle.[1]
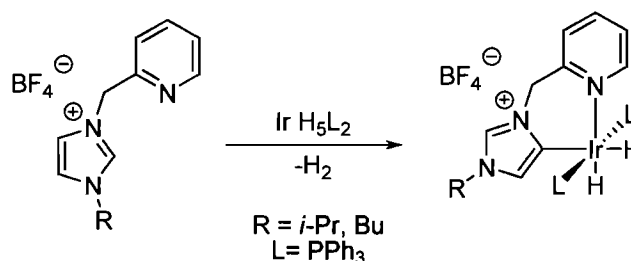
Figure 5-13. Réaction anormale entre un hydrure métallique et un sel d'imidazolium.

L'iridium semble être le premier élément à avoir effectué une métallation anormale d'un imidazolium.[30] Lors de la réaction entre d'un sel d'imidazolium portant une pyridine et d'un hydrure d'iridium, un complexe anormal se forme (**Figure 5-13**). Le même ligand où la pyridine a été substituée par une phosphine permet aussi dans certaines conditions de former le complexe anormal mais moins efficacement.[31] Il faut noter qu'il n'est pas

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[28] Poyatos, M.; Mate, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. *Organometallics* **2003** *22* 1110.

[29] (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274; (b) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.

[30] (a) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290; (b) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. Organometallics **2004**, *23*, 2461; (c) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.

[31] Stylianides, N.; Danopoulos, A. A. ; Tsoureas, N. *J. Organomet. Chem.* **2005**, *690*, 5948.

nécessaire pour le sel d'imidazolium de porter un groupe pyridine ou phosphine pour que la métallation anormale puisse s'effectuer.[32]

Des composés anormaux de platine ont été observés lors de la réaction entre un complexe norbornène-platine et un sel d'imidazolium en présente d'IMes.[33] Ce dernier coordonne le centre métallique de manière attendue tandis que l'imidazolium subit une métallation anormale. Selon les auteurs, le carbène libre (IMes) coordonnerait le métal pour former une espèce capable d'effectuer une addition oxydante dans un lien C-H sur le squelette du sel d'imidazolium en position C4 ou C5.

Meyer a observé qu'une métallation menant à un complexe anormal de cuivre, dans ce cas, à partir d'un carbène N-hétérocyclique libre était possible (**Figure 5-14**).[34]
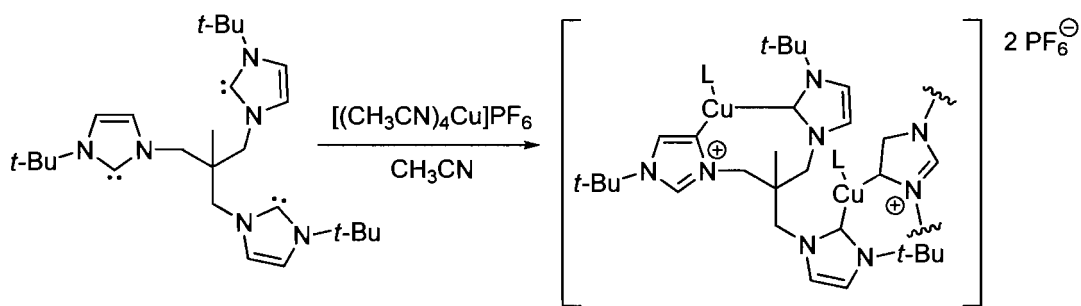
Figure 5-14. Complexe anormal de Meyer.

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[32] Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473.

[33] Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L. *Angew. Chem. Int. Ed.* **2005**, *44*, 5282.

[34] Hu, X.; Castro-Rodrigez, I.; Meyer, K. *Organometallics* **2003**, *22*, 3016.

Il existe un exemple où la déprotonation d'un atome d'hydrogène en position C4 ou C5 d'un CNH lié au potassium par la position C2 mène à une métallation en position anormal bien que dans ce cas, la position C2 était préalablement métallée.[35]

5.2.3.   Explications pour la formation des complexes anormaux.

Le système dans lequel la coordination anormale d'un CNH a été le plus étudiée est celui de Crabtree impliquant l'iridium. Selon Crabtree, le contre-ion du sel d'imidazolium jouerait un rôle important dans la chimiosélectivité de la métallation. L'utilisation de contre-ions qui ont une interaction plus forte avec l'hydrogène en C2 mènerait à la formation de complexes normaux. Les autres contre-ions mèneraient à la formation de complexes anormaux. Du point de vue électronique, lors d'une étude comparative, il fut démontré que les complexes anormaux subissaient une plus importante donation d'électrons par le ligand imidazolium (le CNH anormal) comparativement aux complexes CNH normaux correspondants. [30a,b] De plus, des calculs DFT ont déterminé que les « carbènes anormaux libres » seraient 84 kJ/mol plus énergétiques que le carbène normal libre correspondant.[30c] Des calculs ont aussi démontré que dans le cas de l'iridium, les complexes anormaux seraient isoénergétiques à ceux des complexes normaux.[36] Par contre, cette différence d'énergie serait éliminée lorsque les calculs tenaient compte des contre-ions utilisés. Dans le cas de l'iridium, puisque l'inter-conversion d'un complexe normal en complexe anormal ou vice-versa n'a pas été observée, la croyance actuelle est que le mécanisme de formation des complexes anormaux serait sous contrôle cinétique.[37]

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[35] Arnold, P. L.; Liddle, S. T. *Organometallics* **2006**, *25,* 1485.

[36] Hahn, F. E.; Holtgrewe, C.; Pape, T.; Martin, M.; Sola, E.; Oro, L. A. *Organometallics* **2005**, *24,* 2203.

[37] Kovacevic, A.; Gründemann, S.; Miecznikowski, J. R.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *Chem. Commun.* **2002** *21,* 2580.

Dans les exemples impliquant le fer, le cuivre et l'iridium, il semblerait que la formation de complexes anormaux serait favorisée lorsqu'elle mène à une diminution de l'encombrement stérique autour du centre métallique. Pour le complexe anormal de cuivre de Meyer, la migration d'un atome d'hydrogène est postulée pour expliquer la formation d'un imidazolium à partir du carbène libre. Des raisons strictement stériques seraient à l'origine de la formation de ce complexe anormal.

5.3. Mise en perspective des travaux de recherche

Le nombre de communications impliquant des CNH est en forte croissance d'années en années.[38] L'utilisation en catalyse de complexes de métaux de transition et de CNH est aussi en nombre croissant. Plusieurs catalyseurs sont générés *in situ* et la nature exacte d'une forte proportion d'entre eux demeure inconnue. Il est attendu que pour des CNH dérivés de sels d'imidazolium (la classe la plus importante de CNH), les métaux se lient en position C2 sur le squelette du ligand. Par contre, de plus en plus d'exemples tendent à démontrer que la métallation à d'autres positions est aussi possible dans des conditions communes à la génération de catalyseurs *in situ*.

Nous avons exploré activement plusieurs catalyseurs dans le but d'effectuer des réactions de cyclopropanation catalysées par des complexes de métaux de transition. Nous nous sommes intéressés aux CNH à cause de leur capacité à lier les métaux de transition plus fortement que les phosphines. Bien que le but fût de développer une méthode de cyclopropanation énantiosélective impliquant le diazomethane, nous avions entrepris la synthèse d'un catalyseur ne comportant aucun élément de chiralité soit le IMes$_2$PdCl$_2$. Des résultats inattendus ont été obtenus lors de l'élucidation de la structure exacte du produit obtenu lors de cette synthèse et nous avons entrepris d'explorer de manière plus systématique ces résultats. Cela a mené aux travaux décrits dans les deux prochains chapitres de cette thèse.

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[38] Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596.

Chapitre 6 : Structure and Reactivity of "Unusual" *N*-Heterocyclic Carbene (NHC) Palladium Complexes Synthesized from Imidazolium Salts (Published Article)

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[2] University of New Orleans.

6.1. Article

Recently, a number of new transition metal-catalyzed processes have been developed and optimized through high-throughput and combinatorial methods.[3] Such strategies are particularly efficient for the screening of a large number of transition metal-ligand combinations under various sets of reaction conditions. However, under these *in situ* conditions, the exact nature of the catalytic species is not always precisely known. Indeed, the assumption of a normal mode of binding between ligand and transition metal is most often assumed and may be misleading.

During the course of our studies focusing on ligands suitable to induce enantioselectivity in transition metal-catalyzed processes,[4] we became interested in testing *N*-heterocyclic carbene (NHC)-metal complexes. A number of simple NHC palladium-based complexes have recently emerged as effective catalysts for a variety of cross-coupling reactions.[5] Our

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[3] For recent reviews: (a) Francis, M. B.; Jamison, T. F.; Jacobsen, E. N. *Curr. Opin. Chem. Biol.* **1998**, *2*, 422; (b) Shimizu, K. D.; Snapper, M. L.; Hoveyda, A. H. *Chem. Eur. J.* **1998**, *4*, 1885; (c) Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. H. *Curr. Opin. Chem. Biol.* **1999**, *3*, 313; (d) Reetz, M. T. *Angew. Chem. Int. Ed.* **2001**, *40*, 284; (e) Dahmen, S.; Brase, S. *Synthesis* **2001**, 1431; (f) Traverse, J. F.; Snapper, M. L. *Drug Discov. Today* **2002**, *7*, 1002; (g) Berkowitz, D. B.; Bose, M.; Choi, S. *Angew. Chem., Int. Edit.* **2002**, *41*, 1603; (h) de Vries, J. G.; de Vries, A. H. M. *Eur. J. Org. Chem.* **2003**, 799.

[4] (a) Grasa, G. A.; Moore, Z.; Martin, K. L.; Stevens, E. D.; Nolan, S. P.; Paquet, V.; Lebel, H. *J. Organomet. Chem.* **2002**, *658*, 126; (b) Charette, A. B.; Janes, M. K.; Lebel, H. *Tetrahedron: Asymmetry* **2003**, *14*, 867.

[5] (a) Huang, J. K.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889; (b) Fürstner, A.; Leitner, A. *Synlett* **2001**, 290; (c) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C. P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617*, 616; (d) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1077; (e) Viciu, M. S.; Grasa, G. A.; Nolan, S. P. *Organometallics* **2001**, *20*, 3607; (f) Grasa, G. A.; Viciu, M. S.; Huang, J. K.; Zhang, C. M.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866; (g) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C. L.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69; (h) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez,

study of the exact structure of various palladium NHC species reveals that the metalation site on the imidazolium salt is strongly influenced by the presence of base. We now report the synthesis and structure of novel palladium complexes bearing NHC ligands in "normal" and "abnormal" binding motifs. The binding mode of the NHC to Pd is shown to substantially affect the catalytic behavior of the palladium complexes.

It has been reported that palladium(II)-NHC complexes could be easily prepared from palladium(II) acetate and the corresponding imidazolium salts.[6] Metal binding at the C(2) position is usually observed and complexes bearing two NHCs can potentially exist as *trans* or *cis* isomers depending on the steric hindrance of the nitrogen substituent R. We first attempted to synthesize the palladium complex 1 derived from two equiv of N,N'-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes•HCl) (1) and one equiv of palladium(II) acetate under the standard reaction conditions (dioxane, 80 °C, 6 h). The reaction proceeded smoothly leading to the isolation of a single palladium-containing product.
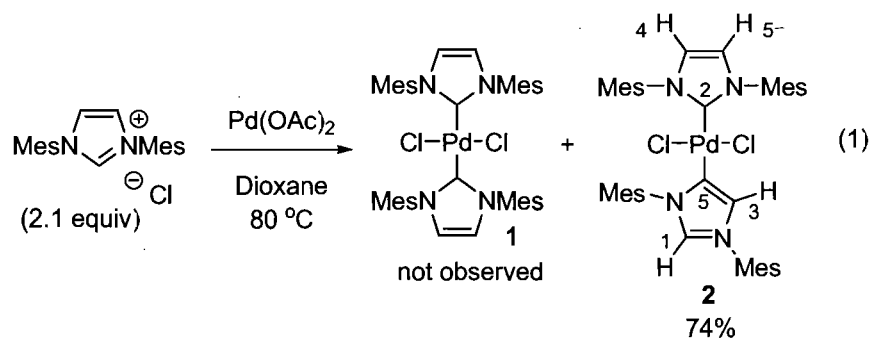
Équation 6-1

The NMR data suggested an unusual coordination mode for the NHC ligands, as indicated by eleven protons and twenty-two carbon signals. In addition to the singlet at 6.85 ppm for

O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470; (i) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.

[6] Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem. Int. Ed.* **1995**, *34*, 2371.

H(4) and H(5) of a presumably C(2) bound IMes ligand, the ^{1}H NMR spectrum displayed two doublets at 6.57 and 7.47 ppm ($J = 1.7$ Hz) corresponding to H(3) and the carbene H(1) of a possibly C(5) bound IMes ligand. Furthermore, the ^{13}C NMR spectrum showed two carbon signals at 175.9 and 150.7 ppm that we assign to C(2) and C(5) bound to the palladium center. Two carbon signals for C(4) and C(5), and for C(3) at respectively 122.8 and 125.5 ppm were also observed. Based on the NMR data, we proposed the reaction product to have the structure **2** (eq 1). To unambiguously establish this structure, single crystals were grown by slow diffusion of hexanes into a saturated solution of **2** in acetone. The single-crystal X-ray analysis provided the ORTEP diagram shown in **Figure 6-1**. The ORTEP reveals that the palladium is C(2) bound to one NHC ligand (the normal binding mode) whereas the second ligand is attached through the C(5) carbon of the second imidazolium. Both Pd-C distances are equivalent (2.019 and 2.021 Å) and are consistent with Pd-C single bonds. The ORTEP shows a square-planar coordination around the palladium center, with the two chlorine atoms bound to the palladium. Here again, no distortion in the Pd-Cl distances is observed (2.289 and 2.302 Å).

Complex **2**, isolated in good yields (74%), is a rare example of C(5) coordination of an IMes ligand and constitutes the first example of an organometallic complex containing one C(2) NHC ligand and one C(5) bound imidazolium ligand.[7,8]

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[7] For the only example of a C-5 IMes, see: (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274; (b) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.

[8] For selected early examples of a C(2) bound IMes, see: (a) Huang, J.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 2674; (b) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370; (c) Jafarpour, L; Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 3760.
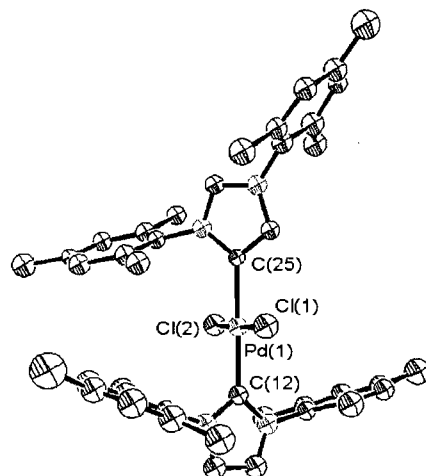
Figure 6-1. ORTEP diagram of palladium complex **2**.

Selected bond lengths (Å) and angles (deg): Pd(1)-C(12), 2.019(13); Pd(1)-C(25), 2.021(11); Pd(1)-Cl(1), 2.289(4); Pd(1)-Cl(2), 2.302(4); C(12)-Pd(1)-C(25), 179.4(5); C(12)-Pd(1)-Cl(1), 93.3(4); C(25)-Pd(1)-Cl(1), 87.3(3); C(12)-Pd(1)-Cl(2), 88.6(4); C(25)-Pd(1)-Cl(2), 90.9(3); Cl(1)-Pd(1)-Cl(2), 177.23(18).

Surprisingly, when a mixture of cesium carbonate, palladium(II) acetate and IMes•HCl was stirred at 80 °C in dioxane, the formation of **2** was not observed and the normal C(2) complex **1** was formed together with (IMes)$_2$Pd(OAc)$_2$.[9] Complex **1** was also isolated in 68% from palladium(II) chloride, cesium carbonate and 2 equiv of IMes•HCl (eq 2). The structure of complex **1** was also unambiguously established by single-crystal X-ray analysis (see supporting information). Attempts to convert complex **2** into the C(2) isomer **1** in the presence of a base were unsuccessful.[10]

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[9] The normal C(2) complex **1** and (IMes)$_2$Pd(OAc)$_2$ were obtained as an inseparable mixture.

[10] The related unusual C(2)-C(5) complex was also obtained with *N,N'*-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr•HCl).
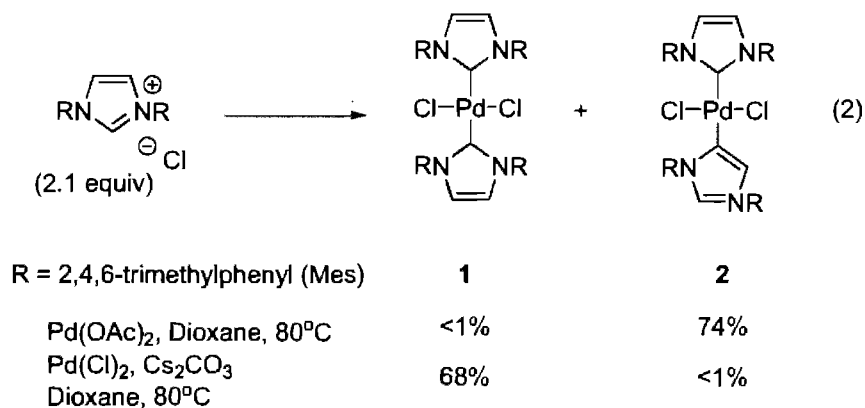
Équation 6-2

The reactivity of **1** and **2** was studied and compared with the *in situ* formed catalyst (from Pd(OAc)₂ (1 equiv) and IMes•HCl (2 equiv)) for the Suzuki-Miyaura (Table 1) and Heck reactions (Table 2).

Tableau 6-1. Palladium-Catalyzed Suzuki-Miyaura Reactions.
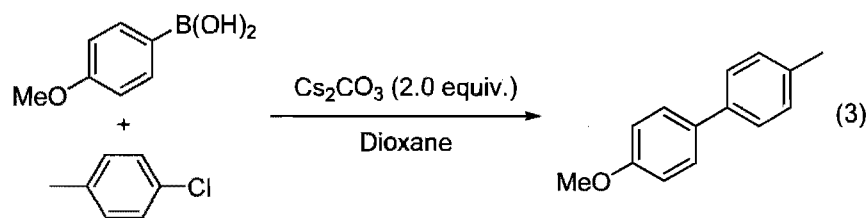
entry	catalyst (2 mol%)	temp.	yield
1	Complex **1**	80 °C	<5%
2	Complex **2**	80 °C	44%
3	IMes•HCl, Pd(OAc)₂	80 °C	76%

Complex **1** proved to be an inactive catalyst for both coupling reactions, while complex **2** lead to the desired product. In Suzuki-Miyaura reactions, complex **2** was not as efficient as the *in situ* formed catalyst.[11] In sharp contrast, the highest isolated yield for the Heck coupling reaction was obtained with **2**.

Table 6-1. Palladium-Catalyzed Heck Reactions.
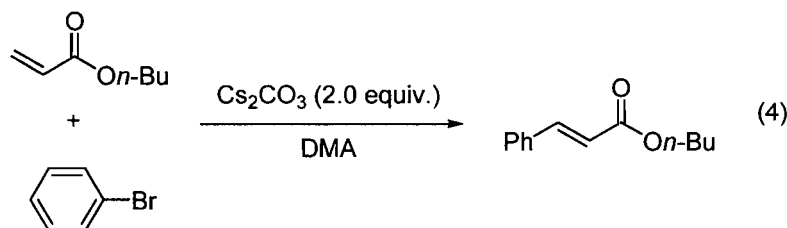
entry	catalyst (2 mol%)	temp.	yield
1	Complex 1	120 °C	<5%
2	Complex 2	120 °C	77%
3	IMes•HCl, Pd(OAc)$_2$	120 °C	66%

In conclusion, these findings highlight the importance of the procedure used for the generation of a catalytically active species in cross-coupling reactions. It appears that the catalytically active species precursor in cross-coupling reactions is not complex **1** in both Suzuki and Heck coupling. Although complex **2** showed a difference in reactivity when compared to the *in situ* generated catalyst, it was found to be a more suitable precursor for

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[11] It should be noted that the optimum Pd:L ratio used in Suzuki-Miyaura was determined to be 1:1 and that well-defined complexes bearing only one NHC are better catalysts than those bearing two. See ref 3f.

Suzuki and Heck coupling reactions. Work aimed at unveiling the nature of catalytically active species in *in situ* generated NHC-Pd systems is ongoing.[12]

6.2. Acknowledgment.

Supporting Information Available: Characterization data for new compounds and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.or

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[12] Lors des travaux de cette thèse, seulement le complexe anormal d'iridium était connu. Le fait qu'un complexe anormal puisse se former impliquant des réactifs simples et courants tels l'acétate de palladium et un sel d'arylimidazolium constituait une importante découverte.

Chapitre 7 :   Abnormal *N*-Heterocyclic Carbene (NHC) Palladium Complexes Bearing a C5-Metallated Arylimidazolium Ligand: Scope and Mechanism (Manuscript)

Hélène Lebel,* Marc K. Janes and André B. Charette*

(Reference to be inserted)

7.1. Abstract

Imidazolium salts react with palladium salts selectively affording unusual (air stable) complexes with abnormally bound imidazolium rings at the C5 position, and bis-*N*-heterocyclic carbene (NHC) complexes. The imidazolium salt's binding mode (C2 vs C5) is strongly influenced by the presence or absence of a base and by the nature of the base. Furthermore, no abnormal complex was observed with *N*-alkyl substituted imidazolium salts.

7.2. Article

Palladium complexes are widely used in catalytic processes such as cross-couplings,[1] alkylations,[2] oxidations,[3] cyclopropanations,[4] and cycloisomerizations.[5] Since applications can be very broad for palladium catalysts, massive efforts have been deployed to develop this field and the search for the next generation of catalysts is ongoing. To control the reactivity of palladium, ligands, such as phosphines, are used extensively. In light of the success of phosphines in controlling the reactivity of palladium, especially in asymmetric processes, a wide array of mono- and bisphosphines have been developed.[6] Furthermore, the use of N-heterocyclic carbenes (NHC's) has allowed many breakthroughs especially in the fields of cross-couplings[7] and alkene metathesis.[8] NHC's are now emerging not only as

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[1] For a recent review on cross-couplings of aryl halides see: Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431. For a historical review on cross couplings see: Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1519 and references cited.

[2] Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813.

[3] (a) Cornell, C. N.; Sigman, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2796; (b) Sigman, M. S.; Shultz, M. J. *Org . Biomol. Chem.* **2004**, *2*, 2551; (c) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400; (d) Nielsen, R. J.; Keith, J. M.; Stoltz, B. M.; Goddard III, W. A. *J. Am. Chem. Soc.* **2004**, *126*, 7967.

[4] (a) Marko, I. E.; Kumamoto, T.; Giard, T. *Adv. Synth. Catal.* **2002**, *344*, 1063 and references cited; (b) Tomilov, Y. V.; Dokichev, V. A.; Dzhemilev, U. M.; (c) Nefedov, O. M. *Russ. Chem. Rev. (Engl. Transl.)*, **1993**, *62*, 799.

[5] (a) Mikami, K.; Hatano, M. *Proc. Nat. Accad. Sci. U.S.A.* **2004**, *101*, 5767; (b) Widenhoefer, R. A. *Acc. Chem. Res.* **2002**, *35*, 905.

[6] (a) Shibasaki, M.; Vogl, E. M.; Ohshima, T. *Adv. Synth. Catal.* **2004**, *346*, 1533; (b) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945

[7] Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195 and references cited.

[8] For a review and historical perspective see: Astruc, D. *New J. Chem.* **2005**, *29*, 42.

phosphine substitutes but also as a powerful class of new ligands in their own right[9] and are starting to show good potential in asymmetric reactions.[10]

In our quest for new palladium catalysts, we previously reported that the reaction between IMesHCl **1a** and Pd(OAc)$_2$ produced an unexpected and abnormal complex **1b** which was isolated instead of the expected complex **1c** (**Equation 7-1**).[11,12]
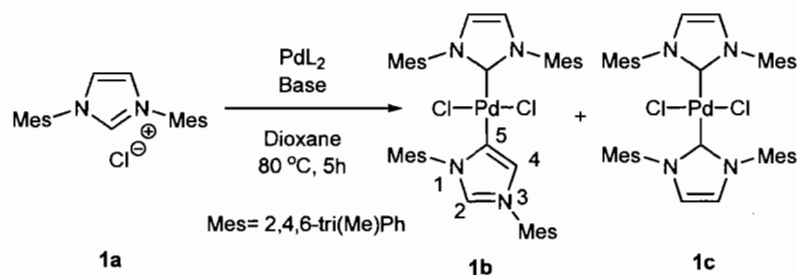
Equation 7-1

Previous reports indicated that the reaction between an imidazolium salt and a palladium salt should have given a normal carbene complex.[13] Complex **1b** was found to be active in

[9] For reviews on the use of NHC ligands in catalysis, see: (a) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247; (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1290; (c) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

[10] For recent reviews see: (a) César, V.; Bellemin-Laponnaz, S.; Gade, H. *Chem. Soc. Rev.* **2004**, *33*, 619; (b) Perry, M. C.; Burgess, K. *Tetrahedron: Asymm.* **2003**, *14*, 951. See also: (c) Bertogg, A.; Camponovo, F.; Togni, A. *Eur. J. Inorg. Chem.* **2005**, 347.

[11] First abnormal complex involving Pd: Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046.

[12] For example of abnormal complexes involving Ir, Cu, or Fe see: (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, *21*, 2274; (b) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473; (c) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *Organometallics* **2003**, *22*, 3016; (d) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166.

cross-coupling reactions such as the Suzuki and Heck reactions. Conversely, the normal carbene complex **1c** was obtained when the reaction between IMesHCl **1a** and PdCl$_2$ was carried out in the presence of cesium carbonate.[14] Surprisingly, the normal biscarbene complex **1c** proved to be completely inactive in cross-coupling reactions. Due to the widespread use of carbene ligands in such important processes and the fact that many reports of *in situ* formation of catalysts are found in the literature,[15] it became important to study the factors influencing the formation of the abnormal versus the normal complexes. Since the mode of binding of the imidazolium salt or NHC to the palladium(II) species influences the catalytic activity of the complex, it is important to study the reaction conditions leading to the abnormal binding.[16]

We had postulated that when a strong enough base was used in the reaction between palladium acetate and an imidazolium chloride, the imidazolium salt was converted to an NHC that could coordinate the palladium leading to a normal complex of type **b** (**Scheme 7-1**). When no base was added, we also postulated that palladium acetate was forced to act as a base and deprotonate the imidazolium salt forming an NHC that could bind to palladium and possibly generate an intermediate "NHC-Pd(II)" complex (**Scheme 7-1**). Complexes similar to the proposed intermediate have been isolated and are known to be potent C-H insertion catalysts (through electrophilic metalation).[17] A protic media is

[13] (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371; (b) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; Rajanbabu, T. V. *Org. Lett.* **2000**, *8*, 1125.

[14] IMesHCl and Pd(OAc)$_2$ reacted in the presence of Cs$_2$CO$_3$ to give an inseparable mixture of normal complexes presumably with different or mixed counter ions (OAc and/or Cl).

[15] (a) Yong, B. S.; Nolan, S. P. *Chemtracts* **2003**, *16*, 205; Hillier, A. C.; (b) Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.

[16] Only *trans* binding around the palladium between the NHC-NHC or NHC-imidazolium ligand was observed in our systems.

[17] (a) Viciu, M. S.; Stevens, E. D.; Petersen J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752. For a review on catalytic functionalization of arenes see: (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. For a review on stœchiometric fuctionalization

required in most examples for such metalation to occur. Involvement of AcOH and AcONa is well precedented for the stoichiometric functionalization of arenes by transition metal complexes including palladium complexes. Since deprotonation of a first imidazolium salt by palladium acetate would lead to the formation of acetic acid, such reaction conditions could favour the C-H insertion and disfavorable for the formation of another NHC ligand. Insertion could occur in two positions with the C5 position being less hindered and possibly more nucleophilic than the C2 position. Abnormal metalation occurs when the C5 position is more reactive. This proposed mechanism is in contrast to those implied for abnormal metalation of copper and iron in which the starting substrate is a NHC and not an imidazolium salt.[18]
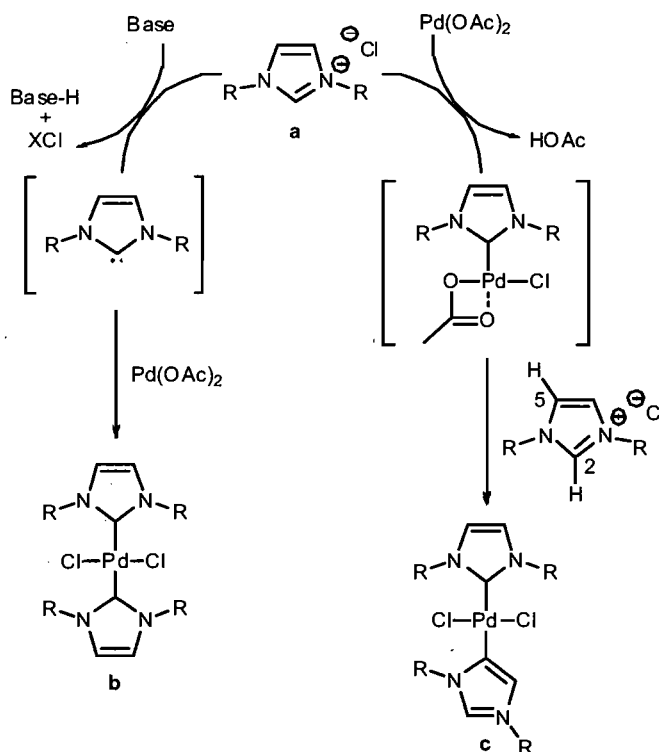
Scheme 7-1. Proposed reaction pathways with or without an added base.

of C-H bond by transtion metals see: (c) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

[18] See ref.: 12c and 12d (of this chapter).

To get indications that would support our hypothesis, different bases were used. We had found that the nature of the base used in the formation of NHC-Pd complexes had a strong influence on the outcome of the reaction. When $Pd(OAc)_2$ was reacted with IMesHCl without a base, the abnormal complex **1b** could be isolated in 74% yield (**Table 7-1**, entry 1). The addition of dimethylaniline or sodium acetate yielded a separable mixture of normal and abnormal complexes **1c** and **1b** in a combined yield of 70% and 97% respectively favouring the abnormal complex (**Table 7-1**, entries 2 and 3). Sodium bicarbonate on the other hand yielded mostly the normal complex in a 2:1 ratio. In contrast, no reaction occurred with hindered tertiary amine bases such as triethylamine or diisopropylethylamine. These strong amine bases could possibly bind to Pd(II) and inhibit the formation of complexes[19] or Pd(II) could get reduced by the amine to Pd(0).

Since we suspected that palladium acetate acted as a base, a less basic palladium salt was used (without the addition of another base). In that case, only unreacted imidazolium salts **1a** was observed by NMR of the crude reaction mixture (**Table 7-1**, entry 5). The imidazolium salt **1a** is also the only product observed when dimethylaniline was used (**Table 7-1**, entry 6). Starting from palladium chloride, the use of sodium acetate yielded a mixture of complexes **1b** and **1c** in a high combined yield favoring the abnormal compound (**Table 7-1**, entry 7).[20] The use of cesium carbonate allowed the exclusive formation of the normal complex when starting from palladium chloride.

We were curious to know if these results were specific to IMesHCl or if other imidazolium salts could exhibit the same reactivity. We turned our attention to an important member of the imidazolium family, IPrHCl **2a.** In the presence of palladium acetate under our typical

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[19] Schultz, M. J.; Park, C. C.; Sigman, M. S. *Chem. Commun.* **2002**, 3034.

[20] The *in situ* formation of palladium acetate is possible.

reaction conditions, this imidazolium formed the corresponding abnormal complex **2b**.[21] In addition, we obtained the palladium chlorodimer **2d** which displays normal binding (**Table 7-1**, entry 1).

Table 7-1. Formation of normal vs. abnormal $IMes_2PdCl_2$ under different reaction conditions.
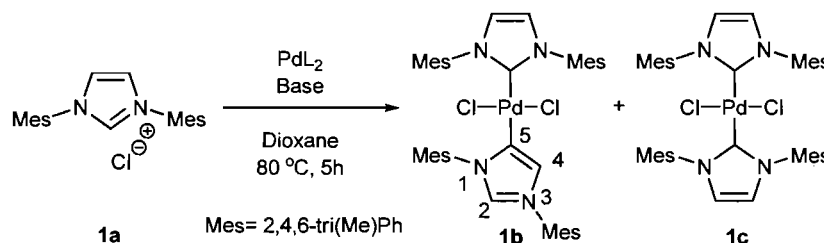
entry	L	base	combined yield b + c (%)^a	ratio^b b : c
1	OAc	--	74	100:0
2	OAc	$PhNMe_2$	70	80:20
3	OAc	NaOAc	97	80:20
4	OAc	$NaHCO_3$	76	33:67
5	Cl	--	nr	--
6	Cl	$PhNMe_2$	nr	--
7	Cl	NaOAc	93	78:22
8	Cl	Cs_2CO_3	68	0:100

^{a} Each isolated separately by a single column chromatography. ^{b} Calculated from the isolated yields of each species. ^{c} No reaction: only the imidazolium salt is observed by NMR.

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[21] Abnormal and normal IPr_2PdCl_2 are also reported in the literature and prepared according to our previously reported procedure: Campeau, L.-C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857.

The formation of palladium dimers by direct reaction of an imidazolium salt with a palladium salt is unprecedented. Compound **2d** was previously reported but synthesized by coordination of the free NHC to palladium.[22] This reaction yielded none of the bis-normal complex of type **c** (**Table 7-1**, entry 1). Similarly to the reaction with IMesHCl, when sodium acetate was used as a base, a high combined yield of normal and abnormal complexes was obtained (**Table 7-1**, entry 2). IPrHCl did not react with palladium chloride in the absence of a base and when cesium carbonate was added to the same reaction, a low yield of the bis-normal IPr$_2$PdCl$_2$ **2c** was obtained (**Table 7-1**, entries 3 and 4).

We then studied alkyl-substituted imidazolium salts. To our surprise, using IAdHCl **4a**, no reaction could be observed with or without the use of base (**Table 7-2**, entries 6 and 7). Possibly the low solubility of IAdHCl in dioxane or tetrahydrofuran may account for this result. However, the addition of dichloromethane to the heterogeneous mixture solubilized the salts, without leading to the conversion of the imidazolium salt into **4b**. The use of ICyHCl **5a** which is soluble under our reaction conditions afforded in a low yield the normal complex **5c** without any trace of the corresponding abnormal complex.[23] To further determine the scope of our findings, an imidazolium salt bearing a (α-Me)Bn group as the nitrogen substituents (compound **6a**) was submitted to our base free conditions. No formation of abnormal complex was observed by NMR analysis of the crude reaction product even if **6a** was consumed (**Table 7-2**, entry 9).[24] The imidazoium salt **6a** bearing 2,6-bis(Me)Ph as a nitrogen substituent reacted to form the normal complex **6c** in 75% yield under similar reaction conditions described previously (**Table 7-2**, entry 5).

[22] (a) Viciu, M. S.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 2229; (b) Jensen, D. R. Sigman, M. S. *Org. Lett.* **2003**, *5*, 63.

[23] IAd$_2$Pd(0) was previously isolated: Gstoettmayr, C. W. K.; Bohm, V. P. W.; Herdtweck, E; Grosche, M.; Herrmann, W. A.; *Angew. Chem. Int. Ed.* **2002**, *41*, 1363.

[24] The corresponding normal complex **6c** was reported earlier: Lebel, H.; del Rayo, M. S. S.; Bélanger-Gariépy, F. *Acta Cryst.* **2004**, *E60*, 755.

Table 7-2. Formation of normal vs. abnormal complexes using imidazolium salts other than IMesHCl.

R= 2,6-bis(*i*-Pr)Ph **2a**
R= 2,6,-bis(Me)Ph **3a**
R= 1-adamantyl **4a**
R= cyclohexyl **5a**
R= (α-Me)Bn **6a**
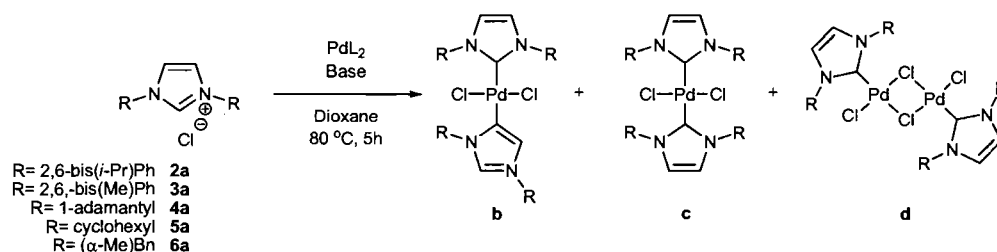
entry	R	L	base	combined yield b + c + d (%)[a]	Ratio[d] b : c : d
1	2,6-bis(*i*-Pr)Ph	OAc	None	60	71:0:29
2	2,6-bis(*i*-Pr)Ph	OAc	NaOAc	65	60:0:40
3	2,6-bis(*i*-Pr)Ph	Cl	none	nr	--
4	2,6-bis(*i*-Pr)Ph	Cl	Cs_2CO_3	33[b]	0:100:0
5	2,6-bis(Me)Ph	OAc	none	75	100:0:0
6	1-adamantyl	OAc	none	nr	--
7	1-adamantyl	Cl	Cs_2CO_3	nr	--
8	cyclohexyl	OAc	none	24	0:100:0
9	(α-Me)Bn	OAc	none	60[c]	0:100:0

[a] Each were isolated separately by a single column chromatography. [b] Reaction time: 20 h. [c]THF was used as solvent. [d]Calculated from the isolated yields of each species

7.3. Conclusion

In conclusion, the formation of abnormal Pd(II) complexes involving one *N*-heterocyclic carbene and one C5 metallated imidazolium as ligands starting from the corresponding

imidazolium salt and palladium salt is not limited to IMesHCl. Other *N*-aryl substituted imidazolium salts can react with or without base to form abnormally bound complexes. The nature of the base as well as of the nitrogen substituents on the imidazolium ring was found to have a profound effect on the selectivity to produce normal or abnormal complexes. Substitution of the nitrogen atoms either by alkyl or benzyl groups prevented the formation of abnormal complexes while it was still possible to form the normal complexes in some cases. We have demonstrated the straightforward synthesis of important palladium(II) complexes starting from commercially available air stable precursors. Abnormal complexes are also air stable and are purified by column chromatography and/or recrystallization without any specific precautions to exclude air or moisture. Applications of our abnormal complexes in catalysis are currently under investigation.

7.4. Acknowledgment.

Chapitre 8 : Conclusion générale

L'utilisation en synthèse de réactifs qui permettent de faciliter la purification est très attrayante pour le chimiste. Ces outils permettent d'optimiser le travail tant en milieu industriel qu'en milieu académique. Nous avons conçu un réactif avec ces enjeux en tête, et développé une synthèse utile du PPh$_3$-NCPS. Nous avons pu confirmer la viabilité de cette voie de synthèse jusqu'à une échelle de 100 g. Ce réactif s'est avéré être un substitut efficace à la triphénylphosphine dans la réaction de formation d'imines ainsi que dans la réaction de Mitsunobu. La concentration en phosphine par masse de réactif est compétitive par rapport aux autres phosphines liées à des supports solubles. La teneur en phosphine est plus grande que la phosphine liée au PEG et moins que la PPh$_3$-CLPS. Ce dernier étant un support solide, des excès de réactifs sont généralement requis pour son utilisation. Par rapport à la triphénylphosphine, notre réactif a un avantage certain lors de réactions régiosélectives. Le fait de pouvoir tirer profit de la matrice polymérique pour augmenter la régiosélectivité a été un atout.

La cyclopropanation énantiosélective d'alcènes est un défi qui est difficile à relever. La nature des méthodes et des réactifs font de cette chimie un art pour lequel il faut maîtriser parfaitement la technique et le savoir. Dans ce contexte, il est compréhensible que malgré le succès des méthodes de cyclopropanation en version racémique, il soit difficile de développer des systèmes catalytiques asymétriques efficaces. Malgré les obstacles, il existe des exemples qui fonctionnent avec des rendements et excès enantiomères élevés. Néanmoins, aucune méthode générale de formation de cyclopropanes énantioenrichis n'existe encore. Une multitude de catalyseurs chiraux sont disponibles pour la décomposition des composés diazo. Ces catalyseurs sont inefficaces devant le plus simple composé diazo: le diazométhane. Nous avons réussi, avec notre protocole réactionnel, à

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obtenir les excès énantiomères les plus élevés observés pour une réaction de cyclopropanation impliquant le diazométhane. Les rendements sont utiles du point de vue synthétique. L'étude de la réaction suggère la formation d'un carbène métallique électrophile. Le fait de diverger de la structure ester cinnamique cause généralement une chute des excès énantiomères.

Le domaine (en émergence) des carbènes *N*-hétérocycliques est très stimulant. Premièrement, le fait d'améliorer des catalyseurs traditionnels grâce à la coordination d'un CNH est remarquable. Deuxièmement, il reste encore des propriétés à découvrir concernant ces espèces ainsi que leurs méthodes de formation. Nous avons montré que des précurseurs de CNH peuvent réagir de façon anormale avec des sels de palladium pour former des ligands de type arylimidazolium. Dans ce processus anormal, un ligand CNH est aussi formé et nous supposons selon notre hypothèse mécanistique qu'il est formé avant que la métallation anormale survienne. Il est important d'avoir un sel d'arylimidazolium pour obtenir une métallation anormale de ce sel. Le fait d'ajouter une base forte au milieu inhibe cette métallation et des complexes normaux sont formés probablement par la génération prépondérante de NHC dans le milieu. Il a été possible d'utiliser des complexes anormaux de palladium pour catalyser des couplages croisés. Nous avons comparé leur réactivité à celle de catalyseurs générés *in situ* dans la réaction de Hecks et de Suzuki. Nous avons déterminé que la réactivité est dépendante des cas (parfois meilleure, parfois moins bonne que celle du catalyseur auquel ils étaient comparés). L'importance de cette découverte réside surtout dans le fait qu'une telle métallation n'avait jamais été observée entre le palladium et un simple sel d'arylimidazolium. Ces deux composés se retrouvent dans une multitude de processus catalytiques et la compréhension de leurs interactions possibles est essentielle à l'évolution de ce domaine de recherche.

Annexe I – Synthesis of "NCPS-PPh₃" (published article and supporting information)

*Note: My contribution to this article involves participation in the development of the synthesis of the NCPS-PPh₃ and on the scale-up procedure (Reproduced with permission from Charette, A. B.; Boezio, A. A.; Janes, M. K. Org. Lett. **2000**, 2, 3777 and supporting information. © 2000 American Chemical Society).*
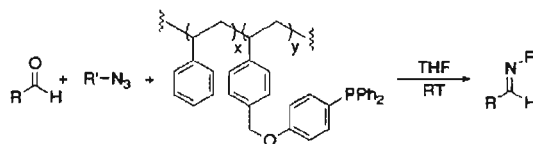
Synthesis of a Triphenylphosphine Reagent on Non-Cross-Linked Polystyrene Support: Application to the Staudinger/Aza-Wittig Reaction

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ABSTRACT

A new triphenylphosphine reagent linked to a linear polystyrene was synthesized. The reactivity of this phosphine-bound polymer is superior to that of the phosphine bound to cross-linked polystyrene. The polymer reacted very rapidly with azides to generate iminophosphoranes which could then react with aldehydes to generate imines in good yields and high purities.

Triphenylphosphine is one of the most widely used phosphorus-containing reagents in organic synthesis for many types of transformations such as the Mitsunobu,[1] the Wittig,[2] and the Staudinger[3] reaction. However, the triphenylphosphine oxide that is usually generated as a byproduct in all these reactions is very difficult to separate from the desired reaction product. Typically, flash chromatography or precipitation of the phosphine oxide by the addition of hexane has been used successfully to remove it. However, these purification techniques require that the desired product is also soluble in hexane or stable to chromatography. Our interest in the development of new synthetic methods for the stereoselective nucleophilic additions to C=N led us to study the reactivity of imines of general structure "YCH₂N=CHR" in which $Y = RO, R_2N$, etc. These imines, which were prepared by the Staudinger reaction,[4,5] are quite sensitive and some of them do not survive purification attempts by chromatography on silica gel. It became obvious

that a method which would allow us to remove triphenylphosphine oxide would be quite useful. One possible solution is to use a triphenylphosphine polymer-bound reagent. Ford[6] has synthesized a triphenylphosphine-bound insoluble cross-linked polystyrene, but this polymer usually requires an excess of one of the reagents. A possible solution would be to use Janda's PEG-bound reagent,[7] but the loading in this case is quite low and the solubility and structural properties were not adequate for our applications.[8] In this Letter, we report the synthesis of a triphenylphosphine-bound non-cross-linked polystyrene soluble support.[9] This polymer should have a reasonably high loading and it should allow stoichiometric reactions to take place between azides and aldehydes.[10] Finally, the removal of the phosphine oxide byproduct should

(1) Mitsunobu, O. *Synthesis* 1981, 1–28.
(2) Maryanoff, R. *Chem. Rev.* 1989, 89, 863–927.
(3) (a) Staudinger, H. *Helv. Chim. Acta* 1919, 2, 635–646. (b) Gololobov, Y. G.; Zhmurova, I. N.; Nasukhin, L. F. *Tetrahedron* 1981, 37, 437–472.
(4) Scriven, E. F. V.; Thurbull, K. *Chem. Rev.* 1988, 88, 297–368.
(5) Johnson, A. W. In *Ylid Chemistry*; Blomquist, A. T., Ed.; Academic Press: New York and London, 1966; Vol. 7, pp 222–236.

(6) Bernard, M.; Ford, W. T. *J. Org. Chem.* 1983, 48, 326–332.
(7) (a) Wentworth, P., Jr.; Vandersteen, A. M.; Janda, K. D. *Chem. Commun.* 1997, 759–760. (b) Sieber, F.; Wentworth, P., Jr.; Toker, J. D.; Wentworth, A. D.; Metz, W. A.; Reed, N. N.; Janda, K. D. *J. Org. Chem.* 1999, 64, 5188–5192.
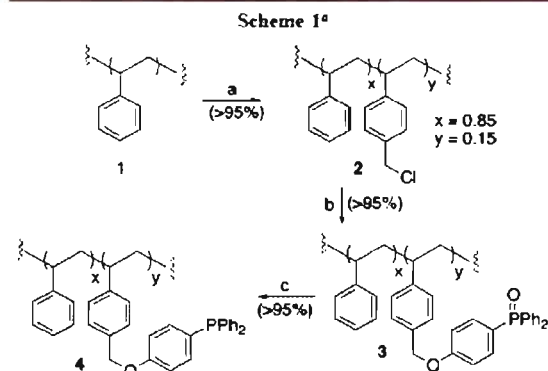(8) The maximum loading of Janda's PPh₃-bound PEG is 0.5 mmol/g.
(9) For recent examples of non-cross-linked polystyrene-supported reagents, see: (a) Enholm, E. J.; Gallagher, M. E.; Moran, K. M.; Lombardi, J. S.; Schulte, J. P. *Org. Lett.* 1999, 1, 689–691. (b) Enholm, E. J.; Schulte, J. P. *Org. Lett.* 1999, 1, 1275–1277.
(10) Reactions involving polymer-supported reagents often require a significant excess of the reagent.

be accomplished by a simple precipitation/filtration or extraction procedure.

The polymer was synthesized in three steps from non-cross-linked polystyrene (1) ($M_w = 230\,000$, $M_n = 140\,000$) (Scheme 1).[11] Tin chloride-mediated chloromethylation of

Scheme 1[a]

[a] (a) MOMCl, SnCl$_4$(cat.), CCl$_4$; (b) p-hydroxyphenyldiphenylphosphine oxide, Cs$_2$CO$_3$, DMF, 60 °C; (c) HSiCl$_3$, N,N-dimethylaniline, p-dioxane, 100 °C.

polystyrene[12] followed by nucleophilic displacement with the cesium phenoxide derived from p-hydroxyphenyldiphenylphosphine oxide[13] gave the phosphine oxide **3**. A subsequent reduction of the phosphine oxide with trichlorosilane and N,N-dimethylaniline at 100 °C led to the phosphine **4** in quantitative yield. The purity of each compound was checked by ^{1}H and ^{31}P NMR, and the final polymer contained less than 5% of the oxide and can be stored for many months on the benchtop at room temperature in a closed bottle. This polymer is highly soluble in DMF, DMSO, THF, p-dioxane, PhH, PhMe, CH$_2$Cl$_2$, CHCl$_3$, and CCl$_4$. It is insoluble in Et$_2$O, MeOH, EtOH, and H$_2$O.

It is important to note that the final loading of the polymer is approximately 1 mmol/g as calculated by ^{1}H NMR. Although we could easily increase the loading to 3 mmol/g, this was not suitable since the solubility and mechanical properties of the phosphine oxide polymer **3** became quite different from those of **4**.

To evaluate the reactivity of the phosphine-bound polymer **4**, the Staudinger/aza-Wittg process was monitored by ^{31}P NMR (Figure 1). A rapid and quantitative conversion to the
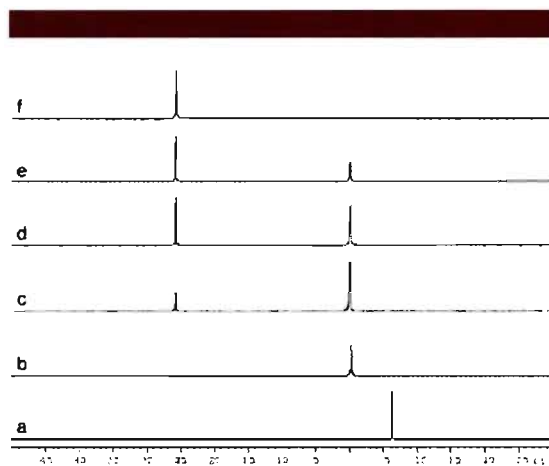
Figure 1. Monitoring of the imine formation process by ^{31}P NMR: (a) polymer **4**; (b) polymer **4** (1.0 equiv) + BnN$_3$ (1.1 equiv), C$_6$D$_6$, rt, 30 min; (c) polymer **4** (1.0 equiv) + BnN$_3$ (1.1 equiv) + PhCHO (1.1 equiv), C$_6$D$_6$, rt, after 2 h; (d) after 9 h; (e) after 18 h; (f) after 24 h.

polymer-supported iminophosphorane was observed within 30 min when 1.0 equiv of the phosphine-bound polystyrene was mixed with 1.1 equiv of the azide at room temperature in C$_6$D$_6$. The imine formation took place quantitatively within 24 h when 1.1 equiv of the aldehyde was added to the iminophosphorane. The rates of both reactions are comparable to those observed when triphenylphosphine is used as the reagent, indicating that the reactivity of the reagent-bound polymer is comparable to that of free triphenylphosphine.

A preparative-scale procedure involves adding a solution of the azide to a mixture of the aldehyde and of the soluble polymer in THF. Nitrogen evolution is quite rapid, and the reactions are generally completed within 24 h (Table 1).

Isolation of the imine was accomplished according to two procedures. Optimal recovery generally requires concentration of the reaction mixture under reduced pressure. The

Table 1. Staudinger/Aza-Wittig Reaction with Phosphine Polymer **4**[a]

entry	R$_1$	R$_2$	yield, %[b]	entry	R$_1$	R$_2$	yield, %[b]
1	phenyl (5a)	benzyl (6a)	89 (7a)	9	3-pyridyl	phenethyl	100 (7i)
2		phenethyl (6b)	96 (7b)	10		(6c)	92 (7j)
3		(6c)	97 (7c)	11		phenyl (6e)	66 (7k)
4		p-anisyl (6d)	75 (7d)	12		p-anisyl	100 (7l)
5	cyclohexyl (5b)	benzyl	90 (7e)	13	cinnamyl (5d)	benzyl	99 (7m)
6		phenetyl	98 (7f)	14		phenethyl	96 (7n)
7		p-anisyl	76 (7g)	15		phenyl	75 (7o)
8	3-pyridyl (5c)	benzyl	94 (7h)	16		p-anisyl	98 (7p)

[a] The conversions were >95% in all cases. [b] Isolated yields of analytically pure imines (^{1}H and ^{13}C NMR).

Scheme 2
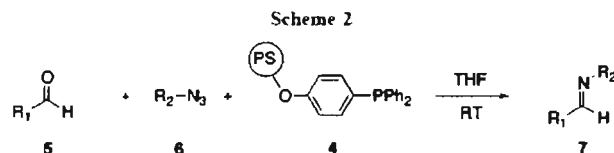
polymeric phosphine oxide crashes upon addition of MeOH. Quantitative extraction of the imine generally requires that the mixture is heated under reflux for a few hours. Alternatively, in cases where the imine is only slightly soluble in MeOH. quantitative imine recovery generally requires extraction of the solid polymeric material in a Soxhlet with MeOH. The phosphine-bound polymer can be quantitatively recovered by reducing the phosphine oxide with trichlorosilane and *N,N*-dimethylaniline.

The scope of the reaction is shown in Table 1. The formation of imines by the reaction of the corresponding azides and aldehydes proceeded smoothly with alkyl- and aryl-substituted aldehydes and azides. Analysis by crude NMR indicated that all the conversions were >95%. The efficiency of the isolation depended upon the nature of the substrate and on the stability of the imine in CH₃OH. For example, imines 7d, 7g, 7k, and 7o were significantly less stable than the others, and the lower isolated yields in these cases are a reflection of partial hydrolysis (Scheme 2). Finally, the imine formation of the more sensitive azide 6c proceeded smoothly to yield 7c and 7j in high yields.
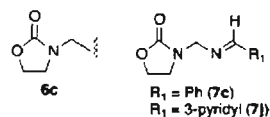

The reaction rate of the Staudinger/aza-Wittig reaction using the soluble polymer was compared to that observed with triphenylphosphine and its cross-linked version (Figure 2). The data show that the reactivity of the soluble polymer by far superior to that of the insoluble polymer. It is even superior to that observed with triphenylphosphine.[14]

In conclusion, we have obtained a variety of imines by the Staudinger/aza-Wittig reaction with a new soluble triphenylphosphine polymer with excellent yields and conversions higher than 95%. Furthermore, the loading of the polymer is about 1 mmol/g, which is superior to that found in PEG-supported triphenylphosphine. This version should

be especially useful when the imine is soluble in MeOH but not in hexane. We are currently testing this polymer in other phosphine-mediated processes, and results will be reported in due course.
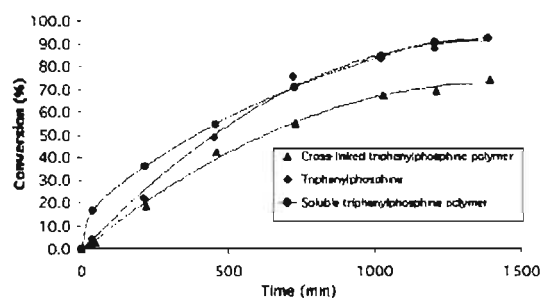
Figure 2. Relative reaction rates of the imine formation using various phosphine reagents.

Supporting Information Available: General procedures and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL006432W

(11) The polystyrene prepared by copolymerization of styrene and 4-vinylbenzyl chloride gave a lower molecular weight polymer that was not as easily manipulated: Kondo, S.; Ohtsuka, T.; Ogura, K.; Tsuda, K. *J. Macromol. Sci.-Chem.* 1979, *A13*, 767−775.

(12) Green, B.; Garson, L. R. *J. Chem. Soc. C* 1969, 401−406.

(13) Senear, A. E.; Valient, W.; Wirth, J. *J. Org. Chem.* 1960, *25*, 2001−2006.

(14) The faster reaction observed with the soluble triphenylphosphine polymer in comparison to triphenylphosphine may be a consequence of the more electron rich phosphine (*p*-RO substituent of the linker).

Supporting information for

Synthesis of a Triphenylphophine Reagent on Non-Cross-Linked Polystyrene Support: Application to the Staudinger/Aza-Wittig Reaction

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General Methods and Materials. NMR spectra were recorded on a Bruker ARX-400 spectrometer operated at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 162 MHz for ^{31}P NMR. IR spectra were recorded on a Perkin Elmer 783 FT-IR. Carbon tetrachloride (ACP Chemical inc.), N,N-dimethylformamide (Anachemia) and p-dioxane (Anachemia) were dried on 4Å molecular sieves for 15 hours prior to use. Tetrahydrofuran (BDH) was glass distilled over sodium/benzophenone under argon atmosphere. Methylene chloride (BDH) was glass distilled over calcium hydride under argon atmosphere. All reactions were carried out in flame dried flasks under argon or nitrogen atmosphere.

Poly(styrene-*co*-4-vinylbenzyl chloride) or non-cross-linked chloromethylated polystyrene (NCPS) (2). [1] NCPS 2 was prepared by adding tin(IV) chloride (8 mL, 68 mmol) to a solution of linear polystyrene (Mw = 230 000, Mn = 140 000), (100 g, 960 mmol) and chloromethyl methyl ether (200 mL, 274 mmol) in carbon tetrachloride (800 mL). *Warning: Extreme care should be taken while manipulating MOMCl which is a suspected carcinogen.* The reaction mixture was stirred vigorously using a mechanical stirrer for exactly 2 hours. The solution was then poured on methyl alcohol (4 L) under vigorous magnetic stirring thus precipitating the polymer. The

polymer suspension was then filtered using a corse sintered glass filter, dissolved in a minimum of benzene (about 1.5 L) and precipitated drop by drop in methyl alcohol (8 L) under vigorous magnetic stirring. Filter polymer as above and place in a vacuum oven at 70 °C for 15 hours. The title compound was obtained as a white solid (106.1 g, 99%). A loading of 1,36 mmol/g was determined by ^{1}H NMR (10 s relaxation time). ^{1}H NMR (CDCl$_3$) δ 7.30-6. 88 (bm, aromatic), 4.62-4.38 (bm, benzylic), 2.31-1.70 (bm, PS-α-methylenes), 1.70-1.16 (bm, PS-β-methylenes); ^{13}C NMR (CDCl$_3$) δ 145.2, 134.9, 127.9, 127.5, 125.6, 46.2, 43.6, 40. IR (KBr) 3025, 2921, 1942, 1871, 1802, 1746, 1601, 1493, 1452, 757, 698 cm^{-1}. Anal. calcd.: C, 87.83; H, 7.37.; found: C, 86.84; H, 7.55.

Poly(styrene-*co*-diphenyl-[4-(4-vinyl-benzyloxy)-phenyl]-phosphine oxide (3). Polymer **3** was prepared by adding *p*-methoxyphenyldiphenylphosphine oxide [2] (31.1 g, 110 mmol) to a solution of NCPS **2** (65 g, 88.4 mmol) in DMF (1 L). Cesium carbonate (57.4 g, 88.4 mmol) was then added to the reaction mixture and heated to 60 °C for 15 hours under vigorous magnetic stirring. The solution was then poured on methyl alcohol (5 L) under vigorous magnetic stirring thus precipitating the polymer. The polymer suspension was then filtered using a corse sintered glass filter, rinsed with water and methyl alcohol to be subsequently placed in a vacuum oven at 70 °C for 15 hours. The title compound **3** was obtained as an off-white solid (87.8 g, 100%). A loading of 0.96 mmol/g was determined by ^{1}H NMR (10 s relaxation time). ^{1}H NMR (CDCl$_3$) δ 7.85-7.33 (bm, aromatic), 7.33-6.82 (bm, aromatic), 6.82-6.25 (bm, aromatic) 5.01-4.82 (bm, benzylic), 2.39-1.70 (bm, PS-α-methylenes), 1.70-1.16 (bm, PS-β-methylenes); ^{13}C NMR (CDCl$_3$) δ 145.1, 134.0, 133.8, 133.5, 132.4, 132.0, 131.9, 131.7, 128.4, 128.3, 127.9, 127.5, 124.3, 114.8, 114.7, 70.0, 42.5, 40.3; ^{31}P NMR (CDCl$_3$) δ 29.35; IR (KBr) 3025, 2921, 1943,

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[1] Modified procedure from: Green, B.; Garson, L. R. *J. Chem. Soc.* **1969**, *C*, 401-406.
[2] Senear, A. E.; Valient, W.; Wirth, J. *J. Org. Chem.* **1960**, *25*, 2001-2006.

1873, 1596, 1493, 1451, 1197, 1178, 1118, 751, 697, 546 cm^{-1}; Anal. calcd.: C, 87.04; H, 6.92; found: C, 85.95; H, 6.88.

Poly(styrene-*co*-diphenyl-[4-(4-vinyl-benzyloxy)-phenyl]-phosphine (4). Polymer **4** was prepared by adding *N,N*-dimethylaniline (100 mL, 790 mmol) to a solution of **3** (82 g, 78.7 mmol) in *p*-dioxane (800 mL). Trichlorosilane (80 g, 790 mmol) was then added to the reaction mixture through a reflux condenser (condenser temperature: -10 °C) and subsequently heated at 100 °C for 15 hours under vigorous magnetic stirring (maintaining the condenser temperature at –10 °C). The solution was then poured on methyl alcohol (5 L) under vigorous magnetic stirring thus precipitating the polymer. The polymer suspension was then filtered using a corse sintered glass filter, rinsed with water and methyl alcohol to be subsequently placed in a vacuum oven at 70 °C for 15 hours. The title compound **4** was obtained as a white solid (80.7 g, 100%). A loading of 0.96 mmol/g was determined by ^{1}H NMR (10 s relaxation time). ^{1}H NMR (CDCl$_3$) δ 7.46-7.27 (bm, aromatic), 7.27-6.86 (bm, aromatic), 6.86-6.30 (bm, aromatic) 5.09-4.84 (bm, benzylic), 2.34-1.72 (bm, PS-α-methylenes), 1.72-1.25 (bm, PS-β-methylenes); ^{13}C NMR (CDCl$_3$) δ 145.1, 137.6, 135.6, 135.5, 133.5, 133.3, 128.5, 128.4, 128.3, 127.9, 127.5, 125.6, 115.0, 69.9, 40.2, 43.0; ^{31}P NMR (CDCl$_3$) δ -6.36. IR (KBr) 3058, 3024, 2921, 1944, 1881, 1805, 1790, 1593, 1494, 1452, 1434, 1242, 1177, 1027, 744, 697, 532 cm^{-1}; Anal. calcd.: C, 88.46; H, 7.04; found: C, 87.33; H, 7.22.

Annexe II - Information supplémentaire pour la partie 4.1

XI

STEREOCHEMISTY ABSTRACT

CATALYTIC ENANTIOSELECTIVE CYCLOPROPANATION OF CINNAMATE DERIVATIVES MEDIATED BY A BIS(OXAZOLINE)-COPPER COMPLEX USING DIAZOMETHANE

André B. Charette[*], Marc K. Janes and Hélène Lebel[†]

Département de Chimie, Université de Montréal, P.O. Box. 6128, Station Downtown, Montréal (Québec), Canada, H3C 3J7
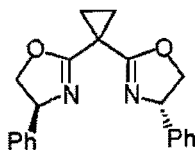
(4S)-4-phenyl-2-{1-[(4S)-4-phenyl-4,5-dihydro-1,3-oxazol-2-yl]cyclopropyl}-4,5-dihydro-1,3-oxazole

$C_{21}H_{20}N_2O_2$

$[\alpha]_D^{20} = -50.2$ (c = 0.62 ,CHCl$_3$)
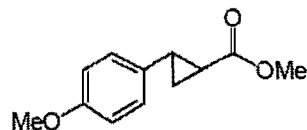
methyl 2-(4-methoxyphenyl)cyclopropanecarboxylate

$C_{12}H_{14}O_3$

E.e. = 55 %
$[\alpha]_D^{20} = -159.13$ (c = 1.15 ,CHCl$_3$)
Chromatographic separation by: SFC
Column: WHELK-O1
Eluent: 2.0% MeOH / CO$_2$ (2.0 mL/min)
Enantiomer R.T.: 6.49 min and 7.25 min

methyl 2-(4-methylphenyl)cyclopropanecarboxylate

$C_{12}H_{14}O_2$

E.e. = 60 %
$[\alpha]_D^{20} = -203.23$ (c= 0.43 ,CHCl$_3$)
Chromatographic separation by: SFC
Column: WHELK-O1
Eluent: 0.9% MeOH / CO$_2$ (0.9 mL/min)
Enantiomer R.T.: 10.20 min and 11.79 min

[*] Corresponding author. Tel.: (514)343-8432; Fax: (514)343-5900; email: █████████
[†] Professor Hélène Lebel.
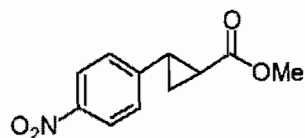
methyl 2-(4-nitrophenyl)cyclopropanecarboxylate

$C_{11}H_{11}NO_4$

E.e. = 80 %
$[\alpha]_D^{20}$ = -131.43 (c= 0.35 ,CHCl$_3$)
Chromatographic separation by : SFC
Column: WHELK-O1
Eluent: 2.0% MeOH / CO$_2$ (2.0 mL/min)
Enantiomer R.T.: 4.27 min and 4.67 min
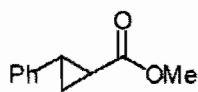
methyl (1S,2S)-2-phenylcyclopropanecarboxylate

$C_{11}H_{12}O_2$

E.e. = 72 %
$[\alpha]_D^{20}$ = -238.06 (c= 1.24 ,CHCl$_3$)
Chromatographic separation by : GC
Column:CYCLODEX G
Eluent: H$_2$ (26 psi), 120°C isotherm
Enantiomer R.T.: 14.20 min and 14.43 min
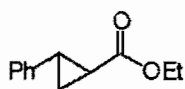
ethyl (1S,2S)-2-phenylcyclopropanecarboxylate

$C_{12}H_{14}O_2$

E.e. = 73 %
$[\alpha]_D^{20}$ = -227.54 (c= 2.7 ,CHCl$_3$)
Chromatographic separation by : SFC
Column: WHELK-O1
Eluent: 0.9% MeOH / CO$_2$ (0.9 mL/min)
Enantiomer R.T.: 8.38 min and 9.32 min

isopropyl 2-phenylcyclopropanecarboxylate

$C_{13}H_{16}O_2$

E.e. = 69 %
$[\alpha]_D^{20}$ = -175.09 (c= 1.32 ,CHCl$_3$)
Chromatographic separation by : SFC
Column: WHELK-O1
Eluent: 0.9% MeOH / CO$_2$ (0.9 mL/min)
Enantiomer R.T.: 8.56 min and 9.82 min

**phenyl 2-
phenylcyclopropanecarboxylate**

$C_{16}H_{14}O_2$

E.e. = 74 %
$[\alpha]_D^{20}$ = -240.00 (c= 0.74 ,CHCl$_3$)
Chromatographic separation by : SFC
Column: WHELK-O1
Eluent: 5.0% MeOH / CO$_2$ (2.0 mL/min)
Enantiomer R.T.: 3.81 min and 4.04 min
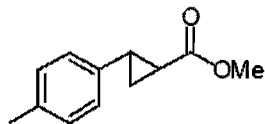

benzyl 2-phenylcyclopropanecarboxylate

$C_{17}H_{16}O_2$

E.e. = 75 %
$[\alpha]_D^{20}$ = -146.49 (c= 1.14 ,CHCl$_3$)
Chromatographic separation by : SFC
Column: WHELK-O1
Eluent: 5.0% MeOH / CO$_2$ (2.0 mL/min)
Enantiomer R.T.: 3.60 min and 3.87 min

CHARACTERIZATION

Bis(oxazoline·copper(I)-catalyzed enantioselective cyclopropanation of cinnamate esters with diazomethane

André B. Charette*, Marc K. Janes and Hélène Lebel†

Département de Chimie, Université de Montréal, P.O. Box. 6128, Station Downtown, Montréal (Québec), Canada, H3C 3J7

$[\alpha]_D^{20}$=-50.2 (c = 0.62, CHCl$_3$)
LRMS (APCI, Pos) calcd for C$_{21}$H$_{20}$N$_2$O$_2$:
332.15, found 333.2

1f

^{1}H-NMR

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* Corresponding author. Tel.: (514)343-8432; Fax: (514)343-5900; email: ▮▮▮▮▮▮▮▮
† Professor Hélène Lebel.

¹³C-NMR

IR

O ‖ Ph ⏜ OPh **2d**	Anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.63; H, 5.57

^{1}H-NMR

^{13}C-NMR

IR
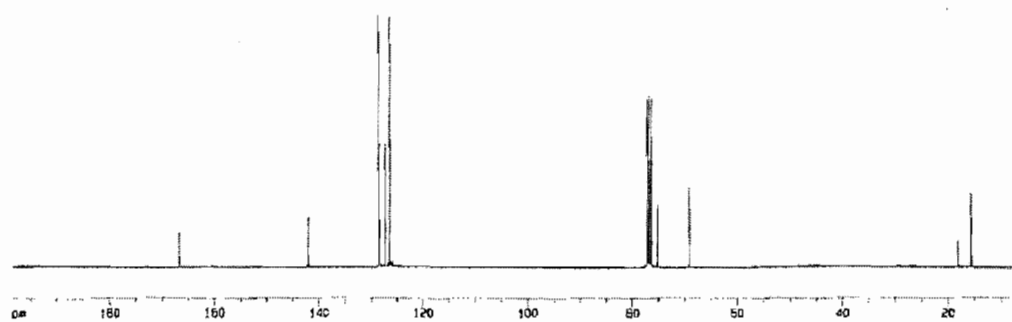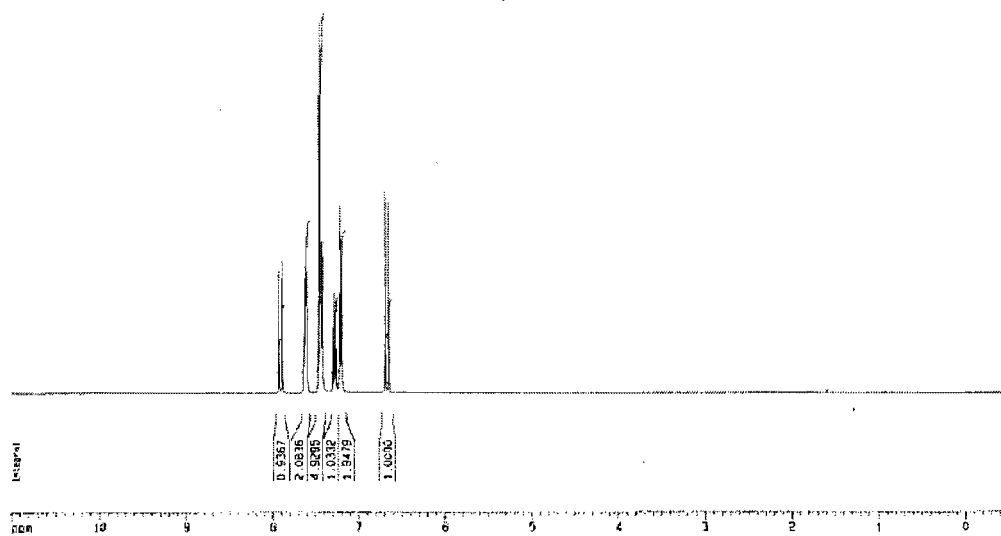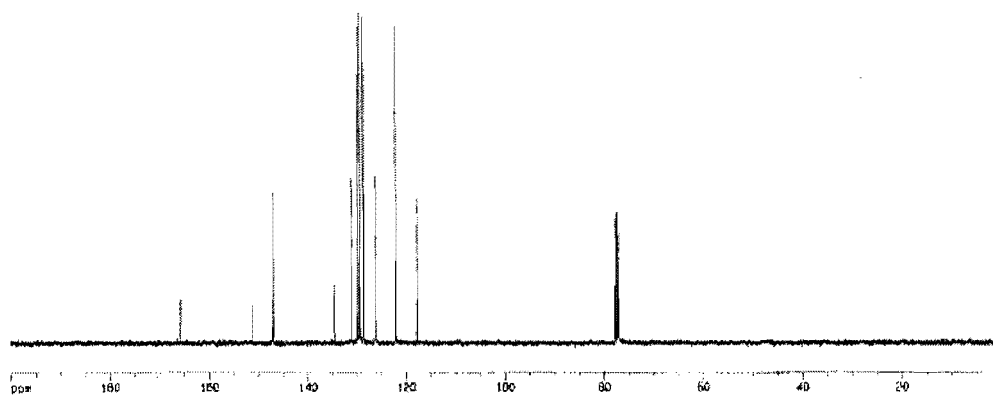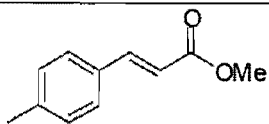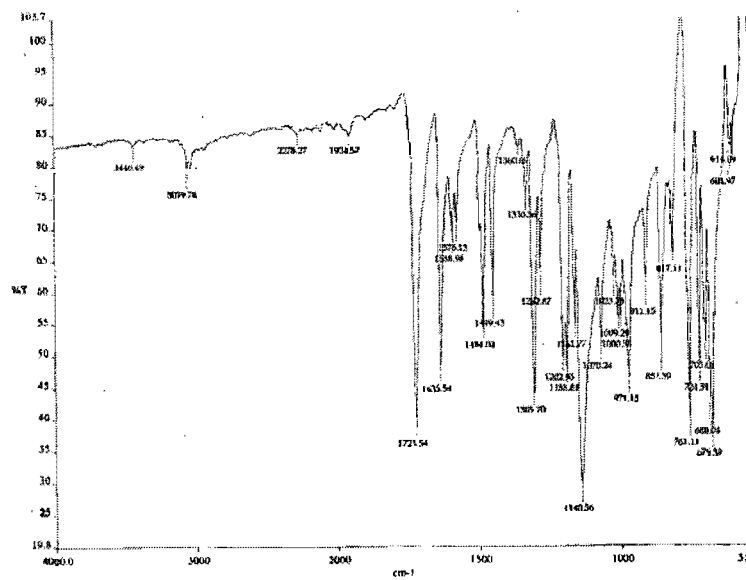
2g (structure: 4-methyl cinnamic acid methyl ester)	Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.36; H, 7.27

^{1}H-NMR

^{13}C-NMR

IR

| | Anal. calcd for C$_{10}$H$_9$NO$_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.91; H, 4.33; N, 6.59 |

2h
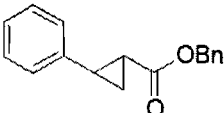
^{1}H-NMR

^{13}C-NMR

IR

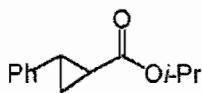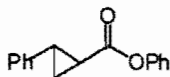|	
C17H16O2 structure with OBn group, 3c	E.e. = 75 % $[\alpha]_D^{20}$ = -146.49 (c= 1.14 ,CHCl3) Chromatographic separation by : SFC Column: WHELK-O1 Eluent: 5.0% MeOH / CO2 (2.0 mL/min) Enantiomer R.T.: 3.60 min and 3.87 min Anal. calcd for C17H16O2: C, 80.93; H, 6.39. Found: C, 80.72; H, 6.78

SFC - RACEMIC MIXTURE


```
********************************************************************
                    Area Percent Report
********************************************************************

Sorted by Signal
Multiplier          :     1.000000

Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak    RT      Type   Width    Area          Height       Area
 #     [min]           [min]    [mAU*sec]     [mAU]        %
|----|-------|------|-------|------------|-----------|----------|
  1    3.555   VF     0.079   16032.35645   3037.61133   47.9394
  2    3.812   FF     0.086   17410.61914   3013.03149   52.0606

Totals :                     33442.97656   6050.64258
```

SFC - PRODUCT


```
══════════════════════════════════════════════════════════════════
                        Area Percent Report
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Sorted by Signal
Multiplier              :      1.000000

Signal 1: DAD1 B, Sig=220,4 Ref=off

  Peak    RT      Type   Width     Area        Height       Area
   #     [min]           [min]   [mAU*sec]     [mAU]          %
 |----|--------|------|-------|------------|------------|----------|
    1    3.602   BV     0.072    314.11063    65.75221    12.5439
    2    3.869   VF     0.081   2189.97168   400.81122    87.4561
```

^{1}H-NMR

^{13}C-NMR

IR

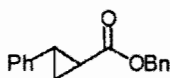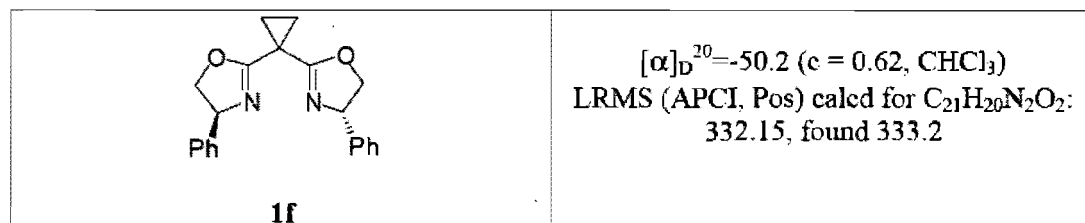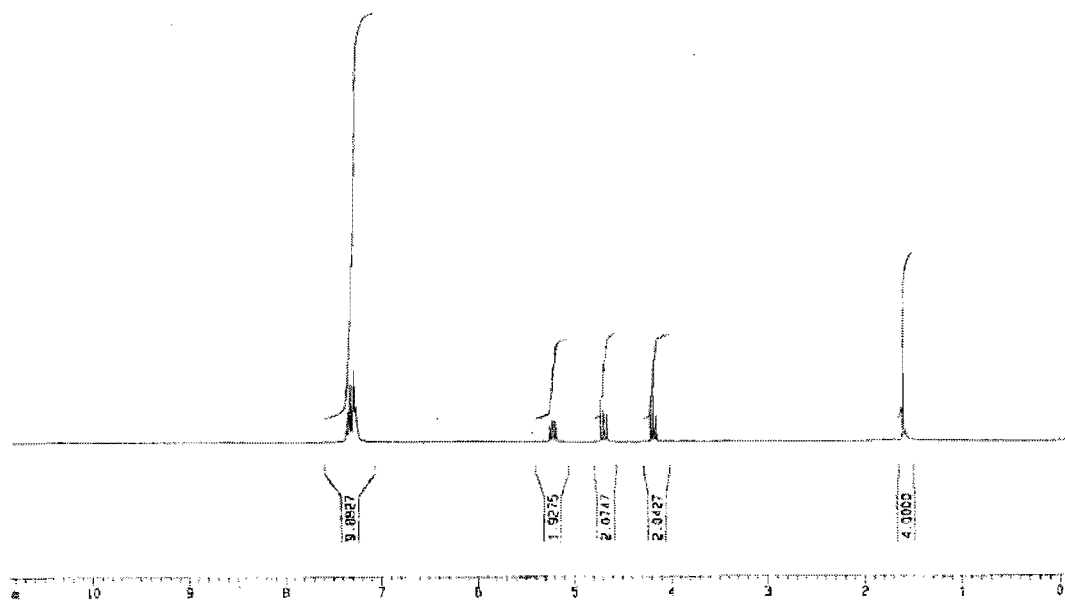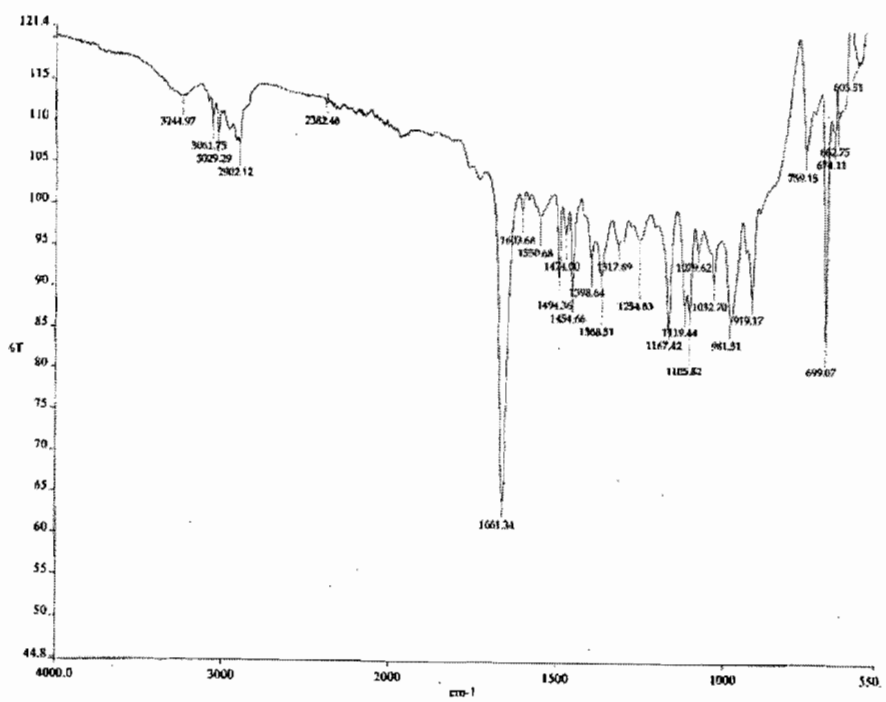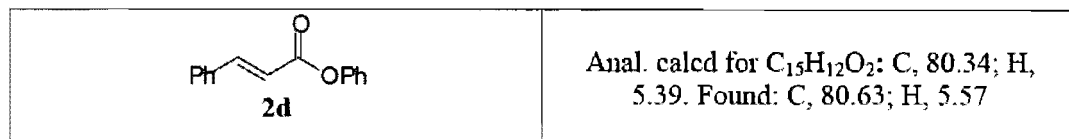|	E.e. = 74 %
$C_{16}H_{14}O_2$ **3d**	$[\alpha]_D^{20}$ = -240.00 (c= 0.74 ,CHCl$_3$) Chromatographic separation by : SFC Column: WHELK-O1 Eluent: 5.0% MeOH / CO$_2$ (2.0 mL/min) Enantiomer R.T.: 3.81 min and 4.04 min HRMS (MAB) calcd for $C_{16}H_{14}O_2$ [M]$^+$: 238.0994, found 238.1006

SFC - RACEMIC MIXTURE


```
                        Area Percent Report


Sorted by Signal
Multiplier          :       1.000000

Signal 1: DAD1 C, Sig=254,30 Ref=off

Peak    RT      Type  Width   Area          Height       Area
#       [min]         [min]   [mAU*sec]     [mAU]        %
|----|---------|------|------|-----------|-----------|-----------|
  1     3.779   BF    0.076   1921.06470    366.51410    48.3065
  2     4.004   FF    0.087   2055.75903    335.98776    51.6935

Totals :                     3976.82373    702.50183
```

SFC - PRODUCT


```
=====================================================
                    Area Percent Report
=====================================================

Sorted by Signal
Multiplier              :     1.000000

Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak   RT     Type  Width   Area        Height      Area
 #    [min]         [min]   [mAU*sec]   [mAU]       %
|----|--------|-----|------|-----------|-----------|---------|
   1   3.812  BF    0.074   1153.91992   254.24184  12.8195
   2   4.036  FB    0.082   7847.37598  1414.93091  87.1805

Totals :                    9001.29590  1649.17273
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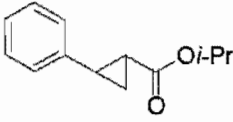
¹H-NMR

^{13}C-NMR

IR

$C_{13}H_{16}O_2$ **3e**	E.e. = 69 % $[\alpha]_D^{20}$ = -175.1 (c= 1.32 ,CHCl$_3$) Chromatographic separation by : SFC Column: WHELK-O1 Eluent: 0.9% MeOH / CO$_2$ (0.9 mL/min) Enantiomer R.T.: 8.56 min and 9.82 min HRMS (MAB) calcd for $C_{13}H_{16}O_2$ [M]$^+$: 204.1150, found 204.1151

SFC - RACEMIC MIXTURE
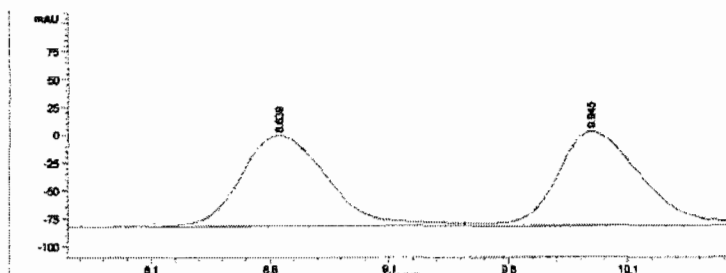
Area Percent Report

Sorted by Signal
Multiplier   :   1.000000

Signal 1: DAD1 C, Sig=254,30 Ref=off

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	8.639	FF	0.393	2063.68286	81.54475	49.9446
2	9.945	FF	0.362	2068.26465	84.88935	50.0554

Totals :   4131.94727   166.43410

SFC - PRODUCT


```
========================================================================
                        Area Percent Report
========================================================================

Sorted by Signal
Multiplier              :       1.000000

Signal 1: DAD1 B, Sig=220,4 Ref=off

  Peak    RT      Type   Width    Area        Height      Area
   #     [min]           [min]   [mAU*sec]     [mAU]        %
 |----|---------|------|-------|------------|-----------|----------|
   1    8.564    BF     0.385   9165.07910   380.27798   14.7110
   2    9.820    FF     0.358   53135.75000  2325.72876  85.2890

Totals :                        62300.82812  2706.00684
```

^{1}H-NMR

^{13}C-NMR

IR

Annexe III – Information supplémentaire pour le Chapitre 6

Structure and Reactivity of "Unusual" *N*-Heterocyclic Carbene (NHC) Palladium Complexes Synthesized from Imidazolium Salts.

Hélène Lebel,*[‡] Marc K. Janes,[‡] André B. Charette,[‡] Steven P. Nolan[§]

Département de chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montréal, Québec, Canada, H3C 3J7; Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148.

Supporting Information

[‡] Université de Montréal.

[§] University of New Orleans.

General: Unless otherwise noted, all reactions were carried out using standard Schlenk techniques under a dry argon atmosphere or in an MBraun glovebox containing dry argon (less than 1 ppm of oxygen and water). Dioxane was distilled over sodium/benzophenone under argon and degassed prior to use. Anhydrous *N,N*-Dimethylacetamide 99.8% was purchased from Aldrich and degassed prior to use. 4-Chlorotoluene was freshly distilled over CaH_2 under argon and degassed prior to use. Bromobenzene was refluxed and freshly distilled from sodium under argon. Cesium carbonate was purchased from Aldrich, dried at 175 °C for 15 hours under vacuum and kept in a glove-box. $Pd(OAc)_2$ and $PdCl_2$ were purchased from Strem, stored in a glove-box under an argon atmosphere and used as received. IMesHCl,[1] 4-MeOPhB(OH)$_2$,[2] butyl acrylate,[3] were synthesized according to literature procedures and are also commercially available from Strem or Aldrich. All reported yields are of isolated pure material obtained from an average of at least two runs. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash chromatography was performed using Silicycle, Ultra Pur Silica Gel 60 Å (230-400 mesh) with the indicated solvent system. ^1H NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). For complex **1** and **2**, deuterated chloroform for NMR analysis was passed through a pad of basic alumina prior to use. Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of deuterated chloroform (77.36 ppm) on the δ scale. The elemental analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal or by the Canadian Microanalytical Service ltd. Melting points are uncorrected.

Synthesis of normal IMes$_2$PdCl$_2$ (1)

Under an argon atmosphere a flask was charged with IMesHCl (150 mg, 0.44 mmol), PdCl$_2$ (37 mg, 0.21 mmol) and Cs$_2$CO$_3$ (681 mg, 2.09 mmol). The flask was then fitted with a condenser and a septum. Dioxane (4.4 mL) was added *via* syringe and the reaction mixture was heated to 80 °C for 5 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (CH$_2$Cl$_2$) afforded **1** as a white solid (112 mg, 68%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.94 (s, 8H, ArH), 6.79 (s, 4H, NCH=CHN), 2.49 (s, 12H, *p*-ArCH$_3$), 1.96 (s, 24H, *o*-ArCH$_3$).

^{13}C NMR (100 MHz, CDCl$_3$) δ 171.2 (s), 137.9 (s), 136.5 (s), 136.1 (s), 129.1 (s), 122.8 (s), 21.6 (s), 19.3 (s).

Calcd. for C$_{42}$H$_{48}$Cl$_2$N$_4$Pd: C, 64.16; H, 6.15; N, 7.13. Found: C, 64.26; H, 6.20; N, 7.00.

Dec. point: ca. 250 °C

Synthesis of abormal IMes$_2$PdCl$_2$ (2)

Under an argon atmosphere, a flask was charged with IMesHCl (109 mg, 0.32 mmol) and Pd(OAc)$_2$ (35 mg, 0.16 mmol). The flask was then fitted with a condenser and a septum. Dioxane (1.6 mL) was added *via* syringe and the reaction mixture was heated to 80 °C for 6 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (100% DCM) afforded **2** as a white solid (91 mg, 74%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, J = 1.7 Hz, 1 H, NCHN), 6.99 (s, 4 H, mes-CH), 6.91 (s, 4 H, mes-CH), 6.85 (s, 2 H, NCH=CHN), 6.57 (d, J = 1.7 Hz, 1 H, CH(=C)N), 2.46 (s, 3 H, mes-CH$_3$), 2.43 (s, 6 H, mes-CH$_3$), 2.30 (s, 3 H, mes-CH$_3$), 2.20 (s, 12 H, mes-CH$_3$), 1.98 (s, 6 H, mes-CH$_3$), 1.95 (s,6 H, mes-CH$_3$).

^{13}C NMR (100 MHz, CDCl$_3$) δ 175.9 (Pd-CN$_3$), 150.7 (Pd-C(=C)N), 139.9 (1 mes-CR$_4$), 137.9 (1+2 mes-CR$_4$), 136.6 (4 mes-CR$_4$), 136.4 (2 mes-CR$_4$), 135.7 (2 mes-CR$_4$), 135.4 (1 mes-CR$_4$), 134.7 (2 mes-CR$_4$), 132.2 (1 mes-CR$_4$), 131.6 (NCHN), 129.3 (2 mes-CH), 129.1 (4 mes-CH), 128.9 (2 mes-CH), 125.5 (CH(=C)N), 122.8 (NCH=CHN), 21.5 (mes-CH$_3$), 21.4 (mes-CH$_3$), 21.2 (mes-CH$_3$), 19.1 (mes-CH$_3$), 18.9 (mes-CH$_3$), 17.6 (mes-CH$_3$).

Calcd. for C$_{42}$H$_{48}$Cl$_2$N$_4$Pd: C, 64.16; H, 6.15; N, 7.13. Found: C, 63.95; H, 6.17; N, 7.10.

Dec. point: ca. 240 °C

Typical Suzuki procedure using preformed catalysts 1 or 2

Under an atmosphere of argon, a flask was charged with abnormal IMes$_2$PdCl$_2$ 2 (20 mg, 0.025 mmol) and Cs$_2$CO$_3$ (652 mg, 2.00 mmol). Dioxane (1 mL) was added *via* syringe, followed by 4-chlorotoluene (119 µL, 1.00 mmol). A solution of 4-MeO-PhB(OH)$_2$ (228 mg, 1.50 mmol) in dioxane (2 mL) was added *via* cannula. The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 80 °C. Stirring was continued for 23 hours. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (20 mL), filtered through a pad of celite using dichloromethane (100 mL). The volatiles were evaporated under reduced pressure. Purification by flash column chromatography (1% EtOAc / Hex) yielded 4-methoxy-4'-methylbiphenyl as a white solid (87 mg, 0.44 mmol, 44%). All coupling products were found to be identical by NMR to literature data.[4]

Typical Suzuki procedure using *in situ* formation of the catalyst[5]

Under an atmosphere of argon, a flask was charged with Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), IMesHCl (17 mg, 0.05 mmol) and Cs$_2$CO$_3$ (652 mg, 2.00 mmol). Dioxane (2 mL) was added *via* syringe. After 30 min at 80 °C, the reaction mixture was cooled to room temperature and 4-chlorotoluene (119 µL, 1.0 mmol) was added to the reaction mixture. A solution of 4-MeO-PhB(OH)$_2$ (228 mg, 1.5 mmol) in dioxane (1 mL) was then added *via* cannula. The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 80 °C. Stirring was continued for 23 hours. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (20 mL), filtered through a pad of celite using dichloromethane (100 mL) and volatiles were evaporated under reduced pressure. Purification by column chromatography (1% EtOAc / Hex) yielded 4-methoxy-4'-methylbiphenyl as a white solid (151 mg, 0.76 mmol, 76%). All coupling products were found to be identical by NMR to literature data.[4]

Typical Heck procedure using preformed catalysts 1 or 2

Under an atmosphere of argon a flask was charged with abnormal IMes$_2$PdCl$_2$ 2 (20 mg, 0.02 mmol) and Cs$_2$CO$_3$ (652 mg, 2.00 mmol). N,N-dimethylacetamide (2 mL) was added *via* syringe followed by butyl acrylate (229 µL, 1.60 mmol) and then bromobenzene (105 µL, 1.00 mmol). The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 120 °C. Stirring was continued for 7 hours. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (20 mL) and washed with water (15 mL). The aqueous phase was then extracted twice with diethyl ether (20 mL), the organic phases were combined and dried over Na$_2$SO$_4$. The volatiles were removed under reduced pressure. Flash column chromatography (4% EtOAc / Hex) yielded n-butylcinnamate as a white solid (157mg, 0.77 mmol, 77%). All coupling products were found to be identical by NMR to literature data.[6]

Typical Heck procedure using *in situ* formation of catalyst[7]

Under an atmosphere of argon, a flask was charged with Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), IMesHCl (13.6 mg, 0.04 mmol) and Cs$_2$CO$_3$ (652 mg, 2.00 mmol). N,N-dimethylacetamide (2 mL) was added *via* syringe and the reaction mixture was stirred for 15 minutes at room temperature. Butyl acrylate (229 µL, 1.60 mmol) was then added, followed by bromobenzene (105 µL, 1.00 mmol). The argon inlet was removed, the septum was covered with parafilm and the reaction vessel was placed in a oil bath at 120 °C. Stirring was continued for 4 hours. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (20 mL) and washed with water (15 mL). The aqueous phase was then extracted twice with diethyl ether (20 mL), the organic phases were combined and dried over Na$_2$SO$_4$. The volatiles were removed under reduced pressure. Flash column chromatography (4% EtOAc / Hex) yielded n-butylcinnamate as a white solid (135 mg, 0.66 mmol, 66%). All coupling products were found to be identical by NMR to literature data.[6]

ORTEP representation of complex 1 (elipsoid drawn at 30% propability level)
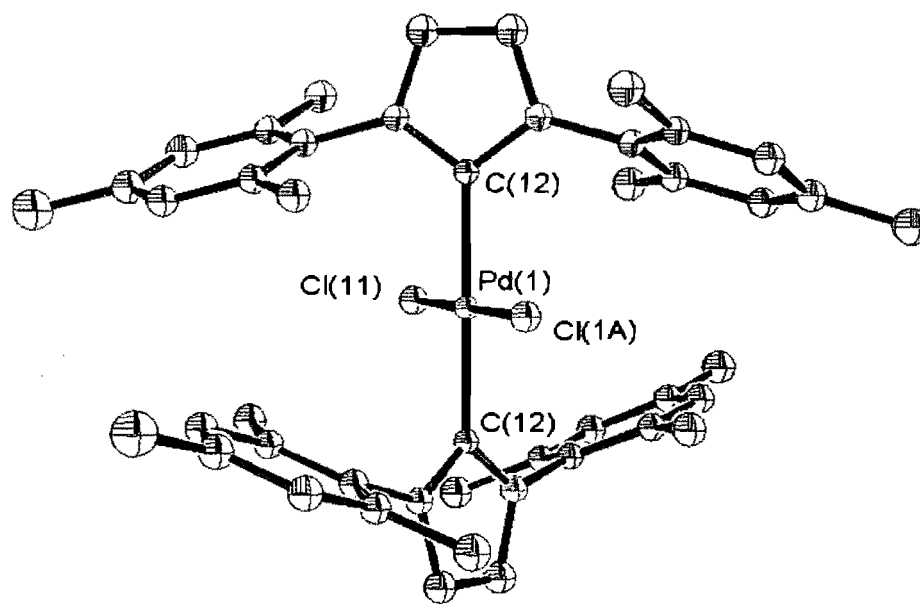
(1) (a) Arduengo, A.J. III. US patent 5 077 414, 1991; (b) Arduengo, A.J. III; Krafczyk, R.; Schmutzler, R. *Tetrahedron*, **1999**, *55*, 14523-14534.

(2) (a) Schmid, M.; Eberhardt, R.; Klinga, M. Leskelä, Rieger, B. *Organometallics*, **2001**, *20*, 2321-2330; (b) Steele, M.; Watkinson, M.; Whiting, A. *J. Chem. Soc., Perkin Trans. 1*, **2001**, *6*, 588-598.

(3) Serra, A.C.; da Silva Corrêa, C.M.M.; do Vale, M.L.C. *Tetrahedron*, **1991**, *47*, 9463-9488.

(4) Farina, V.; Krishnan, B.; Marshall, D.R.; Roth, G.P. *J. Org. Chem.* **1993**, *58*, 5434-5444.

(5) Grasa, G.A.; Viciu, M.S.; Huang, J.; Zhang, C.; Trudell, M.L.; Nolan, S.P. *Organometallics*, **2002**, *21*, 2866-2873.

(6) Feuerstein, M.; Doucer, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923-5925.

(7) Yang, C.; Nolan, S.P. *Synlett*, **2001**, *10*, 1539-1542.

Annexe IV – Information supplémentaire pour le Chapitre 7

Abnormal *N*-Heterocyclic Carbene (NHC) Palladium Complexes Bearing a C5-Metallated Arylimidazolium Ligand: Scope and Mechanism

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Supporting Information

(reference and permissions to be inserted)

General: Unless otherwise noted, all reactions were carried out using standard Schlenk techniques under a dry argon atmosphere or in an MBraun glovebox containing dry argon (less than 1 ppm of oxygen and water). Dioxane was distilled over sodium/benzophenone under argon. Cesium carbonate was purchased from Aldrich, dried at 175 °C for 15 hours under vacuum and kept in a glove-box. $Pd(OAc)_2$ and $PdCl_2$ were purchased from Strem, stored in a glove-box under an argon atmosphere and used as received. IMesHCl, IPrHCl, IAdHCl are commercially available from Strem Chemicals, Inc. and can be synthesized according to literature procedures.[1] IXyHCl, ICyHCl and I(α-Me)BnHCl were synthesized according to literature procedures.[1,2] All reported yields are of isolated pure material obtained from an average of at least two runs. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash chromatography was performed using Silicycle, ultrapur Silica Gel 60 Å (230-400 mesh) with the indicated solvent system. ^1H NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-500, a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (500, 400, 400, 300 and 300 MHz respectively). For all complexes, deuterated chloroform for NMR analysis was passed through a pad of basic alumina prior to use. Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-500, a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (125, 100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of deuterated chloroform (76.9 ppm) on the δ scale. The elemental analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal or by the Canadian Microanalytical Service ltd.

Synthesis of normal IPr₂PdCl₂ (2c)

Under an argon atmosphere a flask was charged with IPrHCl (120 mg, 0.282 mmol), PdCl₂ (24 mg, 0.135 mmol) and Cs₂CO₃ (175 mg, 0.538 mmol). The flask was then fitted with a septum and dioxane (2.8 mL) was added *via* syringe. The flask was sealed with parafilm and the reaction mixture was heated to 80 °C for 20 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (1% acetone/CHCl₃) afforded **2c** as a white solid (43 mg, 33%).

^{1}H NMR (400 MHz, CDCl₃) δ 7.37 (t, *J* = 7.7 Hz, 4H, *p*-ArH), 7.07 (d, *J* = 7.7 Hz, 8H, *m*-ArH), 6.72 (s, 4H, N-CH=C), 2.91 (sep, *J* = 6.7 Hz, 8H, (*i*-Pr)CH), 0.94 (d, *J* = 6.6, 24H, (*i*-Pr)CH₃), 0.87 (d, *J* = 6.9, 24H, (*i*-Pr)CH₃).

^{13}C NMR (100 MHz, CDCl₃) δ 172.5 (s), 146.4 (s), 136.2 (s), 129.1 (s), 124.0 (s), 123.6 (s), 22.1 (s), 26.0 (s), 22.8 (s).

Calcd. for C₅₄H₇₂Cl₂N₄Pd: C, 67.95; H, 7.60; N, 5.87. Found: C, 68.47; H, 7.88; N, 5.70.

Synthesis of normal IPr₂Pd₂Cl₄ (2d) and abnormal IPr₂PdCl₂ (2b)

Under an argon atmosphere a flask was charged with IPrHCl (200 mg, 0.470 mmol) and Pd(OAc)₂ (51 mg, 0.225 mmol). The flask was then fitted with a septum and dioxane (5.0 mL) was added *via* syringe. The flask was sealed with parafilm and the reaction mixture was heated to 80 °C for 5 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (1% acetone/CHCl₃) afforded **2d**[3] as a bright orange solid (89 mg, 35%) and **2b**[4] as a white solid (92 mg, 43%).

For **2b**: ^{1}H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 1.8 Hz, 1 H, NCHN), 7.41-7.33 (m, 4 H, Ar-CH), 7.23 (d, *J* = 7.8 Hz, 2 H, Ar-CH), 7.20 (d, *J* = 7.74 Hz, 4 H, Ar-CH), 7.08 (d, *J* = 7.76 Hz, 2 H, Ar-CH), 6.87 (s, 2 H, NCH=C), 6.51 (d, *J* = 1.8 Hz, 1 H, NCH=C), 3.15 (sep, *J* = 6.8 Hz, 4 H, (*i*-Pr)CH), 2.74 (sep, *J* = 6.8 Hz, 2 H, (*i*-Pr)CH), 2.44 (sep, *J* = 6.8 Hz, 2 H, (*i*-Pr)CH), 1.24 (d, *J* = 6.6 Hz, 12 H, (*i*-Pr)CH₃), 1.19 (d, *J* = 6.7 Hz, 6 H, (*i*-Pr)CH₃), 1.02 (d, *J* = 6.3 Hz, 6 H, (*i*-Pr)CH₃), 1.00 (d, *J* = 6.8 Hz, 12 H, (*i*-Pr)CH₃), 0.92 (d, *J* = 6.6 Hz, 6 H, (*i*-Pr)CH₃), 0.83 (d, *J* = 6.9 Hz, 6 H, (*i*-Pr)CH₃).

^{13}C NMR (100 MHz, CDCl$_3$) δ 178.1 (s), 152.4 (s), 146.6 (s), 146.3 (s), 145.9 (s), 136.3 (s), 134.8 (s), 133.0 (s), 131.4 (s), 130.5 (s), 129.4 (s), 129.2 (s), 126.2 (s), 124.0 (s), 123.7 (s), 123.6 (s), 123.4 (s), 28.3 (s), 28.1 (s), 28.0 (s) , 26.4 (s), 26.0 (s), 24.8 (s), 24.7 (s), 23.2 (s), 22.8 (s).

Calcd. for C$_{38}$H$_{40}$Cl$_2$N$_4$Pd: C, 67.95; H, 7.60; N, 5.87 Found: C, 67.60; H, 7.74; N, 5.67.

Synthesis of abormal IXy$_2$PdCl$_2$ (3b)

Under an argon atmosphere, a flask was charged with IXyHCl (90 mg, 0.288 mmol) and Pd(OAc)$_2$ (31 mg, 0.137 mmol). The flask was then fitted with a septum and dioxane (2.8 mL) was added *via* syringe. The flask was sealed with parafilm and the reaction mixture was heated to 80 °C for 5 hours. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure. Purification by flash column chromatography (100% DCM) afforded 3b as a white solid (75 mg, 75%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, J = 1.5 Hz, 1 H, NCHN), 7.33-7.27 (m, 3 H, ArH), 7.24 (t, J = 7.6 Hz, 1 H, ArH), 7.17 (d, J = 7.5 Hz,4 H, ArH), 7.09 (d, J = 7.6 Hz, 4 H, ArH), 6.88 (s, 2 H, NCH=C), 6.57 (d, J = 1.5 Hz, 1 H, NCH=C), 2.24 (s, 12 H. ArCH$_3$), 2.01 (s, 6 H, ArCH$_3$), 1.99 (s, 6 H, ArCH$_3$).

^{13}C NMR (100 MHz, CDCl$_3$) δ 175.1 (s), 150.1 (s), 138.2 (s), 137.2 (s), 136.4 (s), 135.4 (s), 134.5 (s), 134.1 (s), 130.8 (s), 129.5 (s), 128.1 (2 overlapped s), 128.0 (s), 127.9 (s), 127.8 (s), 124.7 (s), 122.1 (s), 18.7 (s), 18.5 (s), 17.2 (s).

Calcd. for C$_{38}$H$_{40}$Cl$_2$N$_4$Pd·H$_2$O: C, 61.01; H, 5.66; N, 7.49. Found: C, 61.27; H, 5.33; N, 7.28.
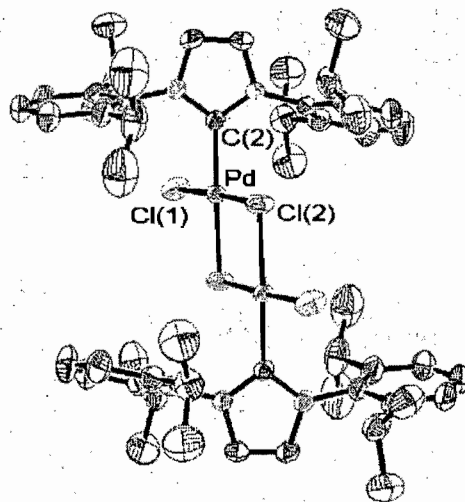
Thermal ellipsoid (30% prob.) plot of normal IPr$_2$Pd$_2$Cl$_4$ **2d**. Selected bond lengths (Å) and angles (deg): C(2)-Pd, 1.96(2); Cl(1)-Pd, 2.267(7); Cl(2)-Pd, 2.315(6); C(2)-Pd-Cl(1), 89.57(7); C(2)-Pd-Cl(2), 93.18(7); Cl(1)-Pd-Cl(2), 177.16(2).
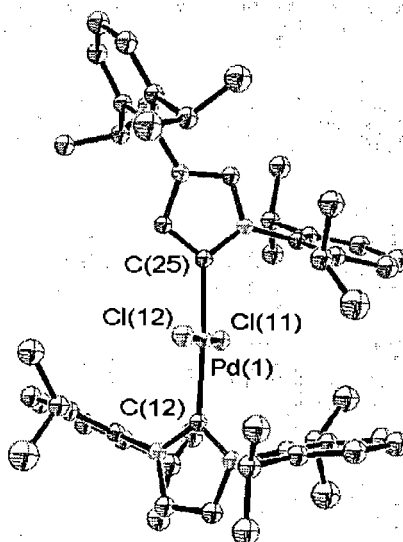
Thermal ellipsoid (30% prob.) plot of abnormal IPr₂PdCl₂ **2b**. Selected bond lengths (Å) and angles (deg): Pd(1)-C(25), 2.022(19); Pd(1)-C(12), 2.0534(19); Pd(1)-Cl(11), 2.2932(5); Pd(1)-Cl(12), 2.3202(5); C(12)-Pd(1)-C(25), 176.79(7); C(12)-Pd(1)-Cl(11), 91.74(5); C(12)-Pd(1)-Cl(12), 90.54(5); Cl(11)-Pd(1)-Cl(12), 177.526(17).

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[1] Arduengo, A.J. III. US patent 5 077 414, 1991; (b) Arduengo, A.J. III; Krafczyk, R.; Schmutzler, R. *Tetrahedron*, **1999**, *55*, 14523-14534.

[2] Lebel, H.; del Rayo, M. S. S.; Bélanger-Gariépy, F. *Acta Cryst.* **2004**, *E60*, 755.

[3] **2d** was found to be identical by NMR to literature data: M.S. Viciu, R.M. Kissling, E.D. Stevens, S.P. Nolan, *Org. Lett.*, 2002, 4, 2229; D.R. Jensen, M.S. Sigman, *Org. Lett.*, 2003, 5, 63.

[4] Abnormal and normal IPr₂PdCl₂ are also reported in the literature and prepared according to our previously reported procedure: Campeau, L. -C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857.

Annexe V – Analyse crystallographique complète IMes₂PdCl₂ anormal

Structure of CHAR95 with squeeze

ANDR B. CHARETTE, MARC JANES AND FRANCINE BÉLANGER-GARIÉPY

Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: ███████████

Abstract

The crystal stucture of the title compound, recrystallized from ...

Comment

comment

Experimental

Small details about the preparation of the compound.

Crystal data

$C_{42}H_{48}Cl_2N_4Pd$

$M_r = 786.14$

Monoclinic

Cc

$a = 50.400\,(3)$ Å

$b = 10.9732\,(6)$ Å

$c = 32.3863\,(18)$ Å

$\beta = 127.410\,(2)°$

$V = 14226.9\,(14)$ Å^3

$Z = 12$

$D_x = 1.101$ Mg m^{-3}

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 5920 reflections

$\theta = 2.73$–$54.16°$

$\mu = 4.401$ mm^{-1}

$T = 220\,(2)$ K

Needle-like

Colourless

$0.50 \times 0.05 \times 0.05$ mm

Crystal source: synthesized by the authors. See text

Data collection

Bruker AXS Smart 2K/Platform diffractom-
  eter

ω scans

Absorption correction:
  multi-scan Sadabs (Sheldrick,1996)
  $T_{min} = 0.1000$, $T_{max} = 0.2000$

59616 measured reflections

14412 independent reflections

7675 reflections with
  >2sigma(I)

$R_{int} = 0.051$

$\theta_{max} = 55.12°$

$h = -48 \rightarrow 53$

$k = -10 \rightarrow 11$

$l = -30 \rightarrow 34$

250 standard reflections

every ? reflections
  intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0565$

$wR(F^2) = 0.1151$

$S = 0.814$

14412 reflections

730 parameters

H-atom parameters constrained
$w=1/[\sigma^2(F_o^2) + (0.0393P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 0.634$ e Å^{-3}

$\Delta\rho_{min} = -0.318$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables
  for Crystallography* (Vol. C)

Absolute structure: Flack H D (1983), *Acta
  Cryst.* A39, 876-881

Flack parameter = 0.463 (9)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—C12	2.019 (13)	C114—C115	1.358 (14)
Pd1—C25	2.021 (11)	C114—C118	1.548 (15)
Pd1—Cl1	2.289 (4)	C115—C116	1.338 (14)
Pd1—Cl2	2.302 (4)	C116—C119	1.526 (15)
N11—C15	1.310 (14)	C131—C132	1.350 (17)
N11—C12	1.385 (14)	C131—C136	1.386 (15)
N11—C111	1.422 (14)	C132—C133	1.388 (18)
C12—N13	1.355 (13)	C132—C137	1.508 (18)
N13—C14	1.382 (15)	C133—C134	1.413 (17)
N13—C131	1.453 (14)	C134—C135	1.253 (18)
C14—C15	1.359 (16)	C134—C138	1.558 (19)
C111—C116	1.397 (15)	C135—C136	1.440 (18)
C111—C112	1.423 (14)	C136—C139	1.590 (18)
C112—C113	1.372 (15)	N21—C22	1.380 (14)
C112—C117	1.497 (15)	N21—C25	1.398 (13)
C113—C114	1.397 (15)	N21—C211	1.465 (14)

C22—N23	1.313 (13)	C314—C318	1.537 (15)
N23—C24	1.406 (13)	C315—C316	1.362 (14)
N23—C231	1.496 (14)	C316—C319	1.517 (14)
C24—C25	1.312 (13)	C331—C332	1.363 (14)
C211—C212	1.357 (14)	C331—C336	1.395 (14)
C211—C216	1.397 (15)	C332—C333	1.354 (14)
C212—C213	1.401 (14)	C332—C337	1.541 (15)
C212—C217	1.492 (14)	C333—C334	1.415 (15)
C213—C214	1.360 (13)	C334—C335	1.334 (16)
C214—C215	1.400 (14)	C334—C338	1.551 (18)
C214—C218	1.477 (14)	C335—C336	1.356 (15)
C215—C216	1.450 (15)	C336—C339	1.491 (14)
C216—C219	1.523 (15)	N41—C42	1.352 (13)
C231—C236	1.321 (14)	N41—C45	1.397 (13)
C231—C232	1.426 (15)	N41—C411	1.439 (12)
C232—C233	1.426 (15)	C42—N43	1.322 (13)
C232—C237	1.564 (15)	N43—C44	1.350 (13)
C233—C234	1.285 (15)	N43—C431	1.423 (14)
C234—C235	1.340 (15)	C44—C45	1.362 (14)
C234—C238	1.561 (18)	C411—C412	1.367 (13)
C235—C236	1.395 (14)	C411—C416	1.369 (13)
C236—C239	1.487 (14)	C412—C413	1.378 (13)
Pd3—C32	1.941 (14)	C412—C417	1.494 (13)
Pd3—C45	2.005 (12)	C413—C414	1.306 (13)
Pd3—Cl4	2.278 (4)	C414—C415	1.400 (13)
Pd3—Cl3	2.313 (4)	C414—C418	1.498 (14)
N31—C35	1.310 (15)	C415—C416	1.398 (13)
N31—C32	1.395 (14)	C416—C419	1.486 (14)
N31—C311	1.436 (14)	C431—C436	1.368 (15)
C32—N33	1.397 (14)	C431—C432	1.407 (15)
N33—C34	1.363 (13)	C432—C433	1.406 (15)
N33—C331	1.461 (13)	C432—C437	1.489 (15)
C34—C35	1.408 (16)	C433—C434	1.326 (15)
C311—C312	1.318 (14)	C434—C435	1.363 (17)
C311—C316	1.385 (14)	C434—C438	1.544 (19)
C312—C313	1.382 (15)	C435—C436	1.417 (18)
C312—C317	1.549 (16)	C436—C439	1.478 (18)
C313—C314	1.358 (14)	Pd5—C55	1.995 (13)
C314—C315	1.369 (14)	Pd5—C62	2.063 (13)

Pd5—Cl5	2.296 (4)	C536—C539	1.540 (14)
Pd5—Cl6	2.333 (4)	N61—C62	1.358 (14)
N51—C52	1.334 (14)	N61—C65	1.413 (15)
N51—C511	1.377 (13)	N61—C611	1.421 (15)
N51—C55	1.444 (14)	C62—N63	1.336 (14)
C52—N53	1.296 (14)	N63—C64	1.408 (14)
N53—C54	1.418 (13)	N63—C631	1.430 (14)
N53—C531	1.444 (13)	C64—C65	1.327 (15)
C54—C55	1.370 (14)	C611—C616	1.364 (16)
C511—C512	1.407 (14)	C611—C612	1.376 (14)
C511—C516	1.420 (13)	C612—C613	1.391 (16)
C512—C513	1.384 (14)	C612—C617	1.394 (16)
C512—C517	1.518 (15)	C613—C614	1.443 (17)
C513—C514	1.389 (14)	C614—C615	1.314 (16)
C514—C515	1.387 (13)	C614—C618	1.604 (19)
C514—C518	1.551 (15)	C615—C616	1.407 (16)
C515—C516	1.391 (13)	C616—C619	1.522 (15)
C516—C519	1.538 (14)	C631—C636	1.345 (14)
C531—C532	1.351 (14)	C631—C632	1.358 (15)
C531—C536	1.399 (14)	C632—C633	1.394 (15)
C532—C533	1.348 (14)	C632—C637	1.446 (14)
C532—C537	1.425 (14)	C633—C634	1.367 (15)
C533—C534	1.478 (15)	C634—C635	1.385 (15)
C534—C535	1.333 (15)	C634—C638	1.526 (16)
C534—C538	1.550 (16)	C635—C636	1.372 (14)
C535—C536	1.408 (15)	C636—C639	1.503 (14)
C12—PD1—C25	179.4 (5)	C12—N13—C131	125.50 (11)
C12—PD1—CL1	93.3 (4)	C14—N13—C131	124.10 (11)
C25—PD1—CL1	87.3 (3)	C15—C14—N13	107.00 (14)
C12—PD1—CL2	88.6 (4)	N11—C15—C14	106.30 (14)
C25—PD1—CL2	90.9 (3)	C116—C111—N11	120.00 (12)
CL1—PD1—CL2	177.23 (18)	C116—C111—C112	118.90 (13)
C15—N11—C12	113.60 (12)	N11—C111—C112	121.10 (12)
C15—N11—C111	121.50 (11)	C113—C112—C111	118.60 (13)
C12—N11—C111	124.90 (11)	C113—C112—C117	122.20 (13)
N13—C12—N11	102.40 (11)	C111—C112—C117	119.10 (12)
N13—C12—PD1	126.1 (1)	C112—C113—C114	118.90 (13)
N11—C12—PD1	131.4 (1)	C115—C114—C113	122.90 (13)
C12—N13—C14	110.40 (11)	C115—C114—C118	124.20 (13)

C113—C114—C118	112.90 (12)	C215—C214—C218	117.90 (11)
C116—C115—C114	118.50 (13)	C214—C215—C216	119.40 (12)
C115—C116—C111	122.20 (14)	C211—C216—C215	117.00 (13)
C115—C116—C119	117.20 (12)	C211—C216—C219	123.20 (12)
C111—C116—C119	120.30 (13)	C215—C216—C219	119.80 (12)
C132—C131—C136	123.90 (15)	C236—C231—C232	127.70 (13)
C132—C131—N13	122.00 (13)	C236—C231—N23	118.00 (12)
C136—C131—N13	113.90 (13)	C232—C231—N23	114.00 (12)
C131—C132—C133	118.40 (16)	C233—C232—C231	112.50 (13)
C131—C132—C137	120.70 (15)	C233—C232—C237	125.50 (12)
C133—C132—C137	120.90 (16)	C231—C232—C237	121.90 (12)
C132—C133—C134	117.20 (15)	C234—C233—C232	119.70 (13)
C135—C134—C133	124.20 (16)	C233—C234—C235	124.80 (15)
C135—C134—C138	122.30 (17)	C233—C234—C238	117.50 (14)
C133—C134—C138	112.70 (14)	C235—C234—C238	117.40 (14)
C134—C135—C136	120.60 (17)	C234—C235—C236	120.80 (14)
C131—C136—C135	115.10 (15)	C231—C236—C235	114.00 (12)
C131—C136—C139	126.40 (14)	C231—C236—C239	123.50 (12)
C135—C136—C139	118.40 (14)	C235—C236—C239	122.40 (12)
C22—N21—C25	110.40 (11)	C32—PD3—C45	177.8 (5)
C22—N21—C211	121.00 (11)	C32—PD3—CL4	90.4 (4)
C25—N21—C211	128.1 (1)	C45—PD3—CL4	89.0 (3)
N23—C22—N21	106.70 (11)	C32—PD3—CL3	91.2 (4)
C22—N23—C24	107.50 (11)	C45—PD3—CL3	89.4 (3)
C22—N23—C231	123.30 (11)	CL4—PD3—CL3	178.40 (14)
C24—N23—C231	128.1 (1)	C35—N31—C32	115.90 (12)
C25—C24—N23	111.50 (11)	C35—N31—C311	120.70 (12)
C24—C25—N21	103.80 (11)	C32—N31—C311	123.40 (11)
C24—C25—PD1	127.7 (1)	N31—C32—N33	98.0 (1)
N21—C25—PD1	128.5 (9)	N31—C32—PD3	130.5 (1)
C212—C211—C216	123.90 (13)	N33—C32—PD3	131.2 (1)
C212—C211—N21	119.30 (12)	C34—N33—C32	115.80 (11)
C216—C211—N21	116.70 (12)	C34—N33—C331	120.2 (1)
C211—C212—C213	116.90 (12)	C32—N33—C331	123.7 (1)
C211—C212—C217	123.70 (12)	N33—C34—C35	103.00 (13)
C213—C212—C217	119.40 (12)	N31—C35—C34	107.20 (14)
C214—C213—C212	123.80 (12)	C312—C311—C316	120.00 (13)
C213—C214—C215	119.00 (12)	C312—C311—N31	121.40 (13)
C213—C214—C218	123.10 (11)	C316—C311—N31	118.60 (12)

C311—C312—C313	122.10 (14)	C411—C412—C413	117.30 (12)
C311—C312—C317	120.90 (13)	C411—C412—C417	121.80 (11)
C313—C312—C317	116.80 (13)	C413—C412—C417	120.90 (11)
C314—C313—C312	119.50 (13)	C414—C413—C412	122.10 (12)
C313—C314—C315	117.20 (12)	C413—C414—C415	123.10 (12)
C313—C314—C318	120.60 (12)	C413—C414—C418	120.40 (12)
C315—C314—C318	121.90 (12)	C415—C414—C418	116.00 (11)
C316—C315—C314	123.60 (13)	C416—C415—C414	114.90 (12)
C315—C316—C311	117.10 (13)	C411—C416—C415	121.30 (12)
C315—C316—C319	120.20 (13)	C411—C416—C419	120.30 (11)
C311—C316—C319	122.70 (12)	C415—C416—C419	117.90 (11)
C332—C331—C336	121.90 (13)	C436—C431—C432	124.40 (14)
C332—C331—N33	116.50 (12)	C436—C431—N43	119.40 (13)
C336—C331—N33	121.30 (12)	C432—C431—N43	116.00 (12)
C333—C332—C331	119.00 (13)	C433—C432—C431	116.40 (13)
C333—C332—C337	118.60 (13)	C433—C432—C437	120.40 (13)
C331—C332—C337	122.00 (12)	C431—C432—C437	123.10 (13)
C332—C333—C334	120.10 (14)	C434—C433—C432	120.30 (14)
C335—C334—C333	118.20 (14)	C433—C434—C435	122.60 (16)
C335—C334—C338	120.60 (14)	C433—C434—C438	119.60 (15)
C333—C334—C338	121.20 (14)	C435—C434—C438	117.80 (16)
C334—C335—C336	123.90 (14)	C434—C435—C436	121.00 (17)
C335—C336—C331	116.50 (13)	C431—C436—C435	115.20 (16)
C335—C336—C339	122.30 (13)	C431—C436—C439	123.50 (15)
C331—C336—C339	121.20 (12)	C435—C436—C439	121.30 (16)
C42—N41—C45	108.2 (1)	C55—PD5—C62	178.9 (5)
C42—N41—C411	122.7 (1)	C55—PD5—CL5	91.1 (4)
C45—N41—C411	129.1 (1)	C62—PD5—CL5	89.3 (4)
N43—C42—N41	111.30 (12)	C55—PD5—CL6	87.4 (4)
C42—N43—C44	104.40 (11)	C62—PD5—CL6	92.2 (4)
C42—N43—C431	125.90 (11)	CL5—PD5—CL6	177.93 (18)
C44—N43—C431	129.60 (11)	C52—N51—C511	122.8 (1)
N43—C44—C45	113.70 (12)	C52—N51—C55	108.5 (1)
C44—C45—N41	102.40 (11)	C511—N51—C55	128.7 (1)
C44—C45—PD3	128.4 (1)	N53—C52—N51	112.40 (12)
N41—C45—PD3	129.2 (9)	C52—N53—C54	105.80 (12)
C412—C411—C416	121.20 (12)	C52—N53—C531	129.30 (11)
C412—C411—N41	120.00 (11)	C54—N53—C531	123.00 (11)
C416—C411—N41	118.70 (11)	C55—C54—N53	110.60 (12)

C54—C55—N51	102.60 (11)	N63—C62—PD5	125.7 (1)
C54—C55—PD5	130.30 (11)	N61—C62—PD5	125.0 (1)
N51—C55—PD5	127.0 (9)	C62—N63—C64	106.20 (12)
N51—C511—C512	119.00 (12)	C62—N63—C631	129.00 (11)
N51—C511—C516	121.80 (11)	C64—N63—C631	124.7 (1)
C512—C511—C516	118.80 (12)	C65—C64—N63	110.70 (14)
C513—C512—C511	119.60 (12)	C64—C65—N61	105.30 (14)
C513—C512—C517	118.50 (11)	C616—C611—C612	125.80 (15)
C511—C512—C517	121.90 (11)	C616—C611—N61	115.50 (14)
C512—C513—C514	120.00 (12)	C612—C611—N61	118.60 (14)
C515—C514—C513	122.20 (12)	C611—C612—C613	115.90 (14)
C515—C514—C518	119.20 (11)	C611—C612—C617	123.90 (14)
C513—C514—C518	118.40 (11)	C613—C612—C617	120.20 (14)
C514—C515—C516	117.80 (11)	C612—C613—C614	118.90 (14)
C515—C516—C511	121.40 (11)	C615—C614—C613	121.50 (15)
C515—C516—C519	118.90 (11)	C615—C614—C618	121.60 (14)
C511—C516—C519	119.70 (11)	C613—C614—C618	116.40 (14)
C532—C531—C536	124.20 (12)	C614—C615—C616	120.50 (15)
C532—C531—N53	119.70 (12)	C611—C616—C615	116.90 (15)
C536—C531—N53	115.80 (11)	C611—C616—C619	125.20 (14)
C533—C532—C531	116.40 (13)	C615—C616—C619	117.90 (13)
C533—C532—C537	120.30 (13)	C636—C631—C632	125.60 (14)
C531—C532—C537	123.10 (13)	C636—C631—N63	116.60 (13)
C532—C533—C534	122.50 (13)	C632—C631—N63	117.80 (13)
C535—C534—C533	117.60 (13)	C631—C632—C633	114.30 (13)
C535—C534—C538	126.10 (13)	C631—C632—C637	123.30 (13)
C533—C534—C538	115.80 (12)	C633—C632—C637	122.40 (13)
C534—C535—C536	120.90 (14)	C634—C633—C632	123.50 (14)
C531—C536—C535	117.90 (12)	C633—C634—C635	117.90 (14)
C531—C536—C539	121.60 (12)	C633—C634—C638	120.20 (13)
C535—C536—C539	120.30 (12)	C635—C634—C638	121.90 (13)
C62—N61—C65	108.60 (11)	C636—C635—C634	120.50 (13)
C62—N61—C611	128.50 (11)	C631—C636—C635	118.10 (13)
C65—N61—C611	122.80 (11)	C631—C636—C639	123.10 (13)
N63—C62—N61	109.30 (12)	C635—C636—C639	118.70 (12)

Data reduction processing was carried out by the use of the program SAINT (Bruker, 1999), which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS (Sheldrick, 1996) was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The space group was confirmed by XPREP routine in *SHELXTL* program (Sheldrick, 1997). The structure was solved by direct method using *SHELXS97* (Sheldrick, 1997) and difmap synthesis using *SHELXL97* (Sheldrick, 1997). All non-H atoms anisotropic, hydrogen atoms isotropic. H atoms constrained to the parent site using a riding model; *SHELXL97* defaults, C—H 0.93 to 0.97 Å. The isotropic factors, U_{iso}, were adjusted to 50% higher value of the parent site (methyl) and 20% higher (others).

To finish the structure, it was decided to use the *PLATON* (Spek, 2000) facility SQUEEZE to handle the disordered solvent. *PLATON* identified a remarkably large potential solvent volume of 3382 Å^3, or 23.8% of the cell volume. The use of *PLATON*/SQUEEZE resulted in a 3.0% improvement in R1 while correcting for 572 electrons/cell. The reported structure is based on the *PLATON*/SQUEEZE corrected data. The actual solvent content is unknown, so several quantities reported in Table 1 [empirical formula, density, absorption coefficient, F(000)] are incorrect and should be indicated as such in future publications.

Data collection: SAINT (Bruker, 1999). Cell refinement: SMART (Bruker, 1999). Data reduction: SAINT (Bruker, 1999). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: XP (Bruker, 1999). Software used to prepare material for publication: UdMX (local program).

(FO)

Supplementary data for this paper are available from the IUCr electronic archives (Reference:). Services for accessing these data are described at the back of the journal.

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Fig 1 *ORTEP* (*SHELXTL*, 1997) drawing of the molecule. Ellipsoids correspond to 30% probability.

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

http://journals.iucr.org/c/journalhomepage.html

Table *S*1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j a_i.a_j.$$

	x	y	z	U_{eq}
Pd1	0.25760 (2)	−0.01023 (9)	0.26246 (3)	0.0540 (3)
Cl1	0.21651 (10)	−0.0363 (3)	0.27198 (17)	0.0836 (15)
Cl2	0.30065 (9)	0.0186 (3)	0.25707 (16)	0.0717 (13)
N11	0.2648 (3)	−0.2817 (9)	0.2428 (4)	0.064 (3)
C12	0.2480 (3)	−0.1714 (12)	0.2257 (5)	0.053 (4)
N13	0.2228 (3)	−0.1944 (9)	0.1751 (4)	0.063 (3)
C14	0.2255 (3)	−0.3114 (13)	0.1621 (6)	0.071 (4)
H14	0.2122	−0.3464	0.1288	0.085
C15	0.2512 (3)	−0.3660 (15)	0.2067 (5)	0.073 (4)
H15	0.2578	−0.4479	0.2109	0.087
C111	0.2938 (3)	−0.3056 (10)	0.2942 (5)	0.052 (4)
C112	0.3262 (3)	−0.3043 (11)	0.3066 (5)	0.064 (4)
C113	0.3533 (3)	−0.3300 (10)	0.3567 (5)	0.072 (4)
H113	0.3749	−0.3307	0.3660	0.086
C114	0.3481 (3)	−0.3553 (11)	0.3936 (5)	0.068 (4)
C115	0.3173 (3)	−0.3577 (11)	0.3820 (5)	0.065 (4)
H115	0.3147	−0.3749	0.4078	0.079
C116	0.2908 (3)	−0.3351 (11)	0.3331 (5)	0.057 (4)
C117	0.3294 (3)	−0.2828 (11)	0.2642 (5)	0.079 (4)
H11A	0.3279	−0.3599	0.2482	0.118
H11B	0.3508	−0.2452	0.2787	0.118
H11C	0.3116	−0.2292	0.2382	0.118
C118	0.3811 (3)	−0.3770 (13)	0.4487 (5)	0.111 (5)
H11D	0.3988	−0.3959	0.4460	0.167
H11E	0.3782	−0.4446	0.4649	0.167
H11F	0.3869	−0.3042	0.4695	0.167
C119	0.2567 (3)	−0.3302 (12)	0.3220 (5)	0.091 (5)
H11G	0.2471	−0.2497	0.3094	0.136
H11H	0.2594	−0.3471	0.3537	0.136
H11I	0.2420	−0.3906	0.2959	0.136
C131	0.1963 (3)	−0.1100 (13)	0.1391 (5)	0.058 (4)
C132	0.1999 (4)	−0.0271 (14)	0.1120 (6)	0.091 (5)
C133	0.1734 (4)	0.0506 (13)	0.0786 (5)	0.091 (5)
H133	0.1751	0.1128	0.0604	0.109
C134	0.1437 (4)	0.0324 (13)	0.0732 (5)	0.083 (5)
C135	0.1407 (4)	−0.0423 (15)	0.0994 (6)	0.111 (6)
H135	0.1212	−0.0422	0.0971	0.133
C136	0.1669 (4)	−0.1283 (15)	0.1330 (5)	0.096 (5)
C137	0.2321 (4)	−0.0182 (13)	0.1185 (6)	0.106 (6)
H13A	0.2507	−0.0098	0.1551	0.158
H13B	0.2313	0.0522	0.0996	0.158
H13C	0.2351	−0.0914	0.1049	0.158
C138	0.1165 (4)	0.1301 (17)	0.0379 (7)	0.172 (8)
H13D	0.0950	0.0907	0.0146	0.257
H13E	0.1221	0.1718	0.0177	0.257
H13F	0.1156	0.1886	0.0594	0.257
C139	0.1607 (4)	−0.2276 (13)	0.1620 (5)	0.116 (6)
H13G	0.1709	−0.3041	0.1635	0.173
H13H	0.1369	−0.2394	0.1432	0.173
H13I	0.1705	−1/5	0.1970	0.173
N21	0.2714 (2)	0.2658 (9)	0.2841 (4)	0.053 (3)

C22	0.2765 (3)	0.3542 (12)	0.3186 (5)	0.052 (4)
H22	0.2788	0.4384	0.3163	0.063
N23	0.2776 (3)	0.2979 (9)	0.3554 (4)	0.057 (3)
C24	0.2717 (3)	0.1736 (11)	0.3424 (5)	0.051 (4)
H24	0.2709	0.1137	0.3624	0.061
C25	0.2675 (3)	0.1516 (11)	0.2990 (4)	0.040 (3)
C211	0.2665 (3)	0.2986 (10)	0.2361 (5)	0.046 (4)
C212	0.2932 (3)	0.3338 (10)	0.2384 (5)	0.061 (4)
C213	0.2869 (3)	0.3698 (10)	0.1917 (4)	0.056 (4)
H213	0.3051	0.3939	0.1925	0.067
C214	0.2559 (3)	0.3717 (10)	0.1452 (4)	0.041 (3)
C215	0.2284 (3)	0.3364 (11)	0.1431 (5)	0.066 (4)
H215	0.2068	0.3368	0.1114	0.079
C216	0.2336 (3)	0.2992 (11)	0.1905 (5)	0.061 (4)
C217	0.3281 (3)	0.3385 (10)	0.2876 (4)	0.060 (4)
H21A	0.3285	0.3862	0.3133	0.089
H21B	0.3425	0.3759	0.2809	0.089
H21C	0.3358	0.2564	0.3006	0.089
C218	0.2495 (3)	0.4133 (12)	0.0965 (5)	0.086 (5)
H21D	0.2364	0.4875	0.0847	0.129
H21E	0.2374	0.3507	0.0701	0.129
H21F	0.2706	0.4290	0.1027	0.129
C219	0.2038 (3)	0.2620 (11)	0.1888 (5)	0.073 (4)
H21G	0.1996	0.1755	0.1813	0.110
H21H	0.1843	0.3078	0.1618	0.110
H21I	0.2086	0.2788	0.2221	0.110
C231	0.2781 (3)	0.3633 (11)	0.3964 (5)	0.064 (4)
C232	0.3103 (3)	0.3706 (13)	0.4454 (5)	0.074 (4)
C233	0.3096 (3)	0.4288 (10)	0.4841 (5)	0.053 (4)
H233	0.3297	0.4470	0.5168	0.064
C234	0.2815 (4)	0.4564 (12)	0.4740 (6)	0.073 (4)
C235	0.2518 (3)	0.4472 (11)	0.4271 (5)	0.068 (4)
H235	0.2325	0.4753	0.4223	0.081
C236	0.2492 (3)	0.3964 (11)	0.3852 (5)	0.058 (4)
C237	0.3424 (3)	0.3248 (11)	0.4530 (5)	0.081 (5)
H23A	0.3429	0.2365	0.4537	0.121
H23B	0.3621	0.3561	0.4855	0.121
H23C	0.3422	0.3536	0.4244	0.121
C238	0.2822 (4)	0.5167 (13)	0.5183 (6)	0.113 (6)
H23D	0.2906	0.4587	0.5463	0.169
H23E	0.2597	0.5413	0.5048	0.169
H23F	0.2966	0.5877	0.5313	0.169
C239	0.2166 (3)	0.3830 (13)	0.3328 (5)	0.090 (4)
H23G	0.2189	0.4103	0.3066	0.135
H23H	0.1999	0.4317	0.3308	0.135
H23I	0.2099	0.2980	0.3268	0.135
Pd3	0.53072 (3)	0.88318 (8)	0.57417 (4)	0.0622 (3)
Cl3	0.57888 (10)	0.8766 (3)	0.58031 (17)	0.1000 (15)
Cl4	0.48372 (9)	0.8949 (3)	0.56915 (15)	0.0828 (13)
N31	0.5050 (3)	0.6909 (8)	0.4903 (4)	0.084 (4)
C32	0.5168 (3)	0.7251 (12)	0.5403 (5)	0.069 (4)
N33	0.5118 (2)	0.6142 (8)	0.5558 (3)	0.062 (3)
C34	0.4989 (3)	0.5226 (13)	0.5200 (5)	0.080 (4)
H34	0.4935	0.4426	0.5229	0.096
C35	0.4956 (3)	0.5770 (14)	0.4778 (6)	0.094 (5)
H35	0.4881	0.5388	0.4464	0.113
C311	0.5048 (3)	0.7709 (11)	0.4551 (5)	0.068 (4)
C312	0.5282 (3)	0.7647 (12)	0.4487 (5)	0.083 (4)
C313	0.5280 (3)	0.8386 (11)	0.4139 (5)	0.084 (4)
H313	0.5440	0.8277	0.4080	0.101
C314	0.5045 (3)	0.9272 (10)	0.3881 (4)	0.067 (4)
C315	0.4813 (3)	0.9357 (12)	0.3972 (5)	0.089 (4)
H315	0.4658	1.0001	0.3816	0.107
C316	0.4795 (3)	0.8561 (10)	0.4276 (4)	0.062 (4)
C317	0.5558 (3)	0.6657 (13)	0.4766 (6)	0.129 (6)

H31A	0.5690	0.6767	0.5139	0.193
H31B	0.5701	0.6726	0.4662	0.193
H31C	0.5455	0.5856	0.4673	0.193
C318	0.5060 (3)	1.0202 (12)	0.3542 (5)	0.117 (5)
H31D	0.5290	1.0311	0.3674	0.176
H31E	0.4970	1.0975	0.3550	0.176
H31F	0.4930	0.9906	0.3187	0.176
C319	0.4507 (3)	0.8637 (12)	0.4310 (5)	0.105 (5)
H31G	0.4461	0.7831	0.4374	0.158
H31H	0.4311	0.8949	0.3985	0.158
H31I	0.4568	0.9179	0.4591	0.158
C331	0.5223 (3)	0.5904 (10)	0.6081 (5)	0.066 (4)
C332	0.4975 (3)	0.5714 (10)	0.6128 (5)	0.066 (4)
C333	0.5058 (3)	0.5529 (11)	0.6607 (5)	0.089 (4)
H333	0.4889	0.5467	0.6649	0.107
C334	0.5398 (4)	0.5430 (12)	0.7044 (6)	0.099 (5)
C335	0.5629 (4)	0.5534 (10)	0.6969 (6)	0.086 (5)
H335	0.5854	0.5447	0.7258	0.103
C336	0.5559 (3)	0.5757 (11)	0.6500 (5)	0.067 (4)
C337	0.4603 (3)	0.5848 (12)	0.5663 (5)	0.094 (5)
H33A	0.4562	2/3	0.5523	0.141
H33B	0.4467	0.5701	0.5777	0.141
H33C	0.4546	0.5262	0.5396	0.141
C338	0.5500 (4)	0.5203 (16)	0.7596 (6)	0.168 (7)
H33D	0.5669	0.4572	0.7767	0.252
H33E	0.5306	0.4945	0.7569	0.252
H33F	0.5588	0.5949	0.7797	0.252
C339	0.5826 (3)	0.5892 (11)	0.6435 (5)	0.085 (4)
H33G	0.5753	0.5524	0.6108	0.128
H33H	0.6028	0.5490	0.6720	0.128
H33I	0.5871	0.6750	0.6433	0.128
N41	0.5291 (2)	1.1556 (7)	0.5960 (4)	0.054 (3)
C42	0.5480 (3)	1.2364 (12)	0.6351 (5)	0.065 (4)
H42	0.5419	1.3176	0.6344	0.078
N43	0.5764 (2)	1.1863 (9)	0.6743 (4)	0.066 (3)
C44	0.5745 (3)	1.0700 (12)	0.6592 (5)	0.070 (4)
H44	0.5917	1.0127	0.6796	0.084
C45	0.5456 (3)	1.0433 (11)	0.6117 (5)	0.065 (4)
C411	0.4975 (3)	1.1876 (10)	0.5480 (5)	0.056 (3)
C412	0.4710 (3)	1.2171 (10)	0.5477 (4)	0.060 (3)
C413	0.4423 (3)	1.2571 (9)	0.5014 (5)	0.068 (4)
H413	0.4238	1.2780	0.5002	0.081
C414	0.4400 (3)	1.2669 (10)	0.4592 (5)	0.061 (3)
C415	0.4665 (3)	1.2400 (10)	0.4574 (5)	0.067 (4)
H415	0.4650	1.2512	0.4273	0.080
C416	0.4952 (3)	1.1952 (9)	0.5038 (5)	0.058 (4)
C417	0.4732 (3)	1.2096 (11)	0.5957 (4)	0.085 (4)
H41A	0.4873	1.1415	0.6168	0.127
H41B	0.4510	1.1978	0.5861	0.127
H41C	0.4826	1.2845	0.6154	0.127
C418	0.4100 (3)	1.3256 (12)	0.4116 (5)	0.103 (5)
H41D	0.3900	1.2852	0.4023	0.154
H41E	0.4114	1.3185	0.3831	0.154
H41F	0.4093	1.4110	0.4185	0.154
C419	0.5249 (3)	1.1708 (11)	0.5057 (5)	0.090 (4)
H41G	0.5449	1.1974	0.5389	0.135
H41H	0.5229	1.2149	0.4779	0.135
H41I	0.5265	1.0841	0.5015	0.135
C431	0.6025 (3)	1.2467 (11)	0.7207 (5)	0.073 (4)
C432	0.6271 (3)	1.3023 (12)	0.7195 (5)	0.066 (4)
C433	0.6527 (3)	1.3640 (12)	0.7648 (5)	0.091 (4)
H433	0.6703	1.3998	0.7666	0.109
C434	0.6521 (4)	1.3717 (14)	0.8051 (6)	0.097 (5)
C435	0.6277 (4)	1.3188 (15)	0.8054 (7)	0.135 (6)
H435	0.6288	1.3240	0.8353	0.162

C436	0.6007 (4)	1.2561 (13)	0.7611 (6)	0.096 (5)
C437	0.6280 (3)	1.2919 (11)	0.6745 (5)	0.092 (4)
H43A	0.6156	1.2203	0.6542	0.138
H43B	0.6510	1.2848	0.6870	0.138
H43C	0.6180	1.3640	0.6528	0.138
C438	0.6803 (5)	1.4402 (17)	0.8545 (7)	0.174 (8)
H43D	0.7014	1.4243	0.8609	0.261
H43E	0.6814	1.4122	0.8840	0.261
H43F	0.6757	1.5270	0.8498	0.261
C439	0.5740 (4)	1.1998 (15)	0.7608 (6)	0.150 (7)
H43G	0.5531	1.2428	0.7364	0.225
H43H	0.5798	1.2048	0.7954	0.225
H43I	0.5714	1.1151	0.7506	0.225
Pd5	0.38607 (2)	0.48293 (8)	0.65791 (3)	0.0523 (3)
Cl5	0.34256 (10)	0.5038 (3)	0.66244 (16)	0.0688 (13)
Cl6	0.42898 (11)	0.4639 (3)	0.65016 (19)	0.0945 (16)
N51	0.3708 (2)	0.7577 (8)	0.6354 (3)	0.040 (3)
C52	0.3636 (3)	0.8396 (13)	0.5994 (5)	0.062 (4)
H52	0.3603	0.9229	0.6016	0.075
N53	0.3618 (3)	0.7913 (9)	0.5612 (4)	0.062 (3)
C54	0.3694 (3)	0.6661 (11)	0.5737 (5)	0.056 (4)
H54	0.3710	0.6091	0.5537	0.067
C55	0.3742 (3)	0.6397 (12)	0.6192 (5)	0.062 (4)
C511	0.3743 (3)	0.7880 (10)	0.6797 (5)	0.043 (3)
C512	0.4066 (3)	0.7921 (10)	0.7274 (5)	0.050 (4)
C513	0.4106 (3)	0.8290 (10)	0.7718 (5)	0.052 (4)
H513	0.4318	0.8253	0.8043	0.063
C514	0.3834 (3)	0.8715 (11)	0.7684 (5)	0.060 (4)
C515	0.3512 (3)	0.8708 (10)	0.7221 (4)	0.048 (3)
H515	0.3330	0.8983	0.7206	0.057
C516	0.3469 (3)	0.8280 (9)	0.6779 (4)	0.046 (3)
C517	0.4372 (3)	0.7516 (11)	0.7324 (5)	0.072 (4)
H51A	0.4345	0.6672	0.7215	0.108
H51B	0.4568	0.7592	0.7683	0.108
H51C	0.4398	0.8023	0.7105	0.108
C518	0.3898 (3)	0.9303 (11)	0.8173 (5)	0.075 (4)
H51D	0.4112	0.9025	0.8481	0.114
H51E	0.3722	0.9068	0.8196	0.114
H51F	0.3902	1.0183	0.8149	0.114
C519	0.3115 (3)	0.8263 (10)	0.6260 (4)	0.063 (4)
H51G	0.3074	0.9020	0.6075	0.095
H51H	0.2952	0.8174	0.6326	0.095
H51I	0.3094	0.7585	0.6050	0.095
C531	0.3612 (3)	0.8501 (10)	0.5208 (5)	0.047 (3)
C532	0.3318 (3)	0.8658 (11)	0.4732 (5)	0.057 (4)
C533	0.3383 (3)	0.9182 (11)	0.4370 (5)	0.070 (4)
H533	0.3138	0.9216	0.4025	0.084
C534	0.3645 (3)	0.9705 (11)	0.4496 (5)	0.063 (4)
C535	0.3923 (3)	0.9568 (11)	0.4980 (5)	0.068 (4)
H535	0.4126	0.9878	0.5070	0.082
C536	0.3918 (3)	0.8966 (12)	0.5358 (5)	0.066 (4)
C537	0.3008 (3)	0.8217 (11)	0.4595 (5)	0.070 (4)
H53A	0.3033	0.7372	0.4701	0.105
H53B	0.2839	0.8279	0.4222	0.105
H53C	0.2942	0.8700	0.4770	0.105
C538	0.3622 (3)	1.0215 (10)	0.4029 (5)	0.075 (4)
H53D	0.3752	1.0958	0.4133	0.113
H53E	0.3391	1.0389	0.3744	0.113
H53F	0.3709	0.9617	0.3919	0.113
C539	0.4244 (3)	0.8760 (12)	0.5909 (4)	0.079 (4)
H53G	0.4271	0.9402	0.6138	0.118
H53H	0.4431	0.8770	0.5897	0.118
H53I	0.4234	0.7977	0.6039	0.118
N61	0.4238 (3)	0.3015 (9)	0.7477 (4)	0.067 (3)
C62	0.3981 (3)	0.3189 (12)	0.6967 (5)	0.056 (4)

N63	0.3811 (3)	0.2149 (9)	0.6765 (4)	0.057 (3)
C64	0.3970 (3)	0.1293 (14)	0.7173 (5)	0.072 (4)
H64	0.3903	0.0478	0.7141	0.087
C65	0.4229 (3)	0.1795 (13)	0.7608 (6)	0.073 (5)
H65	0.4376	0.1420	0.7934	0.088
C611	0.4497 (4)	0.3841 (14)	0.7832 (5)	0.069 (4)
C612	0.4799 (3)	0.3757 (12)	0.7918 (5)	0.065 (4)
C613	0.5044 (4)	0.4568 (13)	0.8280 (5)	0.090 (5)
H613	0.5261	0.4531	0.8373	0.108
C614	0.4962 (4)	0.5465 (12)	0.8511 (5)	0.082 (5)
C615	0.4674 (4)	0.5444 (12)	0.8434 (5)	0.077 (4)
H615	0.4636	0.5983	0.8619	0.093
C616	0.4422 (4)	0.4621 (12)	0.8077 (5)	0.068 (4)
C617	0.4866 (3)	0.2924 (13)	0.7668 (5)	0.100 (5)
H61A	0.4831	0.2103	0.7736	0.150
H61B	0.5096	0.3013	0.7797	0.150
H61C	0.4718	0.3075	0.7296	0.150
C618	0.5255 (4)	0.6381 (15)	0.8921 (6)	0.147 (7)
H61D	0.5292	0.6320	0.9251	0.220
H61E	0.5192	0.7209	0.8791	0.220
H61F	0.5458	0.6167	0.8967	0.220
C619	0.4094 (3)	0.4653 (12)	0.8002 (5)	0.090 (5)
H61G	0.3940	0.5201	0.7718	0.135
H61H	0.4133	0.4937	0.8318	0.135
H61I	0.3998	0.3840	0.7920	0.135
C631	0.3532 (3)	0.1885 (10)	0.6240 (5)	0.055 (4)
C632	0.3594 (3)	0.1682 (11)	0.5892 (5)	0.056 (4)
C633	0.3311 (3)	0.1413 (12)	0.5391 (5)	0.079 (5)
H633	0.8338	0.1260	0.5138	0.095
C634	0.2996 (3)	0.1360 (12)	0.5254 (5)	0.075 (4)
C635	0.2958 (3)	0.1577 (10)	0.5637 (5)	0.066 (4)
H635	0.2744	0.1562	0.5553	0.080
C636	0.3231 (3)	0.1814 (10)	0.6138 (5)	0.055 (4)
C637	0.3926 (3)	0.1707 (12)	0.6028 (5)	0.080 (5)
H63A	0.3972	0.2515	0.5964	0.119
H63B	0.3939	0.1117	0.5818	0.119
H63C	0.4089	0.1505	0.6393	0.119
C638	0.2697 (3)	0.1115 (13)	0.4691 (5)	0.104 (5)
H63D	0.2770	0.1116	0.4474	0.156
H63E	0.2531	0.1748	0.4573	0.156
H63F	0.2601	0.0328	0.4667	0.156
C639	0.3181 (3)	0.1989 (11)	0.6547 (5)	0.082 (5)
H63G	0.3344	0.1510	0.6852	0.122
H63H	0.2958	0.1727	0.6412	0.122
H63I	0.3208	0.2844	0.6641	0.122

Table S2. Anisotropic displacement parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd1	0.0605 (7)	0.0480 (7)	0.0602 (8)	−0.0008 (6)	0.0401 (6)	−0.0039 (6)
Cl1	0.092 (3)	0.067 (3)	0.145 (4)	−0.014 (2)	0.099 (3)	−0.020 (3)
Cl2	0.070 (3)	0.068 (3)	0.092 (3)	−0.010 (2)	0.056 (3)	−0.015 (2)
N11	0.078 (9)	0.039 (8)	0.060 (9)	0.000 (6)	0.033 (8)	−0.007 (6)
N13	0.090 (9)	0.033 (7)	0.061 (9)	0.003 (6)	0.044 (8)	0.000 (6)
N21	0.051 (8)	0.049 (8)	0.036 (8)	0.011 (6)	0.014 (6)	0.004 (6)
N23	0.088 (9)	0.061 (8)	0.034 (7)	−0.001 (6)	0.044 (7)	0.001 (6)
Pd3	0.0594 (6)	0.0534 (6)	0.0681 (6)	0.0036 (5)	0.0358 (5)	0.0026 (6)
Cl3	0.074 (3)	0.090 (3)	0.143 (4)	0.009 (2)	0.070 (3)	0.002 (2)
Cl4	0.078 (3)	0.066 (3)	0.123 (3)	−0.0134 (19)	0.071 (3)	−0.017 (2)
N31	0.109 (9)	0.013 (6)	0.092 (9)	−0.002 (6)	0.042 (8)	0.015 (6)
N33	0.075 (7)	0.045 (7)	0.061 (8)	−0.002 (6)	0.040 (6)	−0.019 (6)
N41	0.055 (7)	0.027 (6)	0.066 (8)	0.002 (5)	0.029 (6)	0.000 (5)
N43	0.058 (7)	0.071 (8)	0.043 (7)	0.000 (6)	0.018 (6)	−0.011 (6)
Pd5	0.0662 (8)	0.0430 (7)	0.0583 (8)	−0.0009 (6)	0.0434 (7)	0.0022 (6)
Cl5	0.088 (3)	0.061 (3)	0.091 (3)	0.005 (2)	0.071 (3)	0.008 (2)

C16	0.110 (4)	0.072 (3)	0.145 (4)	0.011 (2)	0.101 (4)	0.020 (3)
N51	0.083 (8)	0.033 (6)	0.041 (7)	0.011 (5)	0.057 (7)	0.007 (5)
N53	0.080 (9)	0.036 (7)	0.070 (9)	−0.002 (6)	0.046 (7)	0.001 (6)
N61	0.083 (9)	0.036 (7)	0.071 (9)	−0.007 (6)	0.040 (8)	0.012 (6)
N63	0.071 (8)	0.039 (7)	0.070 (9)	−0.009 (6)	0.047 (8)	0.013 (6)

Table S3. Geometric parameters (Å, °)

Pd1—C12	2.019 (13)	N21—C211	1.465 (14)
Pd1—C25	2.021 (11)	C22—N23	1.313 (13)
Pd1—Cl1	2.289 (4)	C22—H22	0.94
Pd1—Cl2	2.302 (4)	N23—C24	1.406 (13)
N11—C15	1.310 (14)	N23—C231	1.496 (14)
N11—C12	1.385 (14)	C24—C25	1.312 (13)
N11—C111	1.422 (14)	C24—H24	0.94
C12—N13	1.355 (13)	C211—C212	1.357 (14)
N13—O14	1.382 (15)	C211—C216	1.397 (15)
N13—C131	1.453 (14)	C212—C213	1.401 (14)
C14—C15	1.359 (16)	C212—C217	1.492 (14)
C14—H14	0.94	C213—C214	1.360 (13)
C15—H15	0.94	C213—H213	0.94
C111—C116	1.397 (15)	C214—C215	1.400 (14)
C111—C112	1.423 (14)	C214—C218	1.477 (14)
C112—C113	1.372 (15)	C215—C216	1.450 (15)
C112—C117	1.497 (15)	C215—H215	0.94
C113—C114	1.397 (15)	C216—C219	1.523 (15)
C113—H113	0.94	C217—H21a	0.97
C114—C115	1.358 (14)	C217—H21b	0.97
C114—C118	1.548 (15)	C217—H21c	0.97
C115—C116	1.338 (14)	C218—H21d	0.97
C115—H115	0.94	C218—H21e	0.97
C116—C119	1.526 (15)	C218—H21f	0.97
C117—H11a	0.97	C219—H21g	0.97
C117—H11b	0.97	C219—H21h	0.97
C117—H11c	0.97	C219—H21i	0.97
C118—H11d	0.97	C231—C236	1.321 (14)
C118—H11e	0.97	C231—C232	1.426 (15)
C118—H11f	0.97	C232—C233	1.426 (15)
C119—H11g	0.97	C232—C237	1.564 (15)
C119—H11h	0.97	C233—C234	1.285 (15)
C119—H11i	0.97	C233—H233	0.94
C131—C132	1.350 (17)	C234—C235	1.340 (15)
C131—C136	1.386 (15)	C234—C238	1.561 (18)
C132—C133	1.388 (18)	C235—C236	1.395 (14)
C132—C137	1.508 (18)	C235—H235	0.94
C133—C134	1.413 (17)	C236—C239	1.487 (14)
C133—H133	0.94	C237—H23a	0.97
C134—C135	1.253 (18)	C237—H23b	0.97
C134—C138	1.558 (19)	C237—H23c	0.97
C135—C136	1.440 (18)	C238—H23d	0.97
C135—H135	0.94	C238—H23e	0.97
C136—C139	1.590 (18)	C238—H23f	0.97
C137—H13a	0.97	C239—H23g	0.97
C137—H13b	0.97	C239—H23h	0.97
C137—H13c	0.97	C239—H23i	0.97
C138—H13d	0.97	Pd3—C32	1.941 (14)
C138—H13e	0.97	Pd3—C45	2.005 (12)
C138—H13f	0.97	Pd3—Cl4	2.278 (4)
C139—H13g	0.97	Pd3—Cl3	2.313 (4)
C139—H13h	0.97	N31—C35	1.310 (15)
C139—H13i	0.97	N31—C32	1.395 (14)
N21—C22	1.380 (14)	N31—C311	1.436 (14)
N21—C25	1.398 (13)	C32—N33	1.397 (14)

N33—C34	1.363 (13)	C415—C416	1.398 (13)
N33—C331	1.461 (13)	C415—H415	0.94
C34—C35	1.408 (16)	C416—C419	1.486 (14)
C34—H34	0.94	C417—H41a	0.97
C35—H35	0.94	C417—H41b	0.97
C311—C312	1.318 (14)	C417—H41c	0.97
C311—C316	1.385 (14)	C418—H41d	0.97
C312—C313	1.382 (15)	C418—H41e	0.97
C312—C317	1.549 (16)	C418—H41f	0.97
C313—C314	1.358 (14)	C419—H41g	0.97
C313—H313	0.94	C419—H41h	0.97
C314—C315	1.369 (14)	C419—H41i	0.97
C314—C318	1.537 (15)	C431—C436	1.368 (15)
C315—C316	1.362 (14)	C431—C432	1.407 (15)
C315—H315	0.94	C432—C433	1.406 (15)
C316—C319	1.517 (14)	C432—C437	1.489 (15)
C317—H31a	0.97	C433—C434	1.326 (15)
C317—H31b	0.97	C433—H433	0.94
C317—H31c	0.97	C434—C435	1.363 (17)
C318—H31d	0.97	C434—C438	1.544 (19)
C318—H31e	0.97	C435—C436	1.417 (18)
C318—H31f	0.97	C435—H435	0.94
C319—H31g	0.97	C436—C439	1.478 (18)
C319—H31h	0.97	C437—H43a	0.97
C319—H31i	0.97	C437—H43b	0.97
C331—C332	1.363 (14)	C437—H43c	0.97
C331—C336	1.395 (14)	C438—H43d	0.97
C332—C333	1.354 (14)	C438—H43e	0.97
C332—C337	1.541 (15)	C438—H43f	0.97
C333—C334	1.415 (15)	C439—H43g	0.97
C333—H333	0.94	C439—H43h	0.97
C334—C335	1.334 (16)	C439—H43i	0.97
C334—C338	1.551 (18)	Pd5—C55	1.995 (13)
C335—C336	1.356 (15)	Pd5—C62	2.063 (13)
C335—H335	0.94	Pd5—Cl5	2.296 (4)
C336—C339	1.491 (14)	Pd5—Cl6	2.333 (4)
C337—H33a	0.97	N51—C52	1.334 (14)
C337—H33b	0.97	N51—C511	1.377 (13)
C337—H33c	0.97	N51—C55	1.444 (14)
C338—H33d	0.97	C52—N53	1.296 (14)
C338—H33e	0.97	C52—H52	0.94
C338—H93f	0.97	N53—C54	1.418 (13)
C339—H33g	0.97	N53—C531	1.444 (13)
C339—H33h	0.97	C54—C55	1.370 (14)
C339—H33i	0.97	C54—H54	0.94
N41—C42	1.352 (13)	C511—C512	1.407 (14)
N41—C45	1.397 (13)	C511—C516	1.420 (13)
N41—C411	1.439 (12)	C512—C513	1.384 (14)
C42—N43	1.322 (13)	C512—C517	1.518 (15)
C42—H42	0.94	C513—C514	1.389 (14)
N43—C44	1.350 (13)	C513—H513	0.94
N43—C431	1.423 (14)	C514—C515	1.387 (13)
C44—C45	1.362 (14)	C514—C518	1.551 (15)
C44—H44	0.94	C515—C516	1.391 (13)
C411—C412	1.367 (13)	C515—H515	0.94
C411—C416	1.369 (13)	C516—C519	1.538 (14)
C412—C413	1.378 (13)	C517—H51a	0.97
C412—C417	1.494 (13)	C517—H51b	0.97
C413—C414	1.306 (13)	C517—H51c	0.97
C413—H413	0.94	C518—H51d	0.97
C414—C415	1.400 (13)	C518—H51e	0.97
C414—C418	1.498 (14)	C518—H51f	0.97

C519—H51g	0.97	C613—C614	1.443 (17)
C519—H51h	0.97	C613—H613	0.94
C519—H51i	0.97	C614—C615	1.314 (16)
C531—C532	1.351 (14)	C614—C618	1.604 (19)
C531—C536	1.399 (14)	C615—C616	1.407 (16)
C532—C533	1.348 (14)	C615—H615	0.94
C532—C537	1.425 (14)	C616—C619	1.522 (15)
C533—C534	1.478 (15)	C617—H61a	0.97
C533—H533	0.94	C617—H61b	0.97
C534—C535	1.333 (15)	C617—H61c	0.97
C534—C538	1.550 (16)	C618—H61d	0.97
C535—C536	1.408 (15)	C618—H61e	0.97
C535—H535	0.94	C618—H61f	0.97
C536—C539	1.540 (14)	C619—H61g	0.97
C537—H53a	0.97	C619—H61h	0.97
C537—H53b	0.97	C619—H61i	0.97
C537—H53c	0.97	C631—C636	1.345 (14)
C538—H53d	0.97	C631—C632	1.358 (15)
C538—H53e	0.97	C632—C633	1.394 (15)
C538—H53f	0.97	C632—C637	1.446 (14)
C539—H53g	0.97	C633—C634	1.367 (15)
C539—H53h	0.97	C633—H633	0.94
C539—H53i	0.97	C634—C635	1.385 (15)
N61—C62	1.358 (14)	C634—C638	1.526 (16)
N61—C65	1.413 (15)	C635—C636	1.372 (14)
N61—C611	1.421 (15)	C635—H635	0.94
C62—N63	1.336 (14)	C636—C639	1.503 (14)
N63—C64	1.408 (14)	C637—H63a	0.97
N63—C631	1.430 (14)	C637—H63b	0.97
C64—C65	1.327 (15)	C637—H63c	0.97
C64—H64	0.94	C638—H63d	0.97
C65—H65	0.94	C638—H63e	0.97
C611—C616	1.364 (16)	C638—H63f	0.97
C611—C612	1.376 (14)	C639—H63g	0.97
C612—C613	1.391 (16)	C639—H63h	0.97
C612—C617	1.394 (16)	C639—H63i	0.97
C12—PD1—C25	179.4 (5)	C111—C112—C117	119.10 (12)
C12—PD1—CL1	93.3 (4)	C112—C113—C114	118.90 (13)
C25—PD1—CL1	87.3 (3)	C112—C113—H113	120.5
C12—PD1—CL2	88.6 (4)	C114—C113—H113	120.5
C25—PD1—CL2	90.9 (3)	C115—C114—C113	122.90 (13)
CL1—PD1—CL2	177.23 (18)	C115—C114—C118	124.20 (13)
C15—N11—C12	113.60 (12)	C113—C114—C118	112.90 (12)
C15—N11—C111	121.50 (11)	C116—C115—C114	118.50 (13)
C12—N11—C111	124.90 (11)	C116—C115—H115	120.8
N13—C12—N11	102.40 (11)	C114—C115—H115	120.8
N13—C12—PD1	126.1 (1)	C115—C116—C111	122.20 (14)
N11—C12—PD1	131.4 (1)	C115—C116—C119	117.20 (12)
C12—N13—C14	110.40 (11)	C111—C116—C119	120.30 (13)
C12—N13—C131	125.50 (11)	C112—C117—H11A	109.5
C14—N13—C131	124.10 (11)	C112—C117—H11B	109.5
C15—C14—N13	107.00 (14)	H11A—C117—H11B	109.5
C15—C14—H14	126.5	C112—C117—H11C	109.5
N13—C14—H14	126.5	H11A—C117—H11C	109.5
N11—C15—C14	106.30 (14)	H11B—C117—H11C	109.5
N11—C15—H15	126.9	C114—C118—H11D	109.5
C14—C15—H15	126.9	C114—C118—H11E	109.5
C116—C111—N11	120.00 (12)	H11D—C118—H11E	109.5
C116—C111—C112	118.90 (13)	C114—C118—H11F	109.5
N11—C111—C112	121.10 (12)	H11D—C118—H11F	109.5
C113—C112—C111	118.60 (13)	H11E—C118—H11F	109.5
C113—C112—C117	122.20 (13)	C116—C119—H11G	109.5

Atoms	Angle	Atoms	Angle
C116—C119—H11H	109.5	C214—C213—C212	123.80 (12)
H11G—C119—H11H	109.5	C214—C213—H213	118.1
C116—C119—H11I	109.5	C212—C213—H213	118.1
H11G—C119—H11I	109.5	C218—C214—C215	119.00 (12)
H11H—C119—H11I	109.5	C213—C214—C218	123.10 (11)
C132—C131—C136	123.90 (15)	C215—C214—C218	117.90 (11)
C132—C131—N13	122.00 (13)	C214—C215—C216	119.40 (12)
C136—C131—N13	113.90 (13)	C214—C215—H215	120.3
C131—C132—C133	118.40 (16)	C216—C215—H215	120.3
C131—C132—C137	120.70 (15)	C211—C216—C215	117.00 (13)
C133—C132—C137	120.90 (16)	C211—C216—C219	123.20 (12)
C132—C133—C134	117.20 (15)	C215—C216—C219	119.80 (12)
C132—C133—H133	121.4	C212—C217—H21A	109.5
C134—C133—H133	121.4	C212—C217—H21B	109.5
C135—C134—C138	124.20 (16)	H21A—C217—H21B	109.5
C135—C134—C138	122.30 (17)	C212—C217—H21C	109.5
C133—C134—C138	112.70 (14)	H21A—C217—H21C	109.5
C134—C135—C136	120.60 (17)	H21B—C217—H21C	109.5
C134—C135—H135	119.7	C214—C218—H21D	109.5
C136—C135—H135	119.7	C214—C218—H21E	109.5
C131—C136—C135	115.10 (15)	H21D—C218—H21E	109.5
C131—C136—C139	126.40 (14)	C214—C218—H21F	109.5
C135—C136—C139	118.40 (14)	H21D—C218—H21F	109.5
C132—C137—H13A	109.5	H21E—C218—H21F	109.5
C132—C137—H13B	109.5	C216—C219—H21G	109.5
H13A—C137—H13B	109.5	C216—C219—H21H	109.5
C132—C137—H13C	109.5	H21G—C219—H21H	109.5
H13A—C137—H13C	109.5	C216—C219—H21I	109.5
H13B—C137—H13C	109.5	H21G—C219—H21I	109.5
C134—C138—H13D	109.5	H21H—C219—H21I	109.5
C134—C138—H13E	109.5	C236—C231—C232	127.70 (13)
H13D—C138—H13E	109.5	C236—C231—N23	118.00 (12)
C134—C138—H13F	109.5	C232—C231—N23	114.00 (12)
H13D—C138—H13F	109.5	C233—C232—C231	112.50 (13)
H13E—C138—H13F	109.5	C233—C232—C237	125.50 (12)
C136—C139—H13G	109.5	C231—C232—C237	121.90 (12)
C136—C139—H13H	109.5	C234—C233—C232	119.70 (13)
H13G—C139—H13H	109.5	C234—C233—H233	120.2
C136—C139—H13I	109.5	C232—C233—H233	120.2
H13G—C139—H13I	109.5	C233—C234—C235	124.80 (15)
H13H—C139—H13I	109.5	C233—C234—C238	117.50 (14)
C22—N21—C25	110.40 (11)	C235—C234—C238	117.40 (14)
C22—N21—C211	121.00 (11)	C234—C235—C236	120.80 (14)
C25—N21—C211	128.1 (1)	C234—C235—H235	119.6
N23—C22—N21	106.70 (11)	C236—C235—H235	119.6
N23—C22—H22	126.6	C231—C236—C235	114.00 (12)
N21—C22—H22	126.6	C231—C236—C239	123.50 (12)
C22—N23—C24	107.50 (11)	C235—C236—C239	122.40 (12)
C22—N23—C231	123.30 (11)	C232—C237—H23A	109.5
C24—N23—C231	128.1 (1)	C232—C237—H23B	109.5
C25—C24—N23	111.50 (11)	H23A—C237—H23B	109.5
C25—C24—H24	124.3	C232—C237—H23C	109.5
N23—C24—H24	124.3	H23A—C237—H23C	109.5
C24—C25—N21	103.80 (11)	H23B—C237—H23C	109.5
C24—C25—PD1	127.7 (1)	C234—C238—H23D	109.5
N21—C25—PD1	128.5 (9)	C234—C238—H23E	109.5
C212—C211—C216	123.90 (13)	H23D—C238—H23E	109.5
C212—C211—N21	119.30 (12)	C234—C238—H23F	109.5
C216—C211—N21	116.70 (12)	H23D—C238—H23F	109.5
C211—C212—C213	116.90 (12)	H23E—C238—H23F	109.5
C211—C212—C217	123.70 (12)	C236—C239—H23G	109.5
C213—C212—C217	119.40 (12)	C236—C239—H23H	109.5

H23G—C239—H23H	109.5	C332—C331—N33	116.50 (12)
C236—C239—H23I	109.5	C336—C331—N33	121.80 (12)
H23G—C239—H23I	109.5	C333—C332—C331	119.00 (13)
H23H—C239—H23I	109.5	C333—C332—C337	118.60 (13)
C32—PD3—C45	177.8 (5)	C331—C332—C337	122.00 (12)
C32—PD3—CL4	90.4 (4)	C332—C333—C334	120.10 (14)
C45—PD3—CL4	89.0 (3)	C332—C333—H333	120
C32—PD3—CL3	91.2 (4)	C334—C333—H333	120
C45—PD3—CL3	89.4 (3)	C335—C334—C333	118.20 (14)
CL4—PD3—CL3	178.40 (14)	C335—C334—C338	120.60 (14)
C35—N31—C32	115.90 (12)	C333—C334—C338	121.20 (14)
C35—N31—C311	120.70 (12)	C334—C335—C336	123.90 (14)
C32—N31—C311	123.40 (11)	C334—C335—H335	118
N31—C32—N33	98.0 (1)	C336—C335—H335	118
N31—C32—PD3	130.5 (1)	C335—C336—C331	116.50 (13)
N33—C32—PD3	131.2 (1)	C335—C336—C339	122.30 (13)
C34—N33—C32	115.80 (11)	C331—C336—C339	121.20 (12)
C34—N33—C331	120.2 (1)	C332—C337—H33A	109.5
C32—N33—C331	123.7 (1)	C332—C337—H33B	109.5
N33—C34—C35	108.00 (13)	H33A—C337—H33B	109.5
N33—C34—H34	128.5	C332—C337—H33C	109.5
C35—C34—H34	128.5	H33A—C337—H33C	109.5
N31—C35—C34	107.20 (14)	H33B—C337—H33C	109.5
N31—C35—H35	126.4	C334—C338—H33D	109.5
C34—C35—H35	126.4	C334—C338—H33E	109.5
C312—C311—C316	120.00 (13)	H33D—C338—H33E	109.5
C312—C311—N31	121.40 (13)	C334—C338—H33F	109.5
C316—C311—N31	118.60 (12)	H33D—C338—H33F	109.5
C311—C312—C313	122.10 (14)	H33E—C338—H33F	109.5
C311—C312—C317	120.90 (13)	C336—C339—H33G	109.5
C313—C312—C317	116.80 (13)	C336—C339—H33H	109.5
C314—C313—C312	119.50 (13)	H33G—C339—H33H	109.5
C314—C313—H313	120.2	C336—C339—H33I	109.5
C312—C313—H313	120.2	H33G—C339—H33I	109.5
C313—C314—C315	117.20 (12)	H33H—C339—H33I	109.5
C313—C314—C318	120.60 (12)	C42—N41—C45	108.2 (1)
C315—C314—C318	121.90 (12)	C42—N41—C411	122.7 (1)
C316—C315—C314	123.60 (13)	C45—N41—C411	129.1 (1)
C316—C315—H315	118.2	N43—C42—N41	111.80 (12)
C314—C315—H315	118.2	N43—C42—H42	124.4
C315—C316—C311	117.10 (13)	N41—C42—H42	124.4
C315—C316—C319	120.20 (13)	C42—N43—C44	104.40 (11)
C311—C316—C319	122.70 (12)	C42—N43—C431	125.90 (11)
C312—C317—H31A	109.5	C44—N43—C431	129.60 (11)
C312—C317—H31B	109.5	N43—C44—C45	113.70 (12)
H31A—C317—H31B	109.5	N43—C44—H44	123.2
C312—C317—H31C	109.5	C45—C44—H44	123.2
H31A—C317—H31C	109.5	C44—C45—N41	102.40 (11)
H31B—C317—H31C	109.5	C44—C45—PD3	128.4 (1)
C314—C318—H31D	109.5	N41—C45—PD3	129.2 (9)
C314—C318—H31E	109.5	C412—C411—C416	121.20 (12)
H31D—C318—H31E	109.5	C412—C411—N41	120.00 (11)
C314—C318—H31F	109.5	C416—C411—N41	118.70 (11)
H31D—C318—H31F	109.5	C411—C412—C413	117.30 (12)
H31E—C318—H31F	109.5	C411—C412—C417	121.80 (11)
C316—C319—H31G	109.5	C413—C412—C417	120.90 (11)
C316—C319—H31H	109.5	C414—C413—C412	122.10 (12)
H31G—C319—H31H	109.5	C414—C413—H413	118.9
C316—C319—H31I	109.5	C412—C413—H413	118.9
H31G—C319—H31I	109.5	C413—C414—C415	123.10 (12)
H31H—C319—H31I	109.5	C413—C414—C418	120.40 (12)
C332—C331—C336	121.90 (13)	C415—C414—C418	116.00 (11)

C416—C415—C414	114.90 (12)	C62—PD5—CL5	89.3 (4)
C416—C415—H415	122.6	C55—PD5—CL6	87.4 (4)
C414—C415—H415	122.6	C62—PD5—CL6	92.2 (4)
C411—C416—C415	121.30 (12)	CL5—PD5—CL6	177.93 (18)
C411—C416—C419	120.30 (11)	C52—N51—C511	122.8 (1)
C415—C416—C419	117.90 (11)	C52—N51—C55	108.5 (1)
C412—C417—H41A	109.5	C511—N51—C55	128.7 (1)
C412—C417—H41B	109.5	N53—C52—N51	112.40 (12)
H41A—C417—H41B	109.5	N53—C52—H52	123.8
C412—C417—H41C	109.5	N51—C52—H52	123.8
H41A—C417—H41C	109.5	C52—N53—C54	105.80 (12)
H41B—C417—H41C	109.5	C52—N53—C531	129.30 (11)
C414—C418—H41D	109.5	C54—N53—C531	123.00 (11)
C414—C418—H41E	109.5	C55—C54—N53	110.60 (12)
H41D—C418—H41E	109.5	C55—C54—H54	124.7
C414—C418—H41F	109.5	N53—C54—H54	124.7
H41D—C418—H41F	109.5	C54—C55—N51	102.60 (11)
H41E—C418—H41F	109.5	C54—C55—PD5	130.30 (11)
C416—C419—H41G	109.5	N51—C55—PD5	127.0 (9)
C416—C419—H41H	109.5	N51—C511—C512	119.00 (12)
H41G—C419—H41H	109.5	N51—C511—C516	121.80 (11)
C416—C419—H41I	109.5	C512—C511—C516	118.80 (12)
H41G—C419—H41I	109.5	C513—C512—C511	119.60 (12)
H41H—C419—H41I	109.5	C513—C512—C517	118.50 (11)
C436—C431—C432	124.40 (14)	C511—C512—C517	121.90 (11)
C436—C431—N43	119.40 (13)	C512—C513—C514	120.00 (12)
C432—C431—N43	116.00 (12)	C512—C513—H513	120
C433—C432—C431	116.40 (13)	C514—C513—H513	120
C433—C432—C437	120.40 (13)	C515—C514—C513	122.20 (12)
C431—C432—C437	123.10 (13)	C515—C514—C518	119.20 (11)
C434—C433—C432	120.30 (14)	C513—C514—C518	118.40 (11)
C434—C433—H433	119.9	C514—C515—C516	117.80 (11)
C432—C433—H433	119.9	C514—C515—H515	121.1
C433—C434—C435	122.60 (16)	C516—C515—H515	121.1
C433—C434—C438	119.60 (15)	C515—C516—C511	121.40 (11)
C435—C434—C438	117.80 (16)	C515—C516—C519	118.90 (11)
C434—C435—C436	121.00 (17)	C511—C516—C519	119.70 (11)
C434—C435—H435	119.5	C512—C517—H51A	109.5
C436—C435—H435	119.5	C512—C517—H51B	109.5
C431—C436—C435	115.20 (16)	H51A—C517—H51B	109.5
C431—C436—C439	123.50 (15)	C512—C517—H51C	109.5
C435—C436—C439	121.30 (16)	H51A—C517—H51C	109.5
C432—C437—H43A	109.5	H51B—C517—H51C	109.5
C432—C437—H43B	109.5	C514—C518—H51D	109.5
H43A—C437—H43B	109.5	C514—C518—H51E	109.5
C432—C437—H43C	109.5	H51D—C518—H51E	109.5
H43A—C437—H43C	109.5	C514—C518—H51F	109.5
H43B—C437—H43C	109.5	H51D—C518—H51F	109.5
C434—C438—H43D	109.5	H51E—C518—H51F	109.5
C434—C438—H43E	109.5	C516—C519—H51G	109.5
H43D—C438—H43E	109.5	C516—C519—H51H	109.5
C434—C438—H43F	109.5	H51G—C519—H51H	109.5
H43D—C438—H43F	109.5	C516—C519—H51I	109.5
H43E—C438—H43F	109.5	H51G—C519—H51I	109.5
C436—C439—H43G	109.5	H51H—C519—H51I	109.5
C436—C439—H43H	109.5	C532—C531—C536	124.20 (12)
H43G—C439—H43H	109.5	C532—C531—N53	119.70 (12)
C436—C439—H43I	109.5	C536—C531—N53	115.80 (11)
H43G—C439—H43I	109.5	C533—C532—C531	116.40 (13)
H43H—C439—H43I	109.5	C533—C532—C537	120.30 (13)
C55—PD5—C62	178.9 (5)	C531—C532—C537	123.10 (13)
C55—PD5—CL5	91.1 (4)	C532—C533—C534	122.50 (13)

C532—C533—H533	118.7	C616—C615—H615	119.8
C534—C533—H533	118.7	C611—C616—C615	116.90 (15)
C535—C534—C533	117.60 (13)	C611—C616—C619	125.20 (14)
C535—C534—C538	126.10 (13)	C615—C616—C619	117.90 (13)
C533—C534—C538	115.80 (12)	C612—C617—H61A	109.5
C534—C535—C536	120.90 (14)	C612—C617—H61B	109.5
C534—C535—H535	119.6	H61A—C617—H61B	109.5
C536—C535—H535	119.6	C612—C617—H61C	109.5
C531—C536—C535	117.90 (12)	H61A—C617—H61C	109.5
C531—C536—C539	121.60 (12)	H61B—C617—H61C	109.5
C535—C536—C539	120.30 (12)	C614—C618—H61D	109.5
C532—C537—H53A	109.5	C614—C618—H61E	109.5
C532—C537—H53B	109.5	H61D—C618—H61E	109.5
H53A—C537—H53B	109.5	C614—C618—H61F	109.5
C532—C537—H53C	109.5	H61D—C618—H61F	109.5
H53A—C537—H53C	109.5	H61E—C618—H61F	109.5
H53B—C537—H53C	109.5	C616—C619—H61G	109.5
C534—C538—H53D	109.5	C616—C619—H61H	109.5
C534—C538—H53E	109.5	H61G—C619—H61H	109.5
H53D—C538—H53E	109.5	C616—C619—H61I	109.5
C534—C538—H53F	109.5	H61G—C619—H61I	109.5
H53D—C538—H53F	109.5	H61H—C619—H61I	109.5
H53E—C538—H53F	109.5	C636—C631—C632	125.60 (14)
C536—C539—H53G	109.5	C636—C631—N63	116.60 (13)
C536—C539—H53H	109.5	C632—C631—N63	117.80 (13)
H53G—C539—H53H	109.5	C631—C632—C633	114.30 (13)
C536—C539—H53I	109.5	C631—C632—C637	123.30 (13)
H53G—C539—H53I	109.5	C633—C632—C637	122.40 (13)
H53H—C539—H53I	109.5	C634—C633—C632	123.50 (14)
C62—N61—C65	108.60 (11)	C634—C633—H633	118.2
C62—N61—C611	128.50 (11)	C632—C633—H633	118.2
C65—N61—C611	122.80 (11)	C633—C634—C635	117.90 (14)
N63—C62—N61	109.30 (12)	C633—C634—C638	120.20 (13)
N63—C62—PD5	125.7 (1)	C635—C634—C638	121.90 (13)
N61—C62—PD5	125.0 (1)	C636—C635—C634	120.50 (13)
C62—N63—C64	106.20 (12)	C636—C635—H635	119.8
C62—N63—C631	129.00 (11)	C634—C635—H635	119.8
C64—N63—C631	124.7 (1)	C631—C636—C635	118.10 (13)
C65—C64—N63	110.70 (14)	C631—C636—C639	123.10 (13)
C65—C64—H64	124.7	C635—C636—C639	118.70 (12)
N63—C64—H64	124.7	C632—C637—H63A	109.5
C64—C65—N61	105.30 (14)	C632—C637—H63B	109.5
C64—C65—H65	127.3	H63A—C637—H63B	109.5
N61—C65—H65	127.3	C632—C637—H63C	109.5
C616—C611—C612	125.80 (15)	H63A—C637—H63C	109.5
C616—C611—N61	115.50 (14)	H63B—C637—H63C	109.5
C612—C611—N61	118.60 (14)	C634—C638—H63D	109.5
C611—C612—C613	115.90 (14)	C634—C638—H63E	109.5
C611—C612—C617	123.90 (14)	H63D—C638—H63E	109.5
C613—C612—C617	120.20 (14)	C634—C638—H63F	109.5
C612—C613—C614	118.90 (14)	H63D—C638—H63F	109.5
C612—C613—H613	120.5	H63E—C638—H63F	109.5
C614—C613—H613	120.5	C636—C639—H63G	109.5
C615—C614—C613	121.50 (15)	C636—C639—H63H	109.5
C615—C614—C618	121.60 (14)	H63G—C639—H63H	109.5
C613—C614—C618	116.40 (14)	C636—C639—H63I	109.5
C614—C615—C616	120.50 (15)	H63G—C639—H63I	109.5
C614—C615—H615	119.8	H63H—C639—H63I	109.5
C15—N11—C12—N13	−1.10 (15)	C25—PD1—C12—N13	−84 (83)
C111—N11—C12—N13	179.60 (11)	CL1—PD1—C12—N13	79.10 (11)
C15—N11—C12—PD1	−178.4 (1)	CL2—PD1—C12—N13	−102.90 (11)
C111—N11—C12—PD1	2.30 (19)	C25—PD1—C12—N11	92 (82)

CL1—PD1—C12—N11	−104.10 (12)	C211—N21—C25—PD1	5.70 (17)
CL2—PD1—C12—N11	73.80 (12)	C12—PD1—C25—C24	−148 (81)
N11—C12—N13—C14	−2.70 (14)	CL1—PD1—C25—C24	48.70 (11)
PD1—C12—N13—C14	174.8 (9)	CL2—PD1—C25—C24	−129.30 (11)
N11—C12—N13—C131	176.50 (11)	C12—PD1—C25—N21	32 (83)
PD1—C12—N13—C131	−5.90 (19)	CL1—PD1—C25—N21	−131.3 (1)
C12—N13—C14—C15	5.40 (15)	CL2—PD1—C25—N21	50.8 (1)
C131—N13—C14—C15	−173.80 (11)	C22—N21—C211—C212	75.20 (14)
C12—N11—C15—C14	4.40 (16)	C25—N21—C211—C212	−113.70 (14)
C111—N11—C15—C14	−176.30 (11)	C22—N21—C211—C216	−100.50 (13)
N13—C14—C15—N11	−5.80 (15)	C25—N21—C211—C216	70.60 (15)
C15—N11—C111—C116	−97.30 (15)	C216—C211—C212—C213	−1.60 (18)
C12—N11—C111—C116	81.90 (15)	N21—C211—C212—C213	−177.0 (1)
C15—N11—C111—C112	80.50 (16)	C216—C211—C212—C217	177.10 (11)
C12—N11—C111—C112	−100.30 (15)	N21—C211—C212—C217	1.60 (17)
C116—C111—C112—CI13	−1.10 (18)	C211—C212—C213—C214	0.40 (18)
N11—C111—C112—C113	−178.90 (11)	C217—C212—C213—C214	−178.30 (11)
C116—C111—C112—C117	175.10 (11)	C212—C213—C214—C215	0.20 (18)
N11—C111—C112—C117	−2.70 (17)	C212—C213—C214—C218	178.10 (12)
C111—C112—C113—C114	−0.60 (18)	C213—C214—C215—C216	0.20 (17)
C117—C112—C113—C114	−176.70 (11)	C218—C214—C215—C216	−177.80 (11)
C112—C113—C114—C115	1.20 (19)	C212—C211—C216—C215	2.00 (18)
C112—C113—C114—C118	−177.50 (12)	N21—C211—C216—C215	177.5 (1)
C113—C114—C115—C116	0 (2)	C212—C211—C216—C219	−178.60 (11)
C118—C114—C115—C116	178.70 (12)	N21—C211—C216—C219	−3.10 (17)
C114—C115—C116—C111	−2 (2)	C214—C215—C216—C211	−1.20 (17)
C114—C115—C116—C119	−176.10 (12)	C214—C215—C216—C219	179.40 (11)
N11—C111—C116—C115	−179.70 (11)	C22—N23—C231—C236	84.90 (16)
C112—C111—C116—C115	2.50 (19)	C24—N23—C231—C236	−81.60 (16)
N11—C111—C116—C119	−5.80 (18)	C22—N23—C231—C232	−101.40 (14)
C112—C111—C116—C119	176.40 (12)	C24—N23—C231—C232	92.10 (15)
C12—N13—C131—C132	86.40 (17)	C236—C231—C232—C233	−5 (2)
C14—N13—C131—C132	−94.40 (17)	N23—C231—C232—C233	−177.5 (1)
C12—N13—C131—C136	−97.60 (15)	C236—C231—C232—C237	178.60 (12)
C14—N13—C131—C136	81.50 (16)	N23—C231—C232—C237	5.70 (18)
C136—C131—C132—C183	5 (2)	C231—C232—C233—C234	−7.10 (18)
N13—C131—C132—C133	−179.60 (12)	C237—C232—C233—C234	−176.20 (12)
C136—C131—C132—C137	−176.10 (13)	C232—C233—C234—C235	−8 (2)
N13—C131—C132—C137	−1 (2)	C232—C233—C234—C238	178.30 (11)
C131—C132—C133—C134	−4 (2)	C233—C234—C235—C236	5 (2)
C137—C132—C133—C134	177.20 (13)	C238—C234—C235—C236	178.80 (12)
C132—C133—C134—C135	6 (2)	C232—C231—C236—C235	2 (2)
C132—C133—C134—C138	176.10 (14)	N23—C231—C236—C235	174.7 (1)
C133—C134—C135—C136	−9 (3)	C232—C231—C236—C239	−178.80 (13)
C138—C134—C135—C136	−177.80 (14)	N23—C231—C236—C239	−6.10 (19)
C132—C131—C136—C135	−7 (2)	C234—C235—C236—C231	−1.70 (19)
N13—C131—C136—C135	177.20 (11)	C234—C235—C236—C239	179.00 (13)
C132—C131—C136—C139	177.40 (14)	C35—N31—C32—N33	−2.40 (14)
N13—C131—C136—C139	2 (2)	C311—N31—C32—N33	−178.30 (11)
C134—C135—C136—C131	9 (2)	C35—N31—C32—PD3	−175.9 (1)
C134—C135—C136—C139	−175.40 (14)	C311—N31—C32—PD3	8.20 (19)
C25—N21—C22—N23	3.10 (13)	C45—PD3—C32—N31	−178 (100)
C211—N21—C22—N23	175.6 (1)	CL4—PD3—C32—N31	106.00 (12)
N21—C22—N23—C24	−2.30 (13)	CL3—PD3—C32—N31	−71.90 (12)
N21—C22—N23—C231	−171.2 (1)	C45—PD3—C32—N33	11 (15)
C22—N23—C24—C25	0.90 (14)	CL4—PD3—C32—N33	−63.40 (12)
C231—N23—C24—C25	169.00 (12)	CL3—PD3—C32—N33	116.60 (12)
N23—C24—C25—N21	1.00 (13)	N31—C32—N33—C34	0.70 (13)
N23—C24—C25—PD1	−179.0 (8)	PD3—C32—N33—C34	174.1 (9)
C22—N21—C25—C24	−2.50 (13)	N31—C32—N33—C331	175.0 (1)
C211—N21—C25—C24	−174.30 (11)	PD9—C32—N33—C331	−11.50 (18)
C22—N21—C25—PD1	177.5 (8)	C32—N33—C34—C35	1.00 (14)

C331—N33—C34—C35	−173.5 (1)
C32—N31—C35—C34	3.30 (16)
C311—N31—C35—C34	179.30 (11)
N33—C34—C35—N31	−2.40 (14)
C35—N31—C311—C312	−76.20 (17)
C32—N31—C311—C312	99.50 (15)
C35—N31—C311—C316	104.00 (14)
C32—N31—C311—C316	−80.30 (15)
C316—C311—C312—C313	−2 (2)
N31—C311—C312—C313	178.20 (11)
C316—C311—C312—C317	−176.70 (11)
N31—C311—C312—C317	3.50 (19)
C311—C312—C313—C314	5 (2)
C317—C312—C313—C314	−180.00 (11)
C312—C313—C314—C315	−2.00 (18)
C312—C313—C314—C318	172.80 (11)
C313—C314—C315—C316	−4.40 (19)
C318—C314—C315—C316	−179.00 (12)
C314—C315—C316—C311	7.40 (19)
C314—C315—C316—C319	−173.20 (11)
C312—C311—C316—C315	−4.10 (18)
N31—C311—C316—C315	175.80 (11)
C312—C311—C316—C319	176.60 (11)
N31—C311—C316—C319	−3.60 (17)
C34—N33—C331—C332	−71.90 (14)
C32—N33—C331—C332	114.00 (13)
C34—N33—C331—C336	101.80 (14)
C32—N33—C331—C336	−72.30 (15)
C336—C331—C332—C333	8.50 (19)
N33—C331—C332—C333	−177.80 (11)
C336—C331—C332—C337	−178.70 (11)
N33—C331—C332—C337	−5.00 (17)
C331—C332—C333—C334	−5.50 (19)
C337—C332—C333—C334	−178.50 (12)
C332—C333—C334—C335	1 (2)
C332—C333—C334—C338	−179.20 (13)
C333—C334—C335—C336	2 (2)
C338—C334—C335—C336	−178.60 (13)
C334—C335—C336—C331	1.20 (19)
C334—C335—C336—C339	178.70 (12)
C332—C331—C336—C335	−6.40 (18)
N33—C331—C336—C335	−179.7 (1)
C332—C331—C336—C339	176.10 (11)
N33—C331—C336—C339	2.80 (18)
C45—N41—C42—N43	2.60 (13)
C411—N41—C42—N43	−177.9 (1)
N41—C42—N43—C44	−1.00 (13)
N41—C42—N43—C431	177.80 (11)
C42—N43—C44—C45	−1.00 (14)
C431—N43—C44—C45	−179.70 (12)
N43—C44—C45—N41	2.40 (14)
N43—C44—C45—PD3	−177.7 (8)
C42—N41—C45—C44	−2.90 (12)
C411—N41—C45—C44	177.60 (11)
C42—N41—C45—PD3	177.3 (9)
C411—N41—C45—PD3	−2.20 (17)
C32—PD3—C45—C44	49 (14)
CL4—PD3—C45—C44	123.70 (11)
CL3—PD3—C45—C44	−56.40 (11)
C32—PD3—C45—N41	−131 (14)
CL4—PD3—C45—N41	−56.5 (1)
CL3—PD3—C45—N41	123.4 (1)

C42—N41—C411—C412	−66.90 (15)
C45—N41—C411—C412	112.50 (13)
C42—N41—C411—C416	109.10 (12)
C45—N41—C411—C416	−71.50 (15)
C416—C411—C412—C413	−1.40 (17)
N41—C411—C412—C413	174.5 (9)
C416—C411—C412—C417	−179.8 (1)
N41—C411—C412—C417	−3.90 (16)
C411—C412—C413—C414	0.10 (17)
C417—C412—C413—C414	178.50 (11)
C412—C413—C414—C415	−1.20 (18)
C412—C413—C414—C418	−172.20 (11)
C413—C414—C415—C416	3.30 (16)
C418—C414—C415—C416	174.7 (1)
C412—C411—C416—C415	3.80 (17)
N41—C411—C416—C415	−172.2 (1)
C412—C411—C416—C419	175.9 (1)
N41—C411—C416—C419	−0.10 (16)
C414—C415—C416—C411	−4.50 (16)
C414—C415—C416—C419	−176.8 (1)
C42—N43—C431—C436	85.20 (16)
C44—N43—C431—C436	−96.30 (16)
C42—N43—C431—C432	−89.50 (15)
C44—N43—C431—C432	89.00 (15)
C436—C431—C432—C433	5 (2)
N43—C431—C432—C433	178.9 (1)
C436—C431—C432—C437	−179.00 (12)
N43—C431—C432—C437	−4.60 (18)
C431—C432—C433—C434	−2.60 (19)
C437—C432—C433—C434	−179.20 (13)
C432—C433—C434—C435	2 (2)
C432—C433—C434—C438	−179.80 (13)
C433—C434—C435—C436	−3 (3)
C438—C434—C435—C436	179.00 (14)
C432—C431—C436—C435	−5 (2)
N43—C431—C436—C435	−179.40 (12)
C432—C431—C436—C439	178.10 (13)
N43—C431—C436—C439	4 (2)
C434—C435—C436—C431	4 (2)
C434—C435—C436—C439	−179.20 (14)
C511—N51—C52—N53	179.40 (11)
C55—N51—C52—N53	0.00 (15)
N51—C52—N53—C54	−1.80 (15)
N51—C52—N53—C531	−166.40 (11)
C52—N53—C54—C55	3.10 (14)
C531—N53—C54—C55	168.90 (11)
N53—C54—C55—N51	−3.00 (13)
N53—C54—C55—PD5	−178.9 (8)
C52—N51—C55—C54	1.90 (13)
C511—N51—C55—C54	−177.50 (11)
C52—N51—C55—PD5	178.0 (9)
C511—N51—C55—PD5	−1.40 (18)
C62—PD5—C55—C54	−18 (29)
CL5—PD5—C55—C54	−129.40 (12)
CL6—PD5—C55—C54	49.20 (12)
C62—PD5—C55—N51	166 (100)
CL5—PD5—C55—N51	55.6 (1)
CL6—PD5—C55—N51	−125.9 (1)
C52—N51—C511—C512	−105.20 (13)
C55—N51—C511—C512	74.10 (15)
C52—N51—C511—C516	67.70 (15)
C55—N51—C511—C516	−113.00 (13)

N51—C511—C512—C513	176.4 (1)		N61—C62—N63—C631	−176.70 (12)
C516—C511—C512—C513	3.30 (16)		PD5—C62—N63—C631	6 (2)
N51—C511—C512—C517	−6.50 (16)		C62—N63—C64—C65	−0.10 (15)
C516—C511—C512—C517	−179.6 (1)		C631—N63—C64—C65	177.20 (12)
C511—C512—C513—C514	−5.50 (17)		N63—C64—C65—N61	−0.20 (15)
C517—C512—C513—C514	177.30 (11)		C62—N61—C65—C64	0.40 (15)
C512—C513—C514—C515	4.60 (18)		C611—N61—C65—C64	−175.30 (12)
C512—C513—C514—C518	−170.70 (11)		C62—N61—C611—C616	86.30 (17)
C513—C514—C515—C516	−1.30 (17)		C65—N61—C611—C616	−98.90 (15)
C518—C514—C515—C516	174.0 (1)		C62—N61—C611—C612	−96.50 (17)
C514—C515—C516—C511	−0.90 (16)		C65—N61—C611—C612	78.30 (17)
C514—C515—C516—C519	−179.9 (1)		C616—C611—C612—C613	−1 (2)
N51—C511—C516—C515	−173.0 (1)		N61—C611—C612—C613	−178.30 (11)
C512—C511—C516—C515	−0.10 (16)		C616—C611—C612—C617	178.30 (13)
N51—C511—C516—C519	6.00 (15)		N61—C611—C612—C617	1 (2)
C512—C511—C516—C519	178.9 (1)		C611—C612—C613—C614	−3.70 (19)
C52—N53—C531—C532	−100.00 (16)		C617—C612—C613—C614	176.50 (13)
C54—N53—C531—C532	97.80 (14)		C612—C613—C614—C615	8 (2)
C52—N53—C531—C536	74.70 (17)		C612—C613—C614—C618	−179.30 (12)
C54—N53—C531—C536	−87.50 (14)		C613—C614—C615—C616	−7 (2)
C536—C531—C532—C533	7.60 (19)		C618—C614—C615—C616	−179.20 (13)
N53—C531—C532—C533	−178.2 (1)		C612—C611—C616—C615	3 (2)
C536—C531—C532—C537	−177.30 (12)		N61—C611—C616—C615	179.60 (11)
N53—C531—C532—C537	−3.10 (19)		C612—C611—C616—C619	−176.20 (13)
C531—C532—C533—C534	−7.60 (19)		N61—C611—C616—C619	1 (2)
C537—C532—C533—C534	177.10 (11)		C614—C615—C616—C611	2 (2)
C532—C533—C534—C535	4.70 (19)		C614—C615—C616—C619	−179.30 (12)
C532—C533—C534—C538	177.10 (12)		C62—N63—C631—C636	−105.00 (15)
C533—C534—C535—C536	−1.20 (18)		C64—N63—C631—C636	78.40 (15)
C538—C534—C535—C536	−172.70 (11)		C62—N63—C631—C632	77.50 (17)
C532—C531—C536—C535	−4.40 (19)		C64—N63—C631—C632	−99.10 (14)
N53—C531—C536—C535	−178.8 (1)		C636—C631—C632—C633	1.80 (19)
C532—C531—C536—C539	179.70 (12)		N63—C631—C632—C633	179.10 (11)
N53—C531—C536—C539	5.20 (16)		C636—C631—C632—C637	−176.60 (12)
C534—C535—C536—C531	1.00 (19)		N63—C631—C632—C637	0.70 (18)
C534—C535—C536—C539	177.00 (11)		C631—C632—C633—C634	0 (2)
C65—N61—C62—N63	−0.50 (15)		C637—C632—C633—C634	178.70 (13)
C611—N61—C62—N63	174.90 (13)		C632—C633—C634—C635	0 (2)
C65—N61—C62—PD5	176.7 (9)		C632—C633—C634—C638	177.30 (12)
C611—N61—C62—PD5	−8 (2)		C633—C634—C635—C636	−1.20 (19)
C55—PD5—C62—N63	−37 (29)		C638—C634—C635—C636	−178.90 (12)
CL5—PD5—C62—N63	73.60 (11)		C632—C631—C636—C635	−3.50 (19)
CL6—PD5—C62—N63	−105.00 (11)		N63—C631—C636—C635	179.2 (1)
C55—PD5—C62—N61	146 (39)		C632—C631—C636—C639	176.90 (11)
CL5—PD5—C62—N61	−103.10 (11)		N63—C631—C636—C639	−0.40 (17)
CL6—PD5—C62—N61	78.30 (11)		C634—C635—C636—C631	3.10 (18)
N61—C62—N63—C64	0.30 (15)		C634—C635—C636—C639	−177.90 (11)
PD5—C62—N63—C64	−176.8 (8)			

Annexe VI – Analyse crystallographique complète pour IMes₂PdCl₂ normal

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Structure of CHA103

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Abstract

Here should be written a short abstract

Comment

Here should be written the text of the article

Experimental

Small details about the preparation of the compound.

Crystal data

$C_{42}H_{48}Cl_2N_4Pd$

$M_r = 786.14$

Monoclinic

$C2/c$

$a = 20.8588\,(3)$ Å

$b = 20.8678\,(4)$ Å

$c = 19.0273\,(3)$ Å

$\beta = 108.4890\,(10)°$

$V = 7854.7\,(2)$ Å^3

$Z = 8$

$D_x = 1.330$ Mg m^{-3}

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 11273 reflections

$\theta = 4.24–72.73°$

$\mu = 5.314$ mm^{-1}

$T = 220\,(2)$ K

Block

Colourless

$0.24 \times 0.19 \times 0.12$ mm

Crystal source: synthesized by the authors. See text

Data collection

Bruker AXS Smart 2K/Platform diffractometer

ω scans

Absorption correction:

multi-scan Sadabs (Sheldrick,1996)

$T_{min} = 0.3500, T_{max} = 0.6500$

31949 measured reflections

7746 independent reflections

4621 reflections with
$I > 2\sigma(I)$

$R_{int} = 0.042$

$\theta_{max} = 72.93°$

$h = -25 \rightarrow 25$

$k = -23 \rightarrow 25$

$l = -23 \rightarrow 23$

229 standard reflections

every ? reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0415$

$wR(F^2) = 0.0819$

$S = 0.992$

7746 reflections

456 parameters

H-atom parameters constrained

$w=1/[\sigma^2(F_o^2) + (0.0140P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.960$ e Å^{-3}

$\Delta\rho_{min} = -0.474$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—C12^i	2.045 (4)	Pd2—C22^{ii}	2.040 (4)
Pd1—C12	2.045 (4)	Pd2—C22	2.040 (4)
Pd1—Cl11^i	2.3156 (10)	Pd2—Cl22	2.3138 (16)
Pd1—Cl11	2.3156 (10)	Pd2—Cl21	2.3247 (16)
N11—C12	1.350 (5)	N21—C22	1.354 (5)
N11—C15	1.378 (5)	N21—C25	1.376 (5)
N11—C111	1.451 (5)	N21—C211	1.449 (5)
C12—N13	1.343 (5)	C22—N23	1.336 (5)
N13—C14	1.384 (5)	N23—C24	1.388 (5)
N13—C131	1.447 (5)	N23—C231	1.450 (5)
C14—C15	1.329 (6)	C24—C25	1.330 (6)
C111—C116	1.384 (6)	C211—C216	1.384 (6)
C111—C112	1.391 (6)	C211—C212	1.400 (6)
C112—C113	1.383 (6)	C212—C213	1.392 (5)
C112—C117	1.515 (6)	C212—C217	1.505 (5)
C113—C114	1.383 (6)	C213—C214	1.387 (6)
C114—C115	1.382 (6)	C214—C215	1.389 (6)
C114—C118	1.518 (5)	C214—C218	1.509 (6)
C115—C116	1.396 (5)	C215—C216	1.375 (6)
C116—C119	1.508 (5)	C216—C219	1.514 (6)
C131—C136	1.381 (6)	C231—C232	1.385 (6)
C131—C132	1.397 (6)	C231—C236	1.394 (5)
C132—C133	1.387 (5)	C232—C233	1.390 (6)
C132—C137	1.514 (5)	C232—C237	1.501 (6)
C133—C134	1.380 (6)	C233—C234	1.390 (6)
C134—C135	1.380 (6)	C234—C235	1.383 (6)
C134—C138	1.516 (6)	C234—C238	1.510 (5)
C135—C136	1.389 (6)	C235—C236	1.398 (5)
C136—C139	1.499 (6)	C236—C239	1.507 (5)
C12^i—PD1—C12	179.8 (3)	N13—C12—N11	105.5 (4)
C12^i—PD1—CL11^i	90.72 (11)	N13—C12—PD1	127.1 (3)
C12—PD1—CL11^i	89.28 (11)	N11—C12—PD1	127.4 (3)
C12^i—PD1—CL11	89.28 (11)	C12—N13—C14	110.3 (4)
C12—PD1—CL11	90.72 (11)	C12—N13—C131	127.6 (4)
CL11^i—PD1—CL11	179.70 (7)	C14—N13—C131	122.1 (4)
C12—N11—C15	109.9 (4)	C15—C14—N13	106.7 (4)
C12—N11—C111	126.3 (4)	C14—C15—N11	107.5 (4)
C15—N11—C111	123.8 (4)	C116—C111—C112	122.9 (4)

C116—C111—N11	119.2 (4)	N23—C22—N21	105.2 (3)
C112—C111—N11	117.9 (4)	N23—C22—PD2	128.3 (3)
C113—C112—C111	117.5 (4)	N21—C22—PD2	126.5 (3)
C113—C112—C117	120.5 (4)	C22—N23—C24	110.7 (4)
C111—C112—C117	122.0 (4)	C22—N23—C231	126.5 (4)
C114—C113—C112	121.6 (5)	C24—N23—C231	122.8 (4)
C115—C114—C113	119.3 (4)	C25—C24—N23	106.5 (4)
C115—C114—C118	119.5 (5)	C24—C25—N21	107.4 (4)
C113—C114—C118	121.2 (4)	C216—C211—C212	122.4 (4)
C114—C115—C116	121.2 (4)	C216—C211—N21	119.0 (4)
C111—C116—C115	117.4 (4)	C212—C211—N21	118.6 (4)
C111—C116—C119	121.8 (4)	C213—C212—C211	117.3 (4)
C115—C116—C119	120.8 (4)	C213—C212—C217	120.5 (4)
C136—C131—C132	122.2 (4)	C211—C212—C217	122.2 (4)
C136—C131—N13	118.6 (4)	C214—C213—C212	121.7 (5)
C132—C131—N13	119.2 (4)	C213—C214—C215	118.3 (4)
C133—C132—C131	117.7 (4)	C213—C214—C218	120.3 (5)
C133—C132—C137	120.7 (4)	C215—C214—C218	121.3 (5)
C131—C132—C137	121.6 (4)	C216—C215—C214	122.2 (5)
C134—C133—C132	121.7 (5)	C215—C216—C211	118.0 (5)
C135—C134—C133	118.7 (5)	C215—C216—C219	120.2 (5)
C135—C134—C138	120.7 (5)	C211—C216—C219	121.8 (4)
C133—C134—C138	120.6 (5)	C232—C231—C236	122.7 (4)
C134—C135—C136	121.9 (5)	C232—C231—N23	118.6 (4)
C131—C136—C135	117.8 (5)	C236—C231—N23	118.6 (4)
C131—C136—C139	121.9 (4)	C231—C232—C233	117.8 (5)
C135—C136—C139	120.3 (4)	C231—C232—C237	122.0 (4)
C22^{ii}—PD2—C22	179.4 (2)	C233—C232—C237	120.2 (4)
C22^{ii}—PD2—CL22	89.70 (12)	C234—C233—C232	121.6 (5)
C22—PD2—CL22	89.70 (12)	C235—C234—C233	118.6 (4)
C22^{ii}—PD2—CL21	90.30 (12)	C235—C234—C238	120.4 (5)
C22—PD2—CL21	90.30 (12)	C233—C234—C238	121.0 (5)
CL22—PD2—CL21	180	C234—C235—C236	122.0 (4)
C22—N21—C25	110.2 (4)	C231—C236—C235	117.1 (4)
C22—N21—C211	127.2 (4)	C231—C236—C239	122.0 (4)
C25—N21—C211	122.6 (4)	C235—C236—C239	120.9 (4)

Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $-x, y, \frac{3}{2} - z$.

All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters. The H atoms were generated geometrically (C—H 0.93 to 0.97 Å) and were included in the refinement in the riding model approximation; their temperature factors were set to 1.5 times those of the equivalent isotropic temperature factors of the parent site (methyl) and 1.2 times for others. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 2000).

Data collection: SMART (Bruker, 1999). Cell refinement: SMART (Bruker, 1999). Data reduction: SAINT (Bruker, 1999). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: UdMX (local program).

Supplementary data for this paper are available from the IUCr electronic archives (Reference:). Services for accessing these data are described at the back of the journal.

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Fig 1 *ORTEP* view of the title compound. Thermal ellipsoids are shown at 30% probability levels.

Table 1. Selected geometric parameters (Å, °) for the title compound.

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

http://journals.iucr.org/c/journalhomepage.html

Table S1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j a_i.a_j.$$

	x	y	z	U_{eq}
Pd1	1/2	0.42600 (2)	3/4	0.02311 (11)
Cl11	0.38899 (5)	0.42571 (6)	0.75000 (5)	0.0346 (2)
N11	0.52470 (18)	0.37983 (17)	0.90895 (19)	0.0305 (9)
C12	0.5340 (2)	0.4259 (2)	0.8633 (2)	0.0232 (10)
N13	0.57189 (18)	0.47090 (17)	0.90793 (19)	0.0276 (9)
C14	0.5868 (2)	0.4528 (2)	0.9814 (3)	0.0399 (13)
H14	0.6125	0.4762	1.0231	0.048
C15	0.5579 (2)	0.3961 (2)	0.9816 (2)	0.0408 (13)
H15	0.5597	0.3716	1.0236	0.049
C111	0.4858 (2)	0.3214 (2)	0.8868 (2)	0.0281 (10)
C112	0.4228 (2)	0.3181 (2)	0.8970 (2)	0.0290 (11)
C113	0.3859 (2)	0.2623 (2)	0.8755 (2)	0.0359 (12)
H113	0.3429	0.2590	0.8813	0.043
C114	0.4108 (2)	0.2113 (2)	0.8458 (2)	0.0369 (12)
C115	0.4745 (2)	0.2156 (2)	0.8383 (2)	0.0353 (11)
H115	0.4919	0.1805	0.8192	0.042
C116	0.5135 (2)	0.2710 (2)	0.8588 (2)	0.0315 (11)
C117	0.3944 (2)	0.3731 (2)	0.9298 (3)	0.0450 (13)
H11A	0.4217	0.3792	0.9811	0.067
H11B	0.3482	0.3635	0.9273	0.067
H11C	0.3951	0.4120	9.9020	0.067
C118	0.3695 (2)	0.1507 (2)	0.8210 (3)	0.0509 (15)
H11D	0.3328	0.1593	0.7757	0.076
H11E	0.3511	0.1370	0.8594	0.076
H11F	0.3982	0.1172	0.8120	0.076
C119	0.5835 (2)	0.2746 (2)	0.8522 (3)	0.0452 (13)
H11G	0.5845	0.3070	0.8160	0.068
H11H	0.5955	0.2334	0.8365	0.068
H11I	0.6156	0.2858	0.8999	0.068
C131	0.5962 (2)	0.5303 (2)	0.8865 (2)	0.0295 (10)
C132	0.5503 (2)	0.5797 (2)	0.8572 (2)	0.0295 (10)
C133	0.5756 (2)	0.6365 (2)	0.8388 (2)	0.0358 (12)
H133	0.5456	0.6703	0.8186	0.043
C134	0.6437 (3)	0.6448 (2)	0.8492 (3)	0.0416 (13)
C135	0.6873 (2)	0.5949 (2)	0.8789 (3)	0.0422 (13)
H135	0.7338	0.6005	0.8868	0.051
C136	0.6646 (2)	0.5367 (2)	0.8974 (3)	0.0327 (12)
C137	0.4755 (2)	0.5719 (2)	0.8453 (2)	0.0384 (11)
H13A	0.4554	0.5458	0.8016	0.058
H13B	0.4540	0.6137	0.8384	0.058
H13C	0.4691	0.5512	0.8882	0.058
C138	0.6700 (3)	0.7077 (2)	0.8294 (3)	0.0670 (19)
H13D	0.6428	0.7205	0.7799	0.100
H13E	0.7166	0.7024	0.8308	0.100
H13F	0.6675	0.7404	0.8646	0.100
C139	0.7134 (2)	0.4833 (2)	0.9281 (3)	0.0452 (13)
H13C	0.7241	0.4819	0.9816	0.068
H13H	0.7545	0.4905	0.9157	0.068
H13I	0.6933	0.4429	0.9071	0.068
Pd2	0.0000	0.42946 (2)	3/4	0.02312 (11)
Cl21	0.0000	0.54086 (7)	3/4	0.0339 (4)

Cl22	0.0000	0.31856 (7)	3/4	0.0353 (4)
N21	0.00128 (18)	0.40403 (17)	0.90813 (19)	0.0284 (9)
C22	0.0337 (2)	0.4289 (2)	0.8630 (2)	0.0217 (10)
N23	0.09235 (18)	0.45106 (18)	0.90844 (19)	0.0304 (9)
C24	0.0976 (2)	0.4392 (2)	0.9818 (2)	0.0425 (14)
H24	0.1342	0.4498	1.0239	0.051
C25	0.0407 (2)	0.4101 (2)	0.9811 (2)	0.0380 (13)
H25	0.0295	0.3962	1.0227	0.046
C211	−0.0639 (2)	0.3724 (2)	0.8862 (2)	0.0295 (10)
C212	−0.1221 (2)	0.4094 (2)	0.8561 (2)	0.0293 (11)
C213	−0.1841 (2)	0.3779 (2)	0.8371 (2)	0.0360 (11)
H213	−0.2240	0.4016	0.8163	0.043
C214	−0.1886 (2)	0.3126 (2)	0.8481 (3)	0.0423 (13)
C215	−0.1291 (2)	0.2785 (2)	0.8793 (3)	0.0414 (13)
H215	−0.1317	0.2344	0.8882	0.050
C216	−0.0666 (2)	0.3071 (2)	0.8976 (3)	0.0329 (12)
C217	−0.1189 (2)	0.4804 (2)	0.8434 (3)	0.0411 (12)
H21A	−0.0845	0.4995	0.8850	0.062
H21B	−0.1624	0.4996	0.8388	0.062
H21C	−0.1078	0.4878	0.7983	0.062
C218	−0.2567 (2)	0.2801 (3)	0.8276 (3)	0.073 (2)
H21D	−0.2615	0.2516	0.7859	0.109
H21E	−0.2921	0.3122	0.8141	0.109
H21F	−0.2601	0.2556	0.8695	0.109
C219	−0.0032 (2)	0.2674 (2)	0.9293 (3)	0.0469 (14)
H21G	0.0145	0.2739	0.9824	0.070
H21H	0.0305	0.2806	0.9067	0.070
H21I	−0.0138	0.2225	0.9189	0.070
C231	0.1450 (2)	0.4830 (2)	0.8869 (2)	0.0283 (10)
C232	0.1524 (2)	0.5487 (2)	0.8966 (2)	0.0311 (11)
C233	0.2030 (2)	0.5785 (2)	0.8756 (2)	0.0365 (12)
H233	0.2089	0.6230	0.8818	0.044
C234	0.2453 (2)	0.5440 (2)	0.8457 (2)	0.0360 (11)
C235	0.2378 (2)	0.4782 (2)	0.8397 (2)	0.0351 (11)
H235	0.2673	0.4545	0.8211	0.042
C236	0.1878 (2)	0.4459 (2)	0.8603 (2)	0.0307 (11)
C237	0.1079 (2)	0.5873 (2)	0.9290 (3)	0.0461 (13)
H23A	0.1192	0.5780	0.9814	0.069
H23B	0.0609	0.5764	0.9041	0.069
H23C	0.1147	0.6326	0.9222	0.069
C238	0.2986 (2)	0.5774 (2)	0.8209 (3)	0.0509 (14)
H23D	0.3294	0.5458	0.8122	0.076
H23E	0.3236	0.6070	0.8591	0.076
H23F	0.2772	0.6008	0.7755	0.076
C239	0.1816 (2)	0.3740 (2)	0.8544 (3)	0.0442 (13)
H23G	0.1814	0.3564	0.9015	0.066
H23H	0.2196	0.3566	0.8416	0.066
H23I	0.1398	0.3627	0.8162	0.066

Table S2. Anisotropic displacement parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd1	0.0235 (3)	0.0247 (3)	0.0186 (2)	0.000	0.00324 (19)	0.000
Cl11	0.0277 (6)	0.0445 (6)	0.0303 (5)	0.0011 (5)	0.0072 (4)	0.0014 (5)
N11	0.035 (2)	0.031 (2)	0.024 (2)	−0.0079 (18)	0.0062 (18)	0.0000 (17)
C12	0.020 (2)	0.030 (3)	0.020 (2)	0.000 (2)	0.0063 (19)	−0.001 (2)
N13	0.031 (2)	0.029 (2)	0.0194 (19)	−0.0042 (17)	0.0031 (17)	−0.0007 (16)
C14	0.053 (4)	0.042 (3)	0.019 (2)	−0.012 (3)	0.002 (2)	0.002 (2)
C15	0.054 (4)	0.046 (3)	0.017 (2)	−0.012 (3)	0.004 (2)	0.002 (2)
C111	0.033 (3)	0.030 (2)	0.0168 (19)	−0.008 (2)	0.0028 (18)	−0.0013 (19)
C112	0.034 (3)	0.028 (3)	0.023 (2)	0.001 (2)	0.007 (2)	0.003 (2)
C113	0.027 (3)	0.044 (3)	0.033 (3)	−0.005 (2)	0.005 (2)	0.007 (2)
C114	0.035 (3)	0.034 (3)	0.033 (3)	−0.008 (2)	−0.001 (2)	0.009 (2)
C115	0.044 (3)	0.026 (3)	0.035 (3)	0.000 (2)	0.011 (2)	0.001 (2)
C116	0.031 (3)	0.029 (3)	0.031 (2)	−0.003 (2)	0.006 (2)	0.006 (2)

C117	0.045 (3)	0.051 (3)	0.044 (3)	0.003 (3)	0.021 (3)	0.000 (3)
C118	0.046 (3)	0.036 (3)	0.063 (4)	−0.010 (3)	0.005 (3)	0.000 (3)
C119	0.035 (3)	0.043 (3)	0.058 (3)	−0.001 (2)	0.016 (3)	0.001 (3)
C131	0.038 (3)	0.027 (2)	0.020 (2)	−0.009 (2)	0.004 (2)	−0.0055 (18)
C132	0.037 (3)	0.031 (3)	0.022 (2)	−0.005 (2)	0.0115 (19)	−0.005 (2)
C133	0.041 (3)	0.028 (3)	0.036 (3)	0.001 (2)	0.009 (2)	−0.001 (2)
C134	0.045 (3)	0.029 (3)	0.050 (3)	−0.011 (2)	0.014 (3)	−0.001 (2)
C135	0.030 (3)	0.047 (4)	0.046 (3)	−0.010 (2)	0.007 (3)	−0.001 (3)
C136	0.034 (3)	0.033 (3)	0.028 (3)	−0.003 (2)	0.006 (2)	−0.005 (2)
C137	0.040 (3)	0.036 (3)	0.045 (3)	0.003 (2)	0.021 (2)	−0.003 (2)
C138	0.069 (4)	0.032 (3)	0.107 (5)	−0.013 (3)	0.039 (4)	0.011 (3)
C139	0.034 (3)	0.043 (3)	0.048 (3)	−0.004 (2)	−0.002 (2)	−0.001 (3)
Pd2	0.0219 (3)	0.0270 (3)	0.0189 (2)	0.000	0.00417 (19)	0.000
Cl21	0.0391 (10)	0.0287 (8)	0.0308 (8)	0.000	0.0069 (7)	0.000
Cl22	0.0424 (10)	0.0281 (8)	0.0333 (8)	0.000	0.0090 (7)	0.000
N21	0.024 (2)	0.037 (2)	0.0234 (19)	−0.0044 (16)	0.0065 (17)	0.0020 (16)
C22	0.026 (2)	0.023 (2)	0.015 (2)	0.002 (2)	0.0041 (19)	0.0001 (19)
N23	0.026 (2)	0.045 (2)	0.0190 (19)	−0.0095 (18)	0.0060 (16)	0.0044 (17)
C24	0.033 (3)	0.069 (4)	0.021 (2)	−0.015 (3)	0.003 (2)	−0.004 (2)
C25	0.034 (3)	0.057 (4)	0.022 (2)	−0.009 (2)	0.007 (2)	0.004 (2)
C211	0.025 (3)	0.042 (3)	0.021 (2)	−0.008 (2)	0.0075 (19)	−0.001 (2)
C212	0.027 (3)	0.039 (3)	0.022 (2)	−0.003 (2)	0.0087 (19)	−0.0052 (19)
C213	0.029 (3)	0.041 (3)	0.040 (3)	0.000 (2)	0.013 (2)	−0.003 (2)
C214	0.029 (3)	0.044 (3)	0.053 (3)	−0.012 (2)	0.012 (2)	−0.002 (3)
C215	0.041 (3)	0.035 (3)	0.051 (3)	−0.007 (2)	0.017 (3)	0.007 (2)
C216	0.027 (3)	0.044 (3)	0.026 (3)	0.000 (2)	0.007 (2)	0.007 (2)
C217	0.040 (3)	0.036 (3)	0.049 (3)	0.002 (2)	0.016 (3)	−0.007 (2)
C218	0.037 (4)	0.060 (4)	0.116 (6)	−0.016 (3)	0.016 (4)	−0.003 (4)
C219	0.045 (3)	0.045 (3)	0.050 (3)	0.002 (3)	0.016 (3)	0.017 (3)
C231	0.021 (2)	0.038 (3)	0.023 (2)	−0.0093 (19)	0.0033 (19)	0.0006 (19)
C232	0.025 (3)	0.039 (3)	0.024 (2)	0.000 (2)	−0.001 (2)	−0.002 (2)
C233	0.034 (3)	0.032 (3)	0.039 (3)	−0.005 (2)	0.004 (2)	0.006 (2)
C234	0.023 (3)	0.049 (3)	0.032 (3)	−0.007 (2)	0.002 (2)	0.008 (2)
C235	0.025 (3)	0.047 (3)	0.032 (3)	0.003 (2)	0.008 (2)	0.001 (2)
C236	0.024 (2)	0.033 (3)	0.031 (2)	−0.0024 (19)	0.002 (2)	0.0006 (19)
C237	0.043 (3)	0.050 (4)	0.043 (3)	0.001 (3)	0.010 (3)	−0.003 (2)
C238	0.034 (3)	0.057 (4)	0.064 (4)	−0.006 (3)	0.018 (3)	0.013 (3)
C239	0.035 (3)	0.037 (3)	0.060 (3)	0.000 (2)	0.013 (3)	−0.001 (3)

Table S3. *Geometric parameters* (Å, °)

Pd1—C12^i	2.045 (4)	Pd2—C22^{ii}	2.040 (4)
Pd1—C12	2.045 (4)	Pd2—C22	2.040 (4)
Pd1—Cl11^i	2.3156 (10)	Pd2—Cl22	2.3138 (16)
Pd1—Cl11	2.3156 (10)	Pd2—Cl21	2.3247 (16)
N11—C12	1.350 (5)	N21—C22	1.354 (5)
N11—C15	1.378 (5)	N21—C25	1.376 (5)
N11—C111	1.451 (5)	N21—C211	1.449 (5)
C12—N13	1.343 (5)	C22—N23	1.336 (5)
N13—C14	1.384 (5)	N23—C24	1.388 (5)
N13—C131	1.447 (5)	N23—C231	1.450 (5)
C14—C15	1.329 (6)	C24—C25	1.330 (6)
C14—H14	0.94	C24—H24	0.94
C15—H15	0.94	C25—H25	0.94
C111—C116	1.384 (6)	C211—C216	1.384 (6)
C111—C112	1.391 (6)	C211—C212	1.400 (6)
C112—C113	1.383 (6)	C212—C213	1.392 (5)
C112—C117	1.515 (6)	C212—C217	1.505 (5)
C113—C114	1.383 (6)	C213—C214	1.387 (6)
C113—H113	0.94	C213—H213	0.94
C114—C115	1.382 (6)	C214—C215	1.389 (6)
C114—C118	1.518 (5)	C214—C218	1.509 (6)
C115—C116	1.396 (5)	C215—C216	1.375 (6)
C115—H115	0.94	C215—H215	0.94
C116—C119	1.508 (5)	C216—C219	1.514 (6)
C117—H11a	0.97	C217—H21a	0.97
C117—H11b	0.97	C217—H21b	0.97
C117—H11c	0.97	C217—H21c	0.97
C118—H11d	0.97	C218—H21d	0.97
C118—H11e	0.97	C218—H21e	0.97
C118—H11f	0.97	C218—H21f	0.97
C119—H11g	0.97	C219—H21g	0.97
C119—H11h	0.97	C219—H21h	0.97
C119—H11i	0.97	C219—H21i	0.97
C131—C136	1.381 (6)	C231—C232	1.385 (6)
C131—C132	1.397 (6)	C231—C236	1.394 (5)
C132—C133	1.387 (5)	C232—C233	1.390 (6)
C132—C137	1.514 (5)	C232—C237	1.501 (6)
C133—C134	1.380 (6)	C233—C234	1.390 (6)
C133—H133	0.94	C233—H233	0.94
C134—C135	1.380 (6)	C234—C235	1.383 (6)
C134—C138	1.516 (6)	C234—C238	1.510 (5)
C135—C136	1.389 (6)	C235—C236	1.398 (5)
C135—H135	0.94	C235—H235	0.94
C136—C139	1.499 (6)	C236—C239	1.507 (5)
C137—H13a	0.97	C237—H23a	0.97
C137—H13b	0.97	C237—H23b	0.97
C137—H13c	0.97	C237—H23c	0.97
C138—H13d	0.97	C233—H23d	0.97
C138—H13e	0.97	C238—H23e	0.97
C138—H13f	0.97	C238—H23f	0.97
C139—H13g	0.97	C239—H23g	0.97
C139—H13h	0.97	C239—H23h	0.97
C139—H13i	0.97	C239—H23i	0.97
C12^i—PD1—C12	179.8 (3)	C15—N11—C111	123.8 (4)
C12^i—PD1—CL11^i	90.72 (11)	N13—C12—N11	105.5 (4)
C12—PD1—CL11^i	89.28 (11)	N13—C12—PD1	127.1 (3)
C12^i—PD1—CL11	89.28 (11)	N11—C12—PD1	127.4 (3)
C12—PD1—CL11	90.72 (11)	C12—N13—C14	110.3 (4)
CL11^i—PD1—CL11	179.70 (7)	C12—N13—C131	127.6 (4)
C12—N11—C15	109.9 (4)	C14—N13—C131	122.1 (4)
C12—N11—C111	126.3 (4)	C15—C14—N13	106.7 (4)

C15—C14—H14	126.6	C132—C137—H13C	109.5
N13—C14—H14	126.6	H13A—C137—H13C	109.5
C14—C15—N11	107.5 (4)	H13B—C137—H13C	109.5
C14—C15—H15	126.2	C134—C138—H13D	109.5
N11—C15—H15	126.2	C134—C138—H13E	109.5
C116—C111—C112	122.9 (4)	H13D—C138—H13E	109.5
C116—C111—N11	119.2 (4)	C134—C138—H13F	109.5
C112—C111—N11	117.9 (4)	H13D—C138—H13F	109.5
C113—C112—C111	117.5 (4)	H13E—C138—H13F	109.5
C113—C112—C117	120.5 (4)	C136—C139—H13G	109.5
C111—C112—C117	122.0 (4)	C136—C139—H13H	109.5
C114—C113—C112	121.6 (5)	H13G—C139—H13H	109.5
C114—C113—H113	119.2	C136—C139—H13I	109.5
C112—C113—H113	119.2	H13G—C139—H13I	109.5
C115—C114—C113	119.3 (4)	H13H—C139—H13I	109.5
C115—C114—C118	119.5 (5)	C22^{ii}—PD2—C22	179.4 (2)
C113—C114—C118	121.2 (4)	C22^{ii}—PD2—CL22	89.70 (12)
C114—C115—C116	121.2 (4)	C22—PD2—CL22	89.70 (12)
C114—C115—H115	119.4	C22^{ii}—PD2—CL21	90.30 (12)
C116—C115—H115	119.4	C22—PD2—CL21	90.30 (12)
C111—C116—C115	117.4 (4)	CL22—PD2—CL21	180
C111—C116—C119	121.8 (4)	C22—N21—C25	110.2 (4)
C115—C116—C119	120.8 (4)	C22—N21—C211	127.2 (4)
C112—C117—H11A	109.5	C25—N21—C211	122.6 (4)
C112—C117—H11B	109.5	N23—C22—N21	105.2 (3)
H11A—C117—H11B	109.5	N23—C22—PD2	128.3 (3)
C112—C117—H11C	109.5	N21—C22—PD2	126.5 (3)
H11A—C117—H11C	109.5	C22—N23—C24	110.7 (4)
H11B—C117—H11C	109.5	C22—N23—C231	126.5 (4)
C114—C118—H11D	109.5	C24—N23—C231	122.8 (4)
C114—C118—H11E	109.5	C25—C24—N23	106.5 (4)
H11D—C118—H11E	109.5	C25—C24—H24	126.7
C114—C118—H11F	109.5	N23—C24—H24	126.7
H11D—C118—H11F	109.5	C24—C25—N21	107.4 (4)
H11E—C118—H11F	109.5	C24—C25—H25	126.3
C116—C119—H11G	109.5	N21—C25—H25	126.3
C116—C119—H11H	109.5	C216—C211—C212	122.4 (4)
H11G—C119—H11H	109.5	C216—C211—N21	119.0 (4)
C116—C119—H11I	109.5	C212—C211—N21	118.6 (4)
H11G—C119—H11I	109.5	C213—C212—C211	117.3 (4)
H11H—C119—H11I	109.5	C213—C212—C217	120.5 (4)
C136—C131—C132	122.2 (4)	C211—C212—C217	122.2 (4)
C136—C131—N13	118.6 (4)	C214—C213—C212	121.7 (5)
C132—C131—N13	119.2 (4)	C214—C213—H213	119.1
C133—C132—C131	117.7 (4)	C212—C213—H213	119.1
C133—C132—C137	120.7 (4)	C213—C214—C215	118.3 (4)
C131—C132—C137	121.6 (4)	C213—C214—C218	120.3 (5)
C134—C133—C132	121.7 (5)	C215—C214—C218	121.3 (5)
C134—C133—H133	119.1	C216—C215—C214	122.2 (5)
C132—C133—H133	119.1	C216—C215—H215	118.9
C135—C134—C133	118.7 (5)	C214—C215—H215	118.9
C135—C134—C138	120.7 (5)	C215—C216—C211	118.0 (5)
C133—C134—C138	120.6 (5)	C215—C216—C219	120.2 (5)
C134—C135—C136	121.9 (5)	C211—C216—C219	121.8 (4)
C134—C135—H135	119.1	C212—C217—H21A	109.5
C136—C135—H135	119.1	C212—C217—H21B	109.5
C131—C136—C135	117.8 (5)	H21A—C217—H21B	109.5
C131—C136—C139	121.9 (4)	C212—C217—H21C	109.5
C135—C136—C139	120.3 (4)	H21A—C217—H21C	109.5
C132—C137—H13A	109.5	H21B—C217—H21C	109.5
C132—C137—H13B	109.5	C214—C218—H21D	109.5
H13A—C137—H13B	109.5	C214—C218—H21E	109.5

H21D—C218—H21E	109.5	C234—C235—H235	119
C214—C218—H21F	109.5	C236—C235—H235	119
H21D—C218—H21F	109.5	C231—C236—C235	117.1 (4)
H21E—C218—H21F	109.5	C231—C236—C239	122.0 (4)
C216—C219—H21G	109.5	C235—C236—C239	120.9 (4)
C216—C219—H21H	109.5	C232—C237—H23A	109.5
H21G—C219—H21H	109.5	C232—C237—H23B	109.5
C216—C219—H21I	109.5	H23A—C237—H23B	109.5
H21G—C219—H21I	109.5	C232—C237—H23C	109.5
H21H—C219—H21I	109.5	H23A—C237—H23C	109.5
C232—C231—C236	122.7 (4)	H23B—C237—H23C	109.5
C232—C231—N23	118.6 (4)	C234—C238—H23D	109.5
C236—C231—N23	118.6 (4)	C234—C238—H23E	109.5
C231—C232—C233	117.8 (5)	H23D—C238—H23E	109.5
C231—C232—C237	122.0 (4)	C234—C238—H23F	109.5
C233—C232—C237	120.2 (4)	H23D—C238—H23F	109.5
C234—C233—C232	121.6 (5)	H23E—C238—H23F	109.5
C234—C233—H233	119.2	C236—C239—H23G	109.5
C232—C233—H233	119.2	C236—C239—H23H	109.5
C235—C234—C233	118.6 (4)	H23G—C239—H23H	109.5
C235—C234—C238	120.4 (5)	C236—C239—H23I	109.5
C233—C234—C238	121.0 (5)	H23G—C239—H23I	109.5
C234—C235—C236	122.0 (4)	H23H—C239—H23I	109.5

C15—N11—C12—N13	−1.0 (5)	C25—N21—C22—N23	−0.9 (5)
C111—N11—C12—N13	178.9 (4)	C211—N21—C22—N23	−178.3 (4)
C15—N11—C12—PD1	177.4 (3)	C25—N21—C22—PD2	177.5 (3)
C111—N11—C12—PD1	−2.7 (6)	C211—N21—C22—PD2	0.2 (7)
C12^i—PD1—C12—N13	152 (17)	C22^{ii}—PD2—C22—N23	116.4 (4)
CL11^i—PD1—C12—N13	61.7 (4)	CL22—PD2—C22—N23	116.4 (4)
CL11—PD1—C12—N13	−118.6 (4)	CL21—PD2—C22—N23	−63.6 (4)
C12^i—PD1—C12—N11	−27 (17)	C22^{ii}—PD2—C22—N21	−61.7 (4)
CL11^i—PD1—C12—N11	−116.4 (4)	CL22—PD2—C22—N21	−61.7 (4)
CL11—PD1—C12—N11	63.3 (4)	CL21—PD2—C22—N21	118.3 (4)
N11—C12—N13—C14	0.6 (5)	N21—C22—N23—C24	1.1 (5)
PD1—C12—N13—C14	−177.9 (3)	PD2—C22—N23—C24	−177.3 (3)
N11—C12—N13—C131	179.8 (4)	N21—C22—N23—C231	−179.2 (4)
PD1—C12—N13—C131	1.3 (7)	PD2—C22—N23—C231	2.4 (7)
C12—N13—C14—C15	0.1 (6)	C22—N23—C24—C25	−0.8 (6)
C131—N13—C14—C15	−179.2 (4)	C231—N23—C24—C25	179.5 (4)
N13—C14—C15—N11	−0.7 (6)	N23—C24—C25—N21	0.2 (6)
C12—N11—C15—C14	1.1 (6)	C22—N21—C25—C24	0.5 (6)
C111—N11—C15—C14	−178.6 (4)	C211—N21—C25—C24	177.9 (4)
C12—N11—C111—C116	77.0 (6)	C22—N21—C211—C216	110.0 (5)
C15—N11—C111—C116	−103.1 (5)	C25—N21—C211—C216	−67.0 (6)
C12—N11—C111—C112	−105.0 (5)	C22—N21—C211—C212	−71.9 (6)
C15—N11—C111—C112	74.9 (6)	C25—N21—C211—C212	111.1 (5)
C116—C111—C112—C113	−2.3 (7)	C216—C211—C212—C213	−0.5 (7)
N11—C111—C112—C113	179.8 (4)	N21—C211—C212—C213	−178.5 (4)
C116—C111—C112—C117	178.1 (4)	C216—C211—C212—C217	−179.7 (4)
N11—C111—C112—C117	0.2 (6)	N21—C211—C212—C217	2.3 (6)
C111—C112—C113—C114	0.7 (7)	C211—C212—C213—C214	0.7 (7)
C117—C112—C113—C114	−179.7 (4)	C217—C212—C213—C214	179.9 (4)
C112—C113—C114—C115	1.1 (7)	C212—C213—C214—C215	0.4 (7)
C112—C113—C114—C118	−178.8 (4)	C212—C213—C214—C218	179.4 (4)
C113—C114—C115—C116	−1.4 (7)	C213—C214—C215—C216	−1.7 (8)
C118—C114—C115—C116	178.4 (4)	C218—C214—C215—C216	179.2 (5)
C112—C111—C116—C115	1.9 (7)	C214—C215—C216—C211	1.9 (8)
N11—C111—C116—C115	179.8 (4)	C214—C215—C216—C219	−178.1 (5)
C112—C111—C116—C119	−176.6 (4)	C212—C211—C216—C215	−0.8 (7)
N11—C111—C116—C119	1.3 (6)	N21—C211—C216—C215	177.3 (4)
C114—C115—C116—C111	0.0 (7)	C212—C211—C216—C219	179.2 (4)
C114—C115—C116—C119	178.5 (4)	N21—C211—C216—C219	−2.8 (7)
C12—N13—C131—C136	−110.5 (5)	C22—N23—C231—C232	105.1 (5)
C14—N13—C131—C136	68.6 (6)	C24—N23—C231—C232	−75.3 (6)
C12—N13—C131—C132	71.1 (6)	C22—N23—C231—C236	−77.7 (6)
C14—N13—C131—C132	−109.8 (5)	C24—N23—C231—C236	102.0 (5)
C136—C131—C132—C133	0.2 (6)	C236—C231—C232—C233	3.0 (7)
N13—C131—C132—C133	178.6 (4)	N23—C231—C232—C233	−179.9 (4)
C136—C131—C132—C137	179.8 (4)	C236—C231—C232—C237	−176.8 (4)
N13—C131—C132—C137	−1.8 (6)	N23—C231—C232—C237	0.3 (6)
C131—C132—C133—C134	−0.5 (7)	C231—C232—C233—C234	−0.1 (7)
C137—C132—C133—C134	179.9 (4)	C237—C232—C233—C234	179.7 (4)
C132—C133—C134—C135	0.0 (7)	C232—C233—C234—C235	−2.4 (7)
C132—C133—C134—C138	−179.3 (4)	C232—C233—C234—C238	178.1 (4)
C133—C134—C135—C136	0.9 (8)	C233—C234—C235—C236	2.2 (7)
C138—C134—C135—C136	−179.8 (5)	C238—C234—C235—C236	−178.3 (4)
C132—C131—C136—C135	0.7 (7)	C232—C231—C236—C235	−3.2 (7)
N13—C131—C136—C135	−177.8 (4)	N23—C231—C236—C235	179.7 (4)
C132—C131—C136—C139	−179.4 (4)	C232—C231—C236—C239	176.2 (4)
N13—C131—C136—C139	2.2 (7)	N23—C231—C236—C239	−0.8 (6)
C134—C135—C136—C131	−1.2 (7)	C234—C235—C236—C231	0.5 (7)
C134—C135—C136—C139	178.9 (5)	C234—C235—C236—C239	−178.9 (4)

Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $-x, y, \frac{3}{2} - z$.

Annexe VII - Analyse crystallographique complète pour IPr$_2$PdCl$_2$ anormal

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Structure of CHA124

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Abstract

Here should be written a short abstract

Comment

Here should be written the text of the article

Experimental

Small details about the preparation of the compound.

Crystal data

$2(C_{54}H_{72}Cl_2N_4Pd).3(C_3H_6O)$

$M_r = 2083.15$

Triclinic

$P\bar{1}$

$a = 14.0914\,(3)$ Å

$b = 22.0305\,(5)$ Å

$c = 22.0822\,(5)$ Å

$\alpha = 60.7720\,(10)°$

$\beta = 73.7420\,(10)°$

$\gamma = 78.2430\,(10)°$

$V = 5724.8\,(2)$ Å³

$Z = 2$

$D_x = 1.208$ Mg m^{-3}

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 52954 reflections

$\theta = 2.42$–$68.07°$

$\mu = 3.783$ mm^{-1}

$T = 100\,(2)$ K

Chunk

Colourless

$0.35 \times 0.25 \times 0.20$ mm

Crystal source: synthesized by the authors.

　　See text

Data collection

Bruker AXS Smart 4K/Platform diffractom-
 eter

ω scans

Absorption correction:
 multi-scan Sadabs (Sheldrick,1996)
 $T_{min} = 0.4300$, $T_{max} = 0.6100$

73046 measured reflections

20125 independent reflections

19244 reflections with
 $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 68.31°$

$h = -16 \rightarrow 16$

$k = -26 \rightarrow 26$

$l = -25 \rightarrow 26$

506 standard reflections

every ? reflections
 intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0317$

$wR(F^2) = 0.0909$

$S = 1.008$

20125 reflections

1245 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 3.7662P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.004$

$\Delta\rho_{max} = 2.121$ e Å^{-3}

$\Delta\rho_{min} = -0.732$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—C25	2.0225 (19)	C116—C120	1.519 (3)
Pd1—C12	2.0534 (19)	C117—C119	1.525 (3)
Pd1—Cl11	2.2932 (5)	C117—C118	1.531 (4)
Pd1—Cl12	2.3202 (5)	C120—C122	1.526 (3)
N11—C12	1.358 (3)	C120—C121	1.533 (3)
N11—C15	1.391 (3)	C131—C132	1.395 (3)
N11—C111	1.446 (3)	C131—C136	1.406 (3)
C12—N13	1.358 (3)	C132—C133	1.402 (3)
N13—C14	1.386 (3)	C132—C137	1.519 (3)
N13—C131	1.450 (2)	C133—C134	1.383 (3)
C14—C15	1.338 (3)	C134—C135	1.377 (3)
C111—C112	1.401 (3)	C135—C136	1.395 (3)
C111—C116	1.402 (3)	C136—C140	1.521 (3)
C112—C113	1.400 (3)	C137—C139	1.523 (3)
C112—C117	1.519 (3)	C137—C138	1.528 (3)
C113—C114	1.383 (4)	C140—C142	1.527 (3)
C114—C115	1.377 (4)	C140—C141	1.536 (3)
C115—C116	1.398 (3)	N21—C22	1.338 (3)

N21—C25	1.406 (2)	N33—C331	1.454 (2)
N21—C211	1.445 (2)	C34—C35	1.336 (3)
C22—N23	1.331 (3)	C311—C316	1.399 (3)
N23—C24	1.384 (2)	C311—C312	1.400 (3)
N23—C231	1.449 (2)	C312—C313	1.398 (3)
C24—C25	1.373 (3)	C312—C317	1.517 (3)
C211—C216	1.395 (3)	C313—C314	1.380 (3)
C211—C212	1.405 (3)	C314—C315	1.381 (3)
C212—C213	1.399 (3)	C315—C316	1.394 (3)
C212—C217	1.521 (3)	C316—C320	1.525 (3)
C213—C214	1.384 (4)	C317—C318	1.519 (3)
C214—C215	1.382 (3)	C317—C319	1.530 (3)
C215—C216	1.398 (3)	C320—C321	1.525 (3)
C216—C220	1.516 (3)	C320—C322	1.529 (3)
C217—C219	1.522 (3)	N41—C42	1.341 (3)
C217—C218	1.529 (3)	N41—C45	1.398 (3)
C220—C221	1.534 (3)	N41—C411	1.449 (3)
C220—C222	1.537 (3)	C42—N43	1.320 (3)
C231—C236	1.393 (3)	N43—C44	1.389 (3)
C231—C232	1.399 (3)	N43—C431	1.447 (2)
C232—C233	1.399 (3)	C44—C45	1.376 (3)
C232—C237	1.517 (3)	C331—C336	1.400 (3)
C233—C234	1.379 (3)	C331—C332	1.401 (3)
C234—C235	1.387 (3)	C332—C333	1.394 (3)
C235—C236	1.399 (3)	C332—C337	1.518 (3)
C236—C240	1.521 (3)	C333—C334	1.378 (3)
C237—C239	1.531 (3)	C334—C335	1.378 (3)
C237—C238	1.534 (3)	C335—C336	1.392 (3)
C240—C242	1.527 (3)	C336—C340	1.522 (3)
C240—C241	1.531 (3)	C337—C338	1.510 (3)
Pd3—C45	2.0305 (19)	C337—C339	1.517 (3)
Pd3—C32	2.0525 (19)	C340—C341	1.528 (3)
Pd3—Cl32	2.3028 (5)	C340—C342	1.539 (3)
Pd3—Cl31	2.3167 (5)	C411—C416	1.400 (3)
N31—C32	1.363 (3)	C411—C412	1.401 (3)
N31—C35	1.393 (3)	C412—C413	1.395 (3)
N31—C311	1.442 (3)	C412—C420	1.524 (3)
C32—N33	1.355 (3)	C413—C414	1.382 (3)
N33—C34	1.389 (3)	C414—C415	1.377 (4)

C415—C416	1.397 (3)	C437—C438	1.523 (4)
C416—C417	1.521 (3)	C437—C439	1.532 (3)
C417—C419	1.525 (4)	C440—C441	1.524 (3)
C417—C418	1.526 (4)	C440—C442	1.533 (3)
C420—C421	1.528 (3)	O50—C51	1.217 (3)
C420—C422	1.535 (3)	C51—C53	1.494 (4)
C431—C432	1.394 (3)	C51—C52	1.503 (4)
C431—C436	1.399 (3)	O60—C61	1.206 (3)
C432—C433	1.394 (3)	C61—C63	1.484 (5)
C432—C437	1.525 (3)	C61—C62	1.489 (5)
C433—C434	1.385 (3)	O70—C71	1.214 (3)
C434—C435	1.383 (3)	C71—C73	1.490 (3)
C435—C436	1.395 (3)	C71—C72	1.493 (3)
C436—C440	1.517 (3)		
C25—PD1—C12	176.79 (7)	C114—C115—C116	121.3 (2)
C25—PD1—CL11	89.04 (6)	C115—C116—C111	116.8 (2)
C12—PD1—CL11	91.74 (5)	C115—C116—C120	120.8 (2)
C25—PD1—CL12	88.63 (6)	C111—C116—C120	122.36 (19)
C12—PD1—CL12	90.54 (5)	C112—C117—C119	113.0 (2)
CL11—PD1—CL12	177.526 (17	C112—C117—C118	110.0 (2)
C12—N11—C15	111.41 (17)	C119—C117—C118	111.3 (2)
C12—N11—C111	126.82 (16)	C116—C120—C122	112.2 (2)
C15—N11—C111	121.38 (16)	C116—C120—C121	111.13 (18)
N13—C12—N11	103.94 (16)	C122—C120—C121	109.97 (19)
N13—C12—PD1	126.65 (14)	C132—C131—C136	123.23 (19)
N11—C12—PD1	129.26 (15)	C132—C131—N13	119.31 (18)
C12—N13—C14	111.13 (17)	C136—C131—N13	117.37 (18)
C12—N13—C131	126.69 (16)	C131—C132—C133	116.77 (19)
C14—N13—C131	121.57 (17)	C131—C132—C137	122.25 (18)
C15—C14—N13	107.20 (18)	C133—C132—C137	120.90 (19)
C14—C15—N11	106.33 (18)	C134—C133—C132	121.2 (2)
C112—C111—C116	123.30 (19)	C135—C134—C133	120.5 (2)
C112—C111—N11	117.91 (18)	C134—C135—C136	121.0 (2)
C116—C111—N11	118.55 (18)	C135—C136—C131	117.2 (2)
C113—C112—C111	117.2 (2)	C135—C136—C140	119.9 (2)
C113—C112—C117	120.2 (2)	C131—C136—C140	122.86 (19)
C111—C112—C117	122.60 (19)	C132—C137—C139	112.61 (18)
C114—C113—C112	120.7 (2)	C132—C137—C138	109.80 (18)
C115—C114—C113	120.8 (2)	C139—C137—C138	110.2 (2)

C136—C140—C142	113.2 (2)	C233—C234—C235	120.8 (2)
C136—C140—C141	110.32 (19)	C234—C235—C236	120.6 (2)
C142—C140—C141	109.8 (2)	C231—C236—C235	116.89 (19)
C22—N21—C25	110.88 (16)	C231—C236—C240	122.54 (18)
C22—N21—C211	120.92 (16)	C235—C236—C240	120.6 (2)
C25—N21—C211	128.04 (16)	C232—C237—C239	111.54 (17)
N23—C22—N21	107.91 (17)	C232—C237—C238	110.77 (17)
C22—N23—C24	108.45 (16)	C239—C237—C238	110.76 (17)
C22—N23—C231	123.85 (16)	C236—C240—C242	111.50 (18)
C24—N23—C231	127.67 (16)	C236—C240—C241	110.42 (18)
C25—C24—N23	109.34 (16)	C242—C240—C241	110.9 (2)
C24—C25—N21	103.41 (16)	C45—PD3—C32	174.39 (8)
C24—C25—PD1	128.20 (14)	C45—PD3—CL32	89.64 (6)
N21—C25—PD1	128.39 (14)	C32—PD3—CL32	91.49 (5)
C216—C211—C212	123.94 (18)	C45—PD3—CL31	88.67 (6)
C216—C211—N21	118.43 (17)	C32—PD3—CL31	90.32 (5)
C212—C211—N21	117.48 (18)	CL32—PD3—CL31	177.875 (19
C213—C212—C211	116.4 (2)	C32—N31—C35	111.16 (17)
C213—C212—C217	121.89 (19)	C32—N31—C311	127.86 (17)
C211—C212—C217	121.65 (18)	C35—N31—C311	120.97 (16)
C214—C213—C212	121.1 (2)	N33—C32—N31	103.76 (16)
C215—C214—C213	120.7 (2)	N33—C32—PD3	125.90 (14)
C214—C215—C216	120.8 (2)	N31—C32—PD3	130.22 (15)
C211—C216—C215	116.94 (19)	C32—N33—C34	111.53 (17)
C211—C216—C220	124.16 (17)	C32—N33—C331	127.85 (16)
C215—C216—C220	118.90 (19)	C34—N33—C331	120.50 (17)
C212—C217—C219	113.2 (2)	C35—C34—N33	106.80 (19)
C212—C217—C218	111.26 (18)	C34—C35—N31	106.75 (18)
C219—C217—C218	109.5 (2)	C316—C311—C312	122.76 (19)
C216—C220—C221	110.72 (18)	C316—C311—N31	118.72 (18)
C216—C220—C222	111.42 (18)	C312—C311—N31	118.24 (19)
C221—C220—C222	110.23 (18)	C313—C312—C311	117.3 (2)
C236—C231—C232	124.11 (18)	C313—C312—C317	119.89 (19)
C236—C231—N23	117.89 (17)	C311—C312—C317	122.9 (2)
C232—C231—N23	118.00 (18)	C314—C313—C312	121.2 (2)
C231—C232—C233	116.45 (19)	C313—C314—C315	120.1 (2)
C231—C232—C237	122.63 (17)	C314—C315—C316	121.4 (2)
C233—C232—C237	120.92 (18)	C315—C316—C311	117.30 (19)
C234—C233—C232	121.1 (2)	C315—C316—C320	119.94 (19)

C311—C316—C320	122.76 (19)	C413—C412—C411	116.9 (2)
C312—C317—C318	111.4 (2)	C413—C412—C420	119.6 (2)
C312—C317—C319	111.63 (19)	C411—C412—C420	123.42 (19)
C318—C317—C319	110.0 (2)	C414—C413—C412	121.1 (2)
C316—C320—C321	111.21 (18)	C415—C414—C413	120.4 (2)
C316—C320—C322	111.56 (18)	C414—C415—C416	121.3 (2)
C321—C320—C322	111.1 (2)	C415—C416—C411	116.7 (2)
C42—N41—C45	110.60 (16)	C415—C416—C417	119.7 (2)
C42—N41—C411	119.47 (17)	C411—C416—C417	123.48 (19)
C45—N41—C411	129.42 (16)	C416—C417—C419	111.87 (19)
N43—C42—N41	108.22 (17)	C416—C417—C418	110.3 (2)
C42—N43—C44	108.65 (16)	C419—C417—C418	111.0 (2)
C42—N43—C431	123.19 (17)	C412—C420—C421	111.85 (19)
C44—N43—C431	128.11 (17)	C412—C420—C422	110.5 (2)
C45—C44—N43	108.65 (18)	C421—C420—C422	109.97 (19)
C44—C45—N41	103.86 (16)	C432—C431—C436	123.91 (18)
C44—C45—PD3	126.39 (15)	C432—C431—N43	118.01 (17)
N41—C45—PD3	129.75 (14)	C436—C431—N43	118.03 (17)
C336—C331—C332	123.13 (19)	C431—C432—C433	116.93 (19)
C336—C331—N33	117.98 (18)	C431—C432—C437	122.62 (18)
C332—C331—N33	118.63 (17)	C433—C432—C437	120.43 (19)
C333—C332—C331	116.72 (19)	C434—C433—C432	120.8 (2)
C333—C332—C337	120.97 (19)	C435—C434—C433	120.67 (19)
C331—C332—C337	122.28 (18)	C434—C435—C436	120.9 (2)
C334—C333—C332	121.3 (2)	C435—C436—C431	116.69 (19)
C335—C334—C333	120.6 (2)	C435—C436—C440	120.90 (18)
C334—C335—C336	120.8 (2)	C431—C436—C440	122.40 (17)
C335—C336—C331	117.3 (2)	C438—C437—C432	110.86 (18)
C335—C336—C340	119.6 (2)	C438—C437—C439	110.2 (2)
C331—C336—C340	122.95 (19)	C432—C437—C439	111.24 (19)
C338—C337—C339	110.1 (3)	C436—C440—C441	111.60 (18)
C338—C337—C332	110.1 (2)	C436—C440—C442	110.92 (18)
C339—C337—C332	112.1 (2)	C441—C440—C442	111.01 (18)
C336—C340—C341	112.5 (2)	O50—C51—C53	122.5 (3)
C336—C340—C342	109.66 (18)	O50—C51—C52	121.5 (3)
C341—C340—C342	110.11 (19)	C53—C51—C52	116.0 (2)
C416—C411—C412	123.43 (19)	O60—C61—C63	121.1 (3)
C416—C411—N41	117.17 (18)	O60—C61—C62	122.7 (3)
C412—C411—N41	119.09 (18)	C63—C61—C62	116.1 (3)

| O70—C71—C73 | 122.1 (2) | C73—C71—C72 | 115.4 (2) |
| O70—C71—C72 | 122.4 (2) | | |

All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters. The H atoms were generated geometrically (C—H 0.95 to 1.00 Å) and were included in the refinement in the riding model approximation; their temperature factors were set to 1.5 times those of the equivalent isotropic temperature factors of the parent site (methyl) and 1.2 times for others. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 2000).

Data collection: SMART (Bruker, 2001). Cell refinement: SMART (Bruker, 2001). Data reduction: SAINT (Bruker, 2003). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: UdMX (local program).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: PREVIEW). Services for accessing these data are described at the back of the journal.

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Fig 1 *ORTEP* view of the title compound. Thermal ellipsoids are shown at 30% probability levels.

Table 1. Selected geometric parameters (Å, °) for the title compound.

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

http://journals.iucr.org/c/journalhomepage.html

Table S1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j a_i.a_j.$$

	x	y	z	U_{eq}
Pd1	0.639972 (9)	0.281311 (7)	0.272292 (7)	0.01767 (5)
Cl11	0.59983 (3)	0.17900 (2)	0.37283 (3)	0.02563 (10)
Cl12	0.67335 (4)	0.38642 (3)	0.17098 (3)	0.02827 (11)
N11	0.86870 (12)	0.25510 (9)	0.24901 (9)	0.0208 (3)
C12	0.78135 (14)	0.26922 (10)	0.28728 (11)	0.0190 (4)
N13	0.80872 (12)	0.27891 (9)	0.33602 (9)	0.0205 (3)
C14	0.91099 (15)	0.27163 (12)	0.32747 (12)	0.0268 (4)
H14	0.9473	0.2766	0.3549	0.032
C15	0.94895 (15)	0.25632 (11)	0.27334 (12)	0.0265 (4)
H15	1.0171	0.2480	0.2552	0.032
C111	0.88173 (14)	0.23297 (11)	0.19520 (11)	0.0225 (4)
C112	0.86822 (15)	0.16325 (11)	0.21765 (12)	0.0265 (4)
C113	0.89047 (16)	0.14094 (13)	0.16538 (13)	0.0320 (5)
H113	0.8817	0.0941	0.1785	0.038
C114	0.92506 (16)	0.18633 (14)	0.09491 (13)	0.0346 (5)
H114	0.9408	0.1702	0.0602	0.041
C115	0.93698 (16)	0.25470 (13)	0.07446 (12)	0.0317 (5)
H115	0.9602	0.2851	0.0257	0.038
C116	0.91554 (14)	0.28024 (11)	0.12407 (12)	0.0257 (4)
C117	0.83542 (17)	0.11197 (11)	0.29528 (12)	0.0310 (5)
H117	0.8038	0.1398	0.3215	0.037
C118	0.9258 (2)	0.06880 (16)	0.32592 (17)	0.0552 (8)
H11A	0.9595	0.0416	0.3006	0.083
H11B	0.9042	0.0371	0.3764	0.083
H11C	0.9716	0.1001	0.3204	0.083
C119	0.7587 (2)	0.06517 (14)	0.30740 (15)	0.0440 (6)
H11D	0.7026	0.0941	0.2862	0.066
H11E	0.7352	0.0367	0.3585	0.066
H11F	0.7890	0.0346	0.2853	0.066
C120	0.93201 (16)	0.35511 (12)	0.10121 (12)	0.0294 (5)
H120	0.8927	0.3673	0.1397	0.035
C121	1.04143 (17)	0.36309 (13)	0.09212 (14)	0.0393 (6)
H12A	1.0613	0.3348	0.1379	0.059
H12B	1.0506	0.4122	0.0750	0.059
H12C	1.0823	0.3474	0.0577	0.059
C122	0.89630 (19)	0.40650 (13)	0.03306 (13)	0.0391 (6)
H12D	0.9361	0.3987	−0.0066	0.059
H12E	0.9005	0.4543	0.0236	0.059
H12F	0.8274	0.3995	0.0385	0.059
C131	0.74378 (14)	0.28546 (11)	0.39670 (11)	0.0214 (4)
C132	0.69894 (14)	0.35095 (11)	0.38826 (11)	0.0227 (4)
C133	0.64121 (15)	0.35475 (12)	0.44953 (12)	0.0277 (5)
H133	0.6104	0.3985	0.4462	0.033
C134	0.62828 (16)	0.29592 (13)	0.51476 (12)	0.0309 (5)
H134	0.5874	0.2996	0.5553	0.037
C135	0.67415 (16)	0.23212 (12)	0.52135 (12)	0.0303 (5)
H135	0.6650	0.1923	0.5666	0.036
C136	0.73380 (15)	0.22512 (11)	0.46256 (12)	0.0259 (4)
C137	0.71550 (15)	0.41615 (11)	0.31730 (11)	0.0261 (4)
H137	0.7391	0.4013	0.2790	0.031
C138	0.7964 (2)	0.45540 (16)	0.31362 (16)	0.0551 (8)

H13A	0.7757	0.4693	0.3517	0.083
H13B	0.8074	0.4971	0.2675	0.083
H13C	0.8581	0.4250	0.3193	0.083
C139	0.62115 (19)	0.46415 (13)	0.30342 (14)	0.0408 (6)
H13D	0.5702	0.4387	0.3051	0.061
H13E	0.6352	0.5045	0.2565	0.061
H13F	0.5973	0.4802	0.3398	0.061
C140	0.78708 (18)	0.15468 (12)	0.47190 (13)	0.0320 (5)
H140	0.8124	0.1573	0.4237	0.038
C141	0.87678 (19)	0.13927 (13)	0.50530 (15)	0.0409 (6)
H14A	0.9231	0.1755	0.4742	0.061
H14B	0.9101	0.0937	0.5113	0.061
H14C	0.8543	0.1389	0.5517	0.061
C142	0.7197 (2)	0.09474 (13)	0.51603 (14)	0.0423 (6)
H14D	0.6962	0.0896	0.5643	0.063
H14E	0.7569	0.0514	0.5177	0.063
H14F	0.6628	0.1048	0.4944	0.063
N21	0.44628 (11)	0.25418 (8)	0.25230 (9)	0.0191 (3)
C22	0.35444 (14)	0.28281 (10)	0.24426 (10)	0.0199 (4)
H22	0.3057	0.2635	0.2380	0.024
N23	0.34350 (11)	0.34311 (8)	0.24662 (9)	0.0196 (3)
C24	0.43148 (14)	0.35302 (10)	0.25568 (11)	0.0208 (4)
H24	0.4434	0.3922	0.2588	0.025
C25	0.49885 (14)	0.29731 (10)	0.25949 (10)	0.0190 (4)
C211	0.48233 (14)	0.18978 (10)	0.24808 (11)	0.0214 (4)
C212	0.54769 (15)	0.19427 (12)	0.18520 (12)	0.0256 (4)
C213	0.57653 (16)	0.13176 (13)	0.18063 (13)	0.0324 (5)
H213	0.6217	0.1320	0.1395	0.039
C214	0.54033 (17)	0.06954 (12)	0.23496 (14)	0.0346 (5)
H214	0.5606	0.0278	0.2305	0.042
C215	0.47508 (16)	0.06742 (11)	0.29563 (13)	0.0298 (5)
H215	0.4501	0.0244	0.3320	0.036
C216	0.44540 (15)	0.12783 (11)	0.30416 (12)	0.0241 (4)
C217	0.58048 (16)	0.26395 (12)	0.12386 (12)	0.0291 (5)
H217	0.5814	0.2954	0.1444	0.035
C218	0.50696 (18)	0.29643 (13)	0.07457 (14)	0.0390 (6)
H21A	0.5049	0.2690	0.0532	0.058
H21B	0.5281	0.3442	0.0370	0.058
H21C	0.4408	0.3042	0.1019	0.058
C219	0.68420 (19)	0.25839 (17)	0.08081 (16)	0.0525 (7)
H21D	0.7312	0.2361	0.1125	0.079
H21E	0.7035	0.3052	0.0449	0.079
H21F	0.6846	0.2303	0.0573	0.079
C220	0.37556 (16)	0.12257 (11)	0.37239 (11)	0.0262 (4)
H220	0.3746	0.1671	0.3744	0.031
C221	0.26973 (17)	0.11372 (12)	0.37357 (13)	0.0337 (5)
H22A	0.2689	0.0701	0.3720	0.050
H22B	0.2474	0.1531	0.3323	0.050
H22C	0.2253	0.1122	0.4172	0.050
C222	0.41085 (18)	0.06224 (11)	0.43793 (12)	0.0324 (5)
H22D	0.3657	0.0613	0.4811	0.049
H22E	0.4779	0.0690	0.4371	0.049
H22F	0.4115	0.0180	0.4374	0.049
C231	0.25396 (14)	0.38975 (10)	0.23839 (11)	0.0206 (4)
C232	0.18030 (14)	0.37982 (10)	0.29926 (11)	0.0220 (4)
C233	0.09269 (15)	0.42337 (11)	0.28888 (12)	0.0259 (4)
H233	0.0402	0.4181	0.3286	0.031
C234	0.08122 (16)	0.47378 (11)	0.22197 (13)	0.0297 (5)
H234	0.0208	0.5024	0.2162	0.036
C235	0.15697 (16)	0.48328 (11)	0.16303 (12)	0.0288 (5)
H235	0.1483	0.5188	0.1174	0.035
C236	0.24598 (15)	0.44098 (11)	0.17014 (11)	0.0237 (4)
C237	0.19305 (14)	0.32503 (11)	0.37313 (11)	0.0248 (4)
H237	0.2621	0.3025	0.3690	0.029
C238	0.12109 (17)	0.26819 (11)	0.40436 (12)	0.0295 (5)

H23A	0.0528	0.2885	0.4117	0.044
H23B	0.1350	0.2310	0.4499	0.044
H23C	0.1295	0.2488	0.3714	0.044
C239	0.18000 (16)	0.35763 (12)	0.42262 (12)	0.0286 (5)
H23D	0.2266	0.3937	0.4018	0.043
H23E	0.1931	0.3214	0.4688	0.043
H23F	0.1119	0.3786	0.4290	0.043
C240	0.32838 (16)	0.45077 (11)	0.10534 (12)	0.0273 (4)
H240	0.3861	0.4172	0.1220	0.033
C241	0.29471 (19)	0.43385 (15)	0.05546 (14)	0.0398 (6)
H24A	0.2378	0.4660	0.0387	0.060
H24B	0.2756	0.3858	0.0810	0.060
H24C	0.3492	0.4390	0.0148	0.060
C242	0.3628 (2)	0.52442 (14)	0.06639 (15)	0.0464 (7)
H24D	0.4166	0.5287	0.0255	0.070
H24E	0.3867	0.5334	0.0987	0.070
H24F	0.3073	0.5584	0.0499	0.070
Pd3	0.434168 (9)	0.243302 (7)	0.717774 (7)	0.01869 (5)
Cl31	0.37256 (4)	0.33756 (3)	0.74068 (3)	0.03072 (11)
Cl32	0.49953 (3)	0.14848 (3)	0.69765 (3)	0.02871 (11)
N31	0.21204 (12)	0.21405 (9)	0.76010 (9)	0.0231 (4)
C32	0.29634 (14)	0.23534 (10)	0.70929 (11)	0.0191 (4)
N33	0.26774 (12)	0.25534 (9)	0.64803 (9)	0.0209 (3)
C34	0.16783 (15)	0.24716 (12)	0.66025 (12)	0.0285 (5)
H34	0.1313	0.2581	0.6255	0.034
C35	0.13306 (15)	0.22093 (12)	0.73028 (12)	0.0294 (5)
H35	0.0672	0.2092	0.7550	0.035
C311	0.19980 (14)	0.18583 (11)	0.83583 (11)	0.0234 (4)
C312	0.14744 (15)	0.22766 (11)	0.86781 (12)	0.0268 (4)
C313	0.12675 (17)	0.19669 (12)	0.94196 (12)	0.0338 (5)
H313	0.0922	0.2238	0.9653	0.041
C314	0.15565 (17)	0.12744 (13)	0.98184 (12)	0.0333 (5)
H314	0.1395	0.1070	1.0322	0.040
C315	0.20810 (16)	0.08778 (12)	0.94861 (12)	0.0297 (5)
H315	0.2280	0.0403	0.9766	0.036
C316	0.23239 (15)	0.11603 (11)	0.87485 (11)	0.0248 (4)
C317	0.11254 (17)	0.30349 (12)	0.82558 (13)	0.0319 (5)
H317	0.1472	0.3190	0.7748	0.038
C318	0.13932 (19)	0.34975 (13)	0.85054 (14)	0.0387 (6)
H31A	0.1034	0.3372	0.8995	0.058
H31B	0.1210	0.3987	0.8197	0.058
H31C	0.2109	0.3432	0.8485	0.058
C319	0.00084 (19)	0.31271 (14)	0.82915 (17)	0.0465 (7)
H31D	−0.0154	0.2842	0.8110	0.070
H31E	−0.0188	0.3619	0.8002	0.070
H31F	−0.0349	0.2979	0.8785	0.070
C320	0.29174 (16)	0.07101 (11)	0.83996 (12)	0.0275 (4)
H320	0.3246	0.1031	0.7906	0.033
C321	0.22413 (19)	0.02884 (14)	0.83432 (16)	0.0423 (6)
H32A	0.2840	0.0008	0.8113	0.063
H32B	0.1758	0.0607	0.8061	0.063
H32C	0.1891	−0.0021	0.8820	0.063
C322	0.37337 (18)	0.02357 (14)	0.87883 (14)	0.0379 (5)
H32D	0.3433	−0.0124	0.9253	0.057
H32E	0.4122	0.0514	0.8853	0.057
H32F	0.4169	0.0014	0.8508	0.057
N41	0.64103 (12)	0.21300 (9)	0.75627 (9)	0.0215 (3)
C42	0.72327 (15)	0.24458 (11)	0.73930 (11)	0.0226 (4)
H42	0.7798	0.2241	0.7599	0.027
N43	0.71208 (12)	0.30905 (8)	0.68901 (9)	0.0206 (3)
C44	0.61914 (14)	0.31958 (11)	0.67376 (11)	0.0214 (4)
H44	0.5925	0.3616	0.6396	0.026
C45	0.57206 (14)	0.25893 (10)	0.71634 (11)	0.0206 (4)
C331	0.32932 (14)	0.27846 (10)	0.57691 (11)	0.0205 (4)
C332	0.34747 (14)	0.34911 (11)	0.53637 (11)	0.0225 (4)

C333	0.39927 (15)	0.37020 (12)	0.46638 (12)	0.0288 (5)
H333	0.4129	0.4177	0.4371	0.035
C334	0.43114 (16)	0.32352 (13)	0.43882 (12)	0.0321 (5)
H334	0.4665	0.3392	0.3910	0.039
C335	0.41218 (16)	0.25431 (13)	0.48000 (13)	0.0315 (5)
H335	0.4350	0.2227	0.4603	0.038
C336	0.36000 (15)	0.23008 (11)	0.55009 (12)	0.0249 (4)
C337	0.31013 (16)	0.40128 (11)	0.56564 (12)	0.0280 (5)
H337	0.2961	0.3749	0.6186	0.034
C338	0.2146 (3)	0.4401 (2)	0.5433 (3)	0.0808 (13)
H33A	0.2246	0.4614	0.4915	0.121
H33B	0.1944	0.4767	0.5585	0.121
H33C	0.1627	0.4075	0.5653	0.121
C339	0.3862 (3)	0.45248 (19)	0.5423 (2)	0.0714 (11)
H33D	0.3990	0.4802	0.4905	0.107
H33E	0.4479	0.4268	0.5569	0.107
H33F	0.3607	0.4835	0.5643	0.107
C340	0.33462 (17)	0.15439 (11)	0.59284 (13)	0.0317 (5)
H340	0.3125	0.1436	0.6440	0.038
C341	0.4233 (2)	0.10342 (14)	0.58599 (16)	0.0442 (6)
H34A	0.4442	0.1116	0.5365	0.066
H34B	0.4044	0.0555	0.6166	0.066
H34C	0.4782	0.1105	0.6005	0.066
C342	0.2481 (2)	0.14460 (13)	0.56940 (16)	0.0419 (6)
H34D	0.2681	0.1555	0.5192	0.063
H34E	0.1906	0.1759	0.5761	0.063
H34F	0.2307	0.0961	0.5980	0.063
C411	0.62964 (15)	0.14375 (10)	0.81554 (11)	0.0235 (4)
C412	0.68109 (15)	0.08619 (11)	0.80657 (12)	0.0268 (4)
C413	0.67766 (17)	0.02178 (12)	0.86725 (13)	0.0326 (5)
H413	0.7115	−0.0185	0.8633	0.039
C414	0.62584 (18)	0.01559 (12)	0.93295 (13)	0.0353 (5)
H414	0.6255	−0.0286	0.9737	0.042
C415	0.57474 (17)	0.07310 (12)	0.93966 (12)	0.0326 (5)
H415	0.5387	0.0678	0.9851	0.039
C416	0.57482 (16)	0.13908 (11)	0.88100 (12)	0.0274 (4)
C417	0.52114 (19)	0.20182 (12)	0.89116 (12)	0.0332 (5)
H417	0.5263	0.2433	0.8432	0.040
C418	0.5715 (3)	0.21645 (18)	0.9350 (2)	0.0659 (9)
H41A	0.5417	0.2603	0.9361	0.099
H41B	0.6424	0.2203	0.9136	0.099
H41C	0.5627	0.1782	0.9836	0.099
C419	0.4114 (2)	0.19223 (14)	0.92471 (16)	0.0469 (7)
H41D	0.3809	0.1827	0.8957	0.070
H41E	0.3785	0.2349	0.9273	0.070
H41F	0.4042	0.1530	0.9726	0.070
C420	0.74233 (16)	0.09150 (11)	0.73553 (12)	0.0306 (5)
H420	0.7251	0.1384	0.6973	0.037
C421	0.71976 (19)	0.03600 (13)	0.72018 (14)	0.0382 (5)
H42A	0.7387	−0.0104	0.7560	0.057
H42B	0.7574	0.0428	0.6730	0.057
H42C	0.6487	0.0401	0.7217	0.057
C422	0.85349 (18)	0.08550 (13)	0.73358 (14)	0.0394 (6)
H42D	0.8675	0.1215	0.7430	0.059
H42E	0.8917	0.0918	0.6866	0.059
H42F	0.8723	0.0393	0.7699	0.059
C431	0.78594 (14)	0.35880 (10)	0.65907 (11)	0.0216 (4)
C432	0.78004 (15)	0.40124 (10)	0.69069 (11)	0.0241 (4)
C433	0.85583 (16)	0.44539 (11)	0.66396 (12)	0.0280 (5)
H433	0.8549	0.4749	0.6843	0.034
C434	0.93245 (16)	0.44676 (11)	0.60816 (12)	0.0292 (5)
H434	0.9838	0.4768	0.5910	0.035
C435	0.93498 (15)	0.40480 (11)	0.57721 (12)	0.0277 (4)
H435	0.9878	0.4068	0.5386	0.033
C436	0.86115 (14)	0.35959 (11)	0.60183 (11)	0.0233 (4)

C437	0.69697 (15)	0.39913 (11)	0.75309 (12)	0.0276 (5)
H437	0.6471	0.3681	0.7611	0.033
C438	0.73662 (19)	0.36882 (15)	0.82052 (14)	0.0415 (6)
H43A	0.7714	0.3229	0.8295	0.062
H43B	0.6813	0.3641	0.8607	0.062
H43C	0.7827	0.4000	0.8148	0.062
C439	0.64466 (19)	0.47183 (14)	0.73722 (15)	0.0437 (6)
H43D	0.5887	0.4684	0.7766	0.065
H43E	0.6203	0.4911	0.6934	0.065
H43F	0.6915	0.5025	0.7315	0.065
C440	0.86419 (15)	0.31341 (11)	0.56801 (12)	0.0269 (4)
H440	0.8023	0.2882	0.5910	0.032
C441	0.86582 (16)	0.35615 (13)	0.48886 (12)	0.0320 (5)
H44A	0.8099	0.3918	0.4815	0.048
H44B	0.8605	0.3254	0.4698	0.048
H44C	0.9281	0.3787	0.4644	0.048
C442	0.95266 (17)	0.25842 (12)	0.58154 (13)	0.0316 (5)
H44D	1.0145	0.2814	0.5560	0.047
H44E	0.9483	0.2255	0.5648	0.047
H44F	0.9517	0.2332	0.6325	0.047
O50	0.27452 (19)	0.33010 (10)	0.98155 (10)	0.0589 (6)
C51	0.2964 (2)	0.38609 (14)	0.93097 (14)	0.0428 (6)
C52	0.4018 (2)	0.39871 (18)	0.89081 (17)	0.0581 (8)
H52A	0.4470	0.3679	0.9223	0.087
H52B	0.4131	0.4474	0.8737	0.087
H52C	0.4140	0.3891	0.8503	0.087
C53	0.2209 (2)	0.44589 (13)	0.90461 (14)	0.0423 (6)
H53A	0.1545	0.4310	0.9316	0.064
H53B	0.2251	0.4615	0.8542	0.064
H53C	0.2337	0.4844	0.9108	0.064
O60	0.89202 (14)	0.17738 (10)	0.83075 (10)	0.0489 (5)
C61	0.89574 (18)	0.13265 (15)	0.89026 (15)	0.0445 (6)
C62	0.8454 (5)	0.1424 (3)	0.9543 (2)	0.1069 (17)
H62A	0.8228	0.1917	0.9397	0.160
H62B	0.8921	0.1277	0.9855	0.160
H62C	0.7883	0.1141	0.9798	0.160
C63	0.9561 (8)	0.0656 (2)	0.9033 (3)	0.114 (2)
H63A	0.9822	0.0633	0.8583	0.170
H63B	0.9146	0.0267	0.9363	0.170
H63C	1.0113	0.0623	0.9239	0.170
O70	0.20126 (13)	0.21972 (9)	0.20271 (10)	0.0401 (4)
C71	0.22482 (17)	0.19025 (12)	0.16580 (13)	0.0321 (5)
C72	0.33052 (18)	0.17229 (15)	0.13850 (16)	0.0434 (6)
H72A	0.3492	0.2034	0.0875	0.065
H72B	0.3387	0.1238	0.1465	0.065
H72C	0.3731	0.1778	0.1635	0.065
C73	0.1500 (2)	0.17164 (18)	0.1427 (2)	0.0585 (9)
H73A	0.0832	0.1829	0.1653	0.088
H73B	0.1594	0.1216	0.1566	0.088
H73C	0.1583	0.1982	0.0910	0.088

Table *S2. Anisotropic displacement parameters* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd1	0.01237 (8)	0.02024 (8)	0.02081 (8)	−0.00127 (5)	−0.00333 (5)	−0.00984 (6)
Cl11	0.0214 (2)	0.0263 (2)	0.0245 (2)	−0.00556 (18)	−0.00473 (18)	−0.0069 (2)
Cl12	0.0218 (2)	0.0256 (2)	0.0299 (3)	−0.00532 (18)	−0.00694 (19)	−0.0050 (2)
N11	0.0150 (8)	0.0239 (8)	0.0227 (9)	−0.0017 (6)	−0.0040 (6)	−0.0101 (7)
C12	0.0159 (9)	0.0189 (9)	0.0207 (10)	−0.0028 (7)	−0.0050 (7)	−0.0069 (8)
N13	0.0151 (8)	0.0239 (8)	0.0219 (9)	−0.0025 (6)	−0.0041 (6)	−0.0095 (7)
C14	0.0165 (10)	0.0364 (12)	0.0302 (12)	−0.0045 (8)	−0.0063 (8)	−0.0158 (10)
C15	0.0155 (9)	0.0338 (11)	0.0294 (12)	−0.0032 (8)	−0.0047 (8)	−0.0135 (9)
C111	0.0125 (9)	0.0297 (10)	0.0263 (11)	0.0022 (7)	−0.0040 (8)	−0.0151 (9)
C112	0.0176 (10)	0.0313 (11)	0.0324 (12)	0.0011 (8)	−0.0052 (8)	−0.0171 (10)
C113	0.0238 (11)	0.0366 (12)	0.0427 (14)	−0.0003 (9)	−0.0048 (9)	−0.0256 (11)

C114	0.0230 (11)	0.0529 (14)	0.0382 (13)	−0.0008 (10)	−0.0017 (9)	−0.0321 (12)
C115	0.0197 (10)	0.0470 (13)	0.0271 (12)	−0.0009 (9)	−0.0015 (9)	−0.0188 (11)
C116	0.0135 (9)	0.0342 (11)	0.0283 (11)	0.0004 (8)	−0.0033 (8)	−0.0149 (9)
C117	0.0334 (12)	0.0261 (11)	0.0323 (12)	−0.0015 (9)	−0.0076 (10)	−0.0124 (10)
C118	0.0478 (16)	0.0495 (16)	0.0499 (18)	0.0054 (13)	−0.0184 (14)	−0.0081 (14)
C119	0.0526 (16)	0.0380 (13)	0.0428 (15)	−0.0174 (12)	−0.0004 (12)	−0.0195 (12)
C120	0.0232 (11)	0.0328 (11)	0.0260 (11)	−0.0025 (9)	−0.0009 (9)	−0.0108 (9)
C121	0.0274 (12)	0.0385 (13)	0.0410 (14)	−0.0098 (10)	−0.0036 (10)	−0.0092 (11)
C122	0.0353 (13)	0.0386 (13)	0.0304 (13)	0.0002 (10)	−0.0050 (10)	−0.0081 (11)
C131	0.0161 (9)	0.0292 (10)	0.0216 (10)	−0.0060 (8)	−0.0029 (8)	−0.0127 (9)
C132	0.0158 (9)	0.0288 (10)	0.0254 (11)	−0.0059 (8)	−0.0044 (8)	−0.0124 (9)
C133	0.0196 (10)	0.0371 (12)	0.0328 (12)	−0.0026 (8)	−0.0049 (9)	−0.0212 (10)
C134	0.0230 (10)	0.0486 (13)	0.0257 (12)	−0.0094 (9)	−0.0011 (9)	−0.0202 (11)
C135	0.0286 (11)	0.0392 (12)	0.0209 (11)	−0.0123 (9)	−0.0045 (9)	−0.0088 (10)
C136	0.0237 (10)	0.0290 (11)	0.0262 (11)	−0.0089 (8)	−0.0074 (8)	−0.0101 (9)
C137	0.0234 (10)	0.0275 (10)	0.0251 (11)	−0.0036 (8)	−0.0051 (8)	−0.0108 (9)
C138	0.0509 (17)	0.0502 (16)	0.0459 (17)	−0.0296 (13)	−0.0177 (13)	0.0053 (13)
C139	0.0363 (13)	0.0348 (13)	0.0371 (14)	0.0058 (10)	−0.0075 (11)	−0.0091 (11)
C140	0.0369 (12)	0.0273 (11)	0.0292 (12)	−0.0062 (9)	−0.0118 (10)	−0.0070 (10)
C141	0.0381 (13)	0.0333 (12)	0.0480 (16)	−0.0022 (10)	−0.0199 (12)	−0.0107 (11)
C142	0.0541 (16)	0.0301 (12)	0.0389 (14)	−0.0131 (11)	−0.0205 (12)	−0.0038 (11)
N21	0.0144 (7)	0.0220 (8)	0.0225 (9)	−0.0024 (6)	−0.0028 (6)	−0.0117 (7)
C22	0.0164 (9)	0.0225 (9)	0.0222 (10)	−0.0024 (7)	−0.0032 (8)	−0.0114 (8)
N23	0.0146 (8)	0.0202 (8)	0.0230 (9)	0.0002 (6)	−0.0037 (6)	−0.0099 (7)
C24	0.0162 (9)	0.0220 (9)	0.0258 (10)	−0.0021 (7)	−0.0050 (8)	−0.0116 (8)
C25	0.0139 (9)	0.0239 (9)	0.0197 (10)	−0.0030 (7)	−0.0048 (7)	−0.0091 (8)
C211	0.0165 (9)	0.0245 (10)	0.0286 (11)	0.0017 (7)	−0.0078 (8)	−0.0159 (9)
C212	0.0168 (9)	0.0358 (11)	0.0308 (12)	0.0015 (8)	−0.0077 (8)	−0.0202 (10)
C213	0.0257 (11)	0.0432 (13)	0.0375 (13)	0.0047 (9)	−0.0069 (9)	−0.0282 (11)
C214	0.0334 (12)	0.0351 (12)	0.0481 (15)	0.0101 (10)	−0.0143 (11)	−0.0305 (12)
C215	0.0316 (11)	0.0246 (10)	0.0379 (13)	0.0022 (9)	−0.0137 (10)	−0.0162 (10)
C216	0.0216 (10)	0.0246 (10)	0.0311 (12)	0.0028 (8)	−0.0108 (8)	−0.0156 (9)
C217	0.0224 (10)	0.0393 (12)	0.0299 (12)	−0.0067 (9)	−0.0001 (9)	−0.0203 (10)
C218	0.0319 (12)	0.0373 (13)	0.0379 (14)	−0.0064 (10)	−0.0071 (10)	−0.0085 (11)
C219	0.0262 (13)	0.0648 (18)	0.0440 (16)	−0.0012 (12)	0.0030 (11)	−0.0142 (14)
C220	0.0283 (11)	0.0217 (10)	0.0290 (11)	−0.0055 (8)	−0.0037 (9)	−0.0118 (9)
C221	0.0284 (11)	0.0293 (11)	0.0370 (13)	−0.0020 (9)	−0.0044 (10)	−0.0119 (10)
C222	0.0405 (13)	0.0265 (11)	0.0306 (12)	−0.0094 (9)	−0.0091 (10)	−0.0101 (10)
C231	0.0138 (9)	0.0218 (9)	0.0303 (11)	0.0010 (7)	−0.0075 (8)	−0.0139 (9)
C232	0.0164 (9)	0.0244 (10)	0.0290 (11)	−0.0009 (7)	−0.0068 (8)	−0.0143 (9)
C233	0.0162 (9)	0.0315 (11)	0.0318 (12)	0.0012 (8)	−0.0044 (8)	−0.0174 (10)
C234	0.0202 (10)	0.0299 (11)	0.0402 (13)	0.0059 (8)	−0.0106 (9)	−0.0177 (10)
C235	0.0274 (11)	0.0268 (11)	0.0297 (12)	0.0027 (8)	−0.0119 (9)	−0.0098 (9)
C236	0.0211 (10)	0.0240 (10)	0.0286 (11)	−0.0018 (8)	−0.0071 (8)	−0.0131 (9)
C237	0.0145 (9)	0.0298 (10)	0.0277 (11)	0.0009 (8)	−0.0044 (8)	−0.0135 (9)
C238	0.0290 (11)	0.0289 (11)	0.0305 (12)	−0.0031 (9)	−0.0081 (9)	−0.0124 (10)
C239	0.0213 (10)	0.0362 (12)	0.0305 (12)	−0.0046 (9)	−0.0051 (9)	−0.0164 (10)
C240	0.0242 (10)	0.0289 (11)	0.0269 (11)	−0.0008 (8)	−0.0052 (9)	−0.0119 (9)
C241	0.0336 (13)	0.0553 (15)	0.0360 (14)	0.0046 (11)	−0.0100 (10)	−0.0267 (12)
C242	0.0458 (15)	0.0376 (13)	0.0427 (15)	−0.0124 (11)	0.0095 (12)	−0.0148 (12)
Pd3	0.01407 (8)	0.02220 (8)	0.01856 (8)	−0.00496 (5)	−0.00263 (6)	−0.00752 (6)
Cl31	0.0246 (2)	0.0322 (3)	0.0422 (3)	−0.00208 (19)	−0.0072 (2)	−0.0222 (2)
Cl32	0.0199 (2)	0.0323 (2)	0.0321 (3)	−0.00178 (18)	−0.00458 (19)	−0.0185 (2)
N31	0.0159 (8)	0.0293 (9)	0.0221 (9)	−0.0055 (7)	−0.0019 (7)	−0.0101 (7)
C32	0.0161 (9)	0.0208 (9)	0.0211 (10)	−0.0028 (7)	−0.0045 (7)	−0.0094 (8)
N33	0.0157 (8)	0.0250 (8)	0.0206 (9)	−0.0037 (7)	−0.0038 (7)	−0.0086 (7)
C34	0.0168 (10)	0.0395 (12)	0.0298 (12)	−0.0060 (9)	−0.0054 (9)	−0.0146 (10)
C35	0.0161 (10)	0.0408 (12)	0.0289 (12)	−0.0084 (9)	−0.0023 (8)	−0.0132 (10)
C311	0.0168 (9)	0.0303 (10)	0.0219 (10)	−0.0066 (8)	−0.0004 (8)	−0.0111 (9)
C312	0.0218 (10)	0.0278 (11)	0.0285 (11)	−0.0032 (8)	−0.0024 (8)	−0.0121 (9)
C313	0.0313 (12)	0.0374 (12)	0.0306 (12)	0.0002 (9)	0.0022 (9)	−0.0196 (10)
C314	0.0331 (12)	0.0388 (12)	0.0209 (11)	−0.0035 (10)	0.0016 (9)	−0.0118 (10)
C315	0.0293 (11)	0.0287 (11)	0.0247 (11)	−0.0047 (9)	−0.0020 (9)	−0.0085 (9)
C316	0.0200 (10)	0.0282 (10)	0.0248 (11)	−0.0064 (8)	−0.0009 (8)	−0.0116 (9)
C317	0.0280 (11)	0.0287 (11)	0.0340 (13)	−0.0006 (9)	−0.0030 (9)	−0.0132 (10)

C318	0.0352 (13)	0.0333 (12)	0.0458 (15)	−0.0021 (10)	−0.0023 (11)	−0.0203 (11)
C319	0.0317 (13)	0.0394 (14)	0.0634 (19)	0.0023 (11)	−0.0114 (12)	−0.0211 (13)
C320	0.0272 (11)	0.0285 (11)	0.0259 (11)	−0.0032 (8)	−0.0032 (9)	−0.0128 (9)
C321	0.0354 (13)	0.0470 (14)	0.0577 (17)	−0.0036 (11)	−0.0079 (12)	−0.0349 (14)
C322	0.0350 (13)	0.0470 (14)	0.0393 (14)	0.0091 (11)	−0.0106 (10)	−0.0285 (12)
N41	0.0194 (8)	0.0220 (8)	0.0213 (9)	−0.0062 (6)	−0.0046 (7)	−0.0068 (7)
C42	0.0176 (9)	0.0248 (10)	0.0239 (11)	−0.0034 (8)	−0.0051 (8)	−0.0090 (9)
N43	0.0161 (8)	0.0223 (8)	0.0218 (9)	−0.0054 (6)	−0.0020 (6)	−0.0086 (7)
C44	0.0158 (9)	0.0246 (10)	0.0214 (10)	−0.0033 (7)	−0.0040 (7)	−0.0082 (8)
C45	0.0176 (9)	0.0245 (10)	0.0212 (10)	−0.0036 (7)	−0.0057 (8)	−0.0099 (8)
C331	0.0148 (9)	0.0256 (10)	0.0200 (10)	−0.0014 (7)	−0.0050 (7)	−0.0091 (8)
C332	0.0148 (9)	0.0263 (10)	0.0248 (11)	−0.0023 (7)	−0.0072 (8)	−0.0087 (9)
C333	0.0219 (10)	0.0343 (11)	0.0244 (11)	−0.0077 (9)	−0.0071 (8)	−0.0058 (9)
C334	0.0218 (10)	0.0524 (14)	0.0217 (11)	−0.0072 (10)	−0.0030 (8)	−0.0159 (11)
C335	0.0224 (10)	0.0474 (13)	0.0339 (13)	0.0032 (9)	−0.0083 (9)	−0.0265 (11)
C336	0.0190 (10)	0.0292 (11)	0.0296 (12)	0.0031 (8)	−0.0103 (8)	−0.0149 (9)
C337	0.0250 (11)	0.0254 (10)	0.0348 (12)	−0.0032 (8)	−0.0077 (9)	−0.0135 (9)
C338	0.061 (2)	0.078 (2)	0.159 (4)	0.0436 (18)	−0.067 (2)	−0.092 (3)
C339	0.081 (2)	0.071 (2)	0.080 (2)	−0.0507 (19)	0.0240 (19)	−0.053 (2)
C340	0.0357 (12)	0.0265 (11)	0.0386 (13)	0.0033 (9)	−0.0178 (10)	−0.0161 (10)
C341	0.0490 (15)	0.0387 (13)	0.0632 (18)	0.0163 (11)	−0.0343 (14)	−0.0330 (14)
C342	0.0438 (14)	0.0279 (12)	0.0614 (18)	0.0015 (10)	−0.0267 (13)	−0.0194 (12)
C411	0.0223 (10)	0.0225 (10)	0.0223 (11)	−0.0077 (8)	−0.0088 (8)	−0.0036 (8)
C412	0.0230 (10)	0.0255 (10)	0.0279 (12)	−0.0047 (8)	−0.0090 (9)	−0.0063 (9)
C413	0.0282 (11)	0.0268 (11)	0.0347 (13)	−0.0023 (9)	−0.0099 (10)	−0.0063 (10)
C414	0.0343 (12)	0.0294 (11)	0.0282 (12)	−0.0088 (9)	−0.0098 (10)	0.0015 (10)
C415	0.0327 (12)	0.0350 (12)	0.0242 (12)	−0.0118 (9)	−0.0050 (9)	−0.0062 (10)
C416	0.0269 (11)	0.0295 (11)	0.0249 (11)	−0.0098 (9)	−0.0069 (9)	−0.0082 (9)
C417	0.0440 (13)	0.0309 (11)	0.0248 (12)	−0.0119 (10)	−0.0042 (10)	−0.0112 (10)
C418	0.093 (3)	0.0586 (19)	0.070 (2)	−0.0102 (18)	−0.034 (2)	−0.0386 (18)
C419	0.0472 (15)	0.0384 (14)	0.0486 (16)	−0.0068 (12)	0.0059 (13)	−0.0221 (12)
C420	0.0288 (11)	0.0250 (10)	0.0304 (12)	0.0000 (8)	−0.0065 (9)	−0.0077 (9)
C421	0.0425 (14)	0.0334 (12)	0.0377 (14)	0.0005 (10)	−0.0110 (11)	−0.0156 (11)
C422	0.0295 (12)	0.0374 (13)	0.0439 (15)	−0.0026 (10)	−0.0029 (10)	−0.0157 (11)
C431	0.0151 (9)	0.0215 (9)	0.0249 (11)	−0.0049 (7)	−0.0049 (8)	−0.0065 (8)
C432	0.0202 (10)	0.0237 (10)	0.0265 (11)	−0.0026 (8)	−0.0057 (8)	−0.0094 (9)
C433	0.0246 (10)	0.0258 (10)	0.0348 (12)	−0.0060 (8)	−0.0056 (9)	−0.0136 (10)
C434	0.0227 (10)	0.0275 (11)	0.0351 (13)	−0.0104 (8)	−0.0037 (9)	−0.0107 (10)
C435	0.0198 (10)	0.0314 (11)	0.0274 (11)	−0.0084 (8)	−0.0001 (8)	−0.0102 (9)
C436	0.0169 (9)	0.0265 (10)	0.0250 (11)	−0.0036 (8)	−0.0057 (8)	−0.0094 (9)
C437	0.0206 (10)	0.0298 (10)	0.0327 (12)	−0.0065 (8)	0.0007 (9)	−0.0162 (10)
C438	0.0351 (13)	0.0514 (15)	0.0353 (14)	−0.0021 (11)	−0.0012 (11)	−0.0216 (12)
C439	0.0352 (13)	0.0408 (14)	0.0463 (15)	0.0035 (11)	−0.0001 (11)	−0.0203 (12)
C440	0.0194 (10)	0.0339 (11)	0.0291 (12)	−0.0077 (8)	−0.0017 (8)	−0.0154 (10)
C441	0.0230 (11)	0.0442 (13)	0.0312 (12)	−0.0030 (9)	−0.0057 (9)	−0.0192 (11)
C442	0.0306 (12)	0.0328 (12)	0.0332 (13)	−0.0036 (9)	−0.0069 (10)	−0.0160 (10)
O50	0.0919 (16)	0.0396 (11)	0.0367 (11)	−0.0082 (10)	−0.0062 (10)	−0.0137 (9)
C51	0.0596 (17)	0.0411 (14)	0.0309 (13)	−0.0082 (12)	−0.0069 (12)	−0.0186 (12)
C52	0.0547 (18)	0.0647 (19)	0.0464 (18)	0.0027 (15)	−0.0130 (14)	−0.0205 (15)
C53	0.0494 (15)	0.0393 (13)	0.0376 (14)	−0.0110 (11)	−0.0032 (12)	−0.0174 (12)
O60	0.0421 (10)	0.0532 (11)	0.0442 (11)	−0.0116 (8)	−0.0209 (8)	−0.0079 (9)
C61	0.0275 (12)	0.0502 (15)	0.0413 (16)	−0.0157 (11)	−0.0132 (11)	−0.0023 (13)
C62	0.157 (5)	0.093 (3)	0.055 (2)	−0.024 (3)	−0.004 (3)	−0.027 (2)
C63	0.079 (3)	0.070 (3)	0.092 (3)	0.019 (2)	0.016 (2)	0.012 (2)
O70	0.0357 (9)	0.0445 (10)	0.0489 (11)	0.0018 (7)	−0.0153 (8)	−0.0268 (9)
C71	0.0315 (12)	0.0305 (11)	0.0383 (13)	0.0013 (9)	−0.0142 (10)	−0.0167 (11)
C72	0.0306 (13)	0.0489 (15)	0.0574 (17)	−0.0063 (11)	−0.0062 (12)	−0.0298 (14)
C73	0.0338 (14)	0.077 (2)	0.101 (3)	0.0150 (14)	−0.0308 (15)	−0.068 (2)

Table S3. *Geometric parameters* $(\text{Å}, °)$

Pd1—C25	2.0225 (19)	Pd1—Cl11	2.2932 (5)
Pd1—C12	2.0534 (19)	Pd1—Cl12	2.3202 (5)

Bond	Length	Bond	Length
N11—C12	1.358 (3)	C141—H14b	0.98
N11—C15	1.391 (3)	C141—H14c	0.98
N11—C111	1.446 (3)	C142—H14d	0.98
C12—N13	1.358 (3)	C142—H14e	0.98
N13—C14	1.386 (8)	C142—H14f	0.98
N13—C131	1.450 (2)	N21—C22	1.338 (3)
C14—C15	1.338 (3)	N21—C25	1.406 (2)
C14—H14	0.95	N21—C211	1.445 (2)
C15—H15	0.95	C22—N23	1.331 (3)
C111—C112	1.401 (3)	C22—H22	0.95
C111—C116	1.402 (3)	N23—C24	1.384 (2)
C112—C113	1.400 (3)	N23—C231	1.449 (2)
C112—C117	1.519 (3)	C24—C25	1.373 (3)
C113—C114	1.383 (4)	C24—H24	0.95
C113—H113	0.95	C211—C216	1.395 (3)
C114—C115	1.377 (4)	C211—C212	1.405 (3)
C114—H114	0.95	C212—C213	1.399 (3)
C115—C116	1.398 (3)	C212—C217	1.521 (3)
C115—H115	0.95	C213—C214	1.384 (4)
C116—C120	1.519 (8)	C213—H213	0.95
C117—C119	1.525 (3)	C214—C215	1.382 (3)
C117—C118	1.531 (4)	C214—H214	0.95
C117—H117	1	C215—C216	1.398 (3)
C118—H11a	0.98	C215—H215	0.95
C118—H11b	0.98	C216—C220	1.516 (3)
C118—H11c	0.98	C217—C219	1.522 (3)
C119—H11d	0.98	C217—C218	1.529 (3)
C119—H11e	0.98	C217—H217	1
C119—H11f	0.98	C218—H21a	0.98
C120—C122	1.526 (3)	C218—H21b	0.98
C120—C121	1.533 (3)	C218—H21c	0.98
C120—H120	1	C219—H21d	0.98
C121—H12a	0.98	C219—H21e	0.98
C121—H12b	0.98	C219—H21f	0.98
C121—H12c	0.98	C220—C221	1.534 (3)
C122—H12d	0.98	C220—C222	1.537 (3)
C122—H12e	0.98	C220—H220	1
C122—H12f	0.98	C221—H22a	0.98
C131—C132	1.395 (3)	C221—H22b	0.98
C131—C136	1.406 (3)	C221—H22c	0.98
C132—C133	1.402 (3)	C222—H22d	0.98
C132—C137	1.519 (3)	C222—H22e	0.98
C133—C134	1.383 (3)	C222—H22f	0.98
C133—H133	0.95	C231—C236	1.393 (3)
C134—C135	1.377 (3)	C231—C232	1.399 (3)
C134—H134	0.95	C232—C233	1.399 (3)
C135—C136	1.395 (3)	C232—C237	1.517 (3)
C135—H135	0.95	C233—C234	1.379 (3)
C136—C140	1.521 (3)	C233—H233	0.95
C137—C139	1.523 (3)	C234—C235	1.387 (3)
C137—C138	1.528 (3)	C234—H234	0.95
C137—H137	1	C235—C236	1.399 (3)
C138—H13a	0.98	C235—H235	0.95
C138—H13b	0.98	C236—C240	1.521 (3)
C138—H13c	0.98	C237—C239	1.531 (3)
C139—H13d	0.98	C237—C238	1.534 (3)
C139—H13e	0.98	C237—H237	1
C139—H13f	0.98	C238—H23a	0.98
C140—C142	1.527 (3)	C238—H23b	0.98
C140—C141	1.536 (3)	C238—H23c	0.98
C140—H140	1	C239—H23d	0.98
C141—H14a	0.98	C239—H23e	0.98

C239—H23f	0.98	C331—C332	1.401 (3)
C240—C242	1.527 (3)	C332—C333	1.394 (3)
C240—C241	1.531 (3)	C332—C337	1.518 (3)
C240—H240	1	C333—C334	1.378 (3)
C241—H24a	0.98	C333—H333	0.95
C241—H24b	0.98	C334—C335	1.378 (3)
C241—H24c	0.98	C334—H334	0.95
C242—H24d	0.98	C335—C336	1.392 (3)
C242—H24e	0.98	C335—H335	0.95
C242—H24f	0.98	C336—C340	1.522 (3)
Pd3—C45	2.0305 (19)	C337—C338	1.510 (3)
Pd3—C32	2.0525 (19)	C337—C339	1.517 (3)
Pd3—Cl32	2.3028 (5)	C337—H337	1
Pd3—Cl31	2.3167 (5)	C338—H33a	0.98
N31—C32	1.363 (3)	C338—H33b	0.98
N31—C35	1.393 (3)	C338—H33c	0.98
N31—C311	1.442 (3)	C339—H33d	0.98
C32—N33	1.355 (3)	C339—H33e	0.98
N33—C34	1.389 (3)	C339—H33f	0.98
N33—C331	1.454 (2)	C340—C341	1.528 (3)
C34—C35	1.336 (3)	C340—C342	1.539 (3)
C34—H34	0.95	C340—H340	1
C35—H35	0.95	C341—H34a	0.98
C311—C316	1.399 (3)	C341—H34b	0.98
C311—C312	1.400 (3)	C341—H34c	0.98
C312—C313	1.398 (3)	C342—H34d	0.98
C312—C317	1.517 (3)	C342—H34e	0.98
C313—C314	1.380 (3)	C342—H34f	0.98
C313—H313	0.95	C411—C416	1.400 (3)
C314—C315	1.381 (3)	C411—C412	1.401 (3)
C314—H314	0.95	C412—C413	1.395 (3)
C315—C316	1.394 (3)	C412—C420	1.524 (3)
C315—H315	0.95	C413—C414	1.382 (3)
C316—C320	1.525 (3)	C413—H413	0.95
C317—C318	1.519 (3)	C414—C415	1.377 (4)
C317—C319	1.530 (3)	C414—H414	0.95
C317—H317	1	C415—C416	1.397 (3)
C318—H31a	0.98	C415—H415	0.95
C318—H31b	0.98	C416—C417	1.521 (3)
C318—H31c	0.98	C417—C419	1.525 (4)
C319—H31d	0.98	C417—C418	1.526 (4)
C319—H31e	0.98	C417—H417	1
C319—H31f	0.98	C418—H41a	0.98
C320—C321	1.525 (3)	C418—H41b	0.98
C320—C322	1.529 (3)	C418—H41c	0.98
C320—H320	1	C419—H41d	0.98
C321—H32a	0.98	C419—H41e	0.98
C321—H32b	0.98	C419—H41f	0.98
C321—H32c	0.98	C420—C421	1.528 (3)
C322—H32d	0.98	C420—C422	1.535 (3)
C322—H32e	0.98	C420—H420	1
C322—H32f	0.98	C421—H42a	0.98
N41—C42	1.341 (3)	C421—H42b	0.98
N41—C45	1.398 (3)	C421—H42c	0.98
N41—C411	1.449 (3)	C422—H42d	0.98
C42—N43	1.320 (3)	C422—H42e	0.98
C42—H42	0.95	C422—H42f	0.98
N43—C44	1.389 (3)	C431—C432	1.394 (3)
N43—C431	1.447 (2)	C431—C436	1.399 (3)
C44—C45	1.376 (3)	C432—C433	1.394 (3)
C44—H44	0.95	C432—C437	1.525 (3)
C331—C336	1.400 (3)	C433—C434	1.385 (3)

C433—H433	0.95	C51—C52	1.503 (4)
C434—C435	1.383 (3)	C52—H52a	0.98
C434—H434	0.95	C52—H52b	0.98
C435—C436	1.395 (3)	C52—H52c	0.98
C435—H435	0.95	C53—H53a	0.98
C436—C440	1.517 (3)	C53—H53b	0.98
C437—C438	1.523 (4)	C53—H53c	0.98
C437—C439	1.532 (3)	O60—C61	1.206 (3)
C437—H437	1	C61—C63	1.484 (5)
C438—H43a	0.98	C61—C62	1.489 (5)
C438—H43b	0.98	C62—H62a	0.98
C438—H43c	0.98	C62—H62b	0.98
C439—H43d	0.98	C62—H62c	0.98
C439—H43e	0.98	C63—H63a	0.98
C439—H43f	0.98	C63—H63b	0.98
C440—C441	1.524 (3)	C63—H63c	0.98
C440—C442	1.533 (3)	O70—C71	1.214 (3)
C440—H440	1	C71—C73	1.490 (3)
C441—H44a	0.98	C71—C72	1.493 (3)
C441—H44b	0.98	C72—H72a	0.98
C441—H44c	0.98	C72—H72b	0.98
C442—H44d	0.98	C72—H72c	0.98
C442—H44e	0.98	C73—H73a	0.98
C442—H44f	0.98	C73—H73b	0.98
O50—C51	1.217 (3)	C73—H73c	0.98
C51—C53	1.494 (4)		

C25—PD1—C12	176.79 (7)	C115—C116—C111	116.8 (2)
C25—PD1—CL11	89.04 (6)	C115—C116—C120	120.8 (2)
C12—PD1—CL11	91.74 (5)	C111—C116—C120	122.36 (19)
C25—PD1—CL12	88.63 (6)	C112—C117—C119	113.0 (2)
C12—PD1—CL12	90.54 (5)	C112—C117—C118	110.0 (2)
CL11—PD1—CL12	177.526 (17	C119—C117—C118	111.3 (2)
C12—N11—C15	111.41 (17)	C112—C117—H117	107.4
C12—N11—C111	126.82 (16)	C119—C117—H117	107.4
C15—N11—C111	121.38 (16)	C118—C117—H117	107.4
N13—C12—N11	108.94 (16)	C117—C118—H11A	109.5
N13—C12—PD1	126.65 (14)	C117—C118—H11B	109.5
N11—C12—PD1	129.26 (15)	H11A—C118—H11B	109.5
C12—N13—C14	111.13 (17)	C117—C118—H11C	109.5
C12—N13—C131	126.69 (16)	H11A—C118—H11C	109.5
C14—N13—C131	121.57 (17)	H11B—C118—H11C	109.5
C15—C14—N13	107.20 (18)	C117—C119—H11D	109.5
C15—C14—H14	126.4	C117—C119—H11E	109.5
N13—C14—H14	126.4	H11D—C119—H11E	109.5
C14—C15—N11	106.33 (18)	C117—C119—H11F	109.5
C14—C15—H15	126.8	H11D—C119—H11F	109.5
N11—C15—H15	126.8	H11E—C119—H11F	109.5
C112—C111—C116	123.30 (19)	C116—C120—C122	112.2 (2)
C112—C111—N11	117.91 (18)	C116—C120—C121	111.13 (18)
C116—C111—N11	118.55 (18)	C122—C120—C121	109.97 (19)
C113—C112—C111	117.2 (2)	C116—C120—H120	107.8
C113—C112—C117	120.2 (2)	C122—C120—H120	107.8
C111—C112—C117	122.60 (19)	C121—C120—H120	107.8
C114—C113—C112	120.7 (2)	C120—C121—H12A	109.5
C114—C113—H113	119.7	C120—C121—H12B	109.5
C112—C113—H113	119.7	H12A—C121—H12B	109.5
C115—C114—C113	120.8 (2)	C120—C121—H12C	109.5
C115—C114—H114	119.6	H12A—C121—H12C	109.5
C113—C114—H114	119.6	H12B—C121—H12C	109.5
C114—C115—C116	121.3 (2)	C120—C122—H12D	109.5
C114—C115—H115	119.4	C120—C122—H12E	109.5
C116—C115—H115	119.4	H12D—C122—H12E	109.5

C120—C122—H12F	109.5	N21—C22—H22	126
H12D—C122—H12F	109.5	C22—N23—C24	108.45 (16)
H12E—C122—H12F	109.5	C22—N23—C231	123.85 (16)
C132—C131—C136	123.23 (19)	C24—N23—C231	127.67 (16)
C132—C131—N13	118.81 (18)	C25—C24—N23	109.94 (16)
C136—C131—N13	117.37 (18)	C25—C24—H24	125.3
C131—C132—C133	116.77 (19)	N23—C24—H24	125.3
C131—C132—C137	122.25 (18)	C24—C25—N21	103.41 (16)
C133—C132—C137	120.90 (19)	C24—C25—PD1	128.20 (14)
C134—C133—C132	121.2 (2)	N21—C25—PD1	128.39 (14)
C134—C133—H133	119.4	C216—C211—C212	123.94 (18)
C132—C133—H133	119.4	C216—C211—N21	118.43 (17)
C135—C134—C133	120.5 (2)	C212—C211—N21	117.48 (18)
C135—C134—H134	119.7	C213—C212—C211	116.4 (2)
C133—C134—H134	119.7	C213—C212—C217	121.89 (19)
C134—C135—C136	121.0 (2)	C211—C212—C217	121.65 (18)
C134—C135—H135	119.5	C214—C213—C212	121.1 (2)
C136—C135—H135	119.5	C214—C213—H213	119.4
C135—C136—C131	117.2 (2)	C212—C213—H213	119.4
C135—C136—C140	119.9 (2)	C215—C214—C213	120.7 (2)
C131—C136—C140	122.86 (19)	C215—C214—H214	119.6
C132—C137—C139	112.61 (18)	C213—C214—H214	119.6
C132—C137—C138	109.80 (18)	C214—C215—C216	120.8 (2)
C139—C137—C138	110.2 (2)	C214—C215—H215	119.6
C132—C137—H137	108	C216—C215—H215	119.6
C139—C137—H137	108	C211—C216—C215	116.94 (19)
C138—C137—H137	108	C211—C216—C220	124.16 (17)
C137—C138—H13A	109.5	C215—C216—C220	118.90 (19)
C137—C138—H13B	109.5	C212—C217—C219	113.2 (2)
H13A—C138—H13B	109.5	C212—C217—C218	111.26 (18)
C137—C138—H13C	109.5	C219—C217—C218	109.5 (2)
H13A—C138—H13C	109.5	C212—C217—H217	107.5
H13B—C138—H13C	109.5	C219—C217—H217	107.5
C137—C139—H13D	109.5	C218—C217—H217	107.5
C137—C139—H13E	109.5	C217—C218—H21A	109.5
H13D—C139—H13E	109.5	C217—C218—H21B	109.5
C137—C139—H13F	109.5	H21A—C218—H21B	109.5
H13D—C139—H13F	109.5	C217—C218—H21C	109.5
H13E—C139—H13F	109.5	H21A—C218—H21C	109.5
C136—C140—C142	113.2 (2)	H21B—C218—H21C	109.5
C136—C140—C141	110.32 (19)	C217—C219—H21D	109.5
C142—C140—C141	109.8 (2)	C217—C219—H21E	109.5
C136—C140—H140	107.8	H21D—C219—H21E	109.5
C142—C140—H140	107.8	C217—C219—H21F	109.5
C141—C140—H140	107.8	H21D—C219—H21F	109.5
C140—C141—H14A	109.5	H21E—C219—H21F	109.5
C140—C141—H14B	109.5	C216—C220—C221	110.72 (18)
H14A—C141—H14B	109.5	C216—C220—C222	111.42 (18)
C140—C141—H14C	109.5	C221—C220—C222	110.23 (18)
H14A—C141—H14C	109.5	C216—C220—H220	108.1
H14B—C141—H14C	109.5	C221—C220—H220	108.1
C140—C142—H14D	109.5	C222—C220—H220	108.1
C140—C142—H14E	109.5	C220—C221—H22A	109.5
H14D—C142—H14E	109.5	C220—C221—H22B	109.5
C140—C142—H14F	109.5	H22A—C221—H22B	109.5
H14D—C142—H14F	109.5	C220—C221—H22C	109.5
H14E—C142—H14F	109.5	H22A—C221—H22C	109.5
C22—N21—C25	110.88 (16)	H22B—C221—H22C	109.5
C22—N21—C211	120.92 (16)	C220—C222—H22D	109.5
C25—N21—C211	128.04 (16)	C220—C222—H22E	109.5
N23—C22—N21	107.91 (17)	H22D—C222—H22E	109.5
N23—C22—H22	126	C220—C222—H22F	109.5

H22D—C222—H22F	109.5	C32—N31—C35	111.16 (17)
H22E—C222—H22F	109.5	C32—N31—C311	127.86 (17)
C236—C231—C232	124.11 (18)	C35—N31—C311	120.97 (16)
C236—C231—N23	117.89 (17)	N33—C32—N31	103.76 (17)
C232—C231—N23	118.00 (18)	N33—C32—PD3	125.90 (14)
C231—C232—C233	116.45 (19)	N31—C32—PD3	130.22 (15)
C231—C232—C237	122.63 (17)	C32—N33—C34	111.53 (17)
C233—C232—C237	120.92 (18)	C32—N33—C331	127.85 (16)
C234—C233—C232	121.1 (2)	C34—N33—C331	120.50 (17)
C234—C233—H233	119.4	C35—C34—N33	106.80 (19)
C232—C233—H233	119.4	C35—C34—H34	126.6
C233—C234—C235	120.8 (2)	N33—C34—H34	126.6
C233—C234—H234	119.6	C34—C35—N31	106.75 (18)
C235—C234—H234	119.6	C34—C35—H35	126.6
C234—C235—C236	120.6 (2)	N31—C35—H35	126.6
C234—C235—H235	119.7	C316—C311—C312	122.76 (19)
C236—C235—H235	119.7	C316—C311—N31	118.72 (18)
C231—C236—C235	116.89 (19)	C312—C311—N31	118.24 (19)
C231—C236—C240	122.54 (18)	C313—C312—C311	117.3 (2)
C235—C236—C240	120.6 (2)	C313—C312—C317	119.89 (19)
C232—C237—C239	111.54 (17)	C311—C312—C317	122.9 (2)
C232—C237—C238	110.77 (17)	C314—C313—C312	121.2 (2)
C239—C237—C238	110.76 (17)	C314—C313—H313	119.4
C232—C237—H237	107.9	C312—C313—H313	119.4
C239—C237—H237	107.9	C313—C314—C315	120.1 (2)
C238—C237—H237	107.9	C313—C314—H314	120
C237—C238—H23A	109.5	C315—C314—H314	120
C237—C238—H23B	109.5	C314—C315—C316	121.4 (2)
H23A—C238—H23B	109.5	C314—C315—H315	119.3
C237—C238—H23C	109.5	C316—C315—H315	119.3
H23A—C238—H23C	109.5	C315—C316—C311	117.30 (19)
H23B—C238—H23C	109.5	C315—C316—C320	119.94 (19)
C237—C239—H23D	109.5	C311—C316—C320	122.76 (19)
C237—C239—H23E	109.5	C312—C317—C318	111.4 (2)
H23D—C239—H23E	109.5	C312—C317—C319	111.63 (19)
C237—C239—H23F	109.5	C318—C317—C319	110.0 (2)
H23D—C239—H23F	109.5	C312—C317—H317	107.9
H23E—C239—H23F	109.5	C318—C317—H317	107.9
C236—C240—C242	111.50 (18)	C319—C317—H317	107.9
C236—C240—C241	110.42 (18)	C317—C318—H31A	109.5
C242—C240—C241	110.9 (2)	C317—C318—H31B	109.5
C236—C240—H240	108	H31A—C318—H31B	109.5
C242—C240—H240	108	C317—C318—H31C	109.5
C241—C240—H240	108	H31A—C318—H31C	109.5
C240—C241—H24A	109.5	H31B—C318—H31C	109.5
C240—C241—H24B	109.5	C317—C319—H31D	109.5
H24A—C241—H24B	109.5	C317—C319—H31E	109.5
C240—C241—H24C	109.5	H31D—C319—H31E	109.5
H24A—C241—H24C	109.5	C317—C319—H31F	109.5
H24B—C241—H24C	109.5	H31D—C319—H31F	109.5
C240—C242—H24D	109.5	H31E—C319—H31F	109.5
C240—C242—H24E	109.5	C316—C320—C321	111.21 (18)
H24D—C242—H24E	109.5	C316—C320—C322	111.56 (18)
C240—C242—H24F	109.5	C321—C320—C322	111.1 (2)
H24D—C242—H24F	109.5	C316—C320—H320	107.6
H24E—C242—H24F	109.5	C321—C320—H320	107.6
C45—PD3—C32	174.39 (8)	C322—C320—H320	107.6
C45—PD3—CL32	89.64 (6)	C320—C321—H32A	109.5
C32—PD3—CL32	91.49 (5)	C320—C321—H32B	109.5
C45—PD3—CL31	88.67 (6)	H32A—C321—H32B	109.5
C32—PD3—CL31	90.32 (5)	C320—C321—H32C	109.5
CL32—PD3—CL31	177.875 (19	H32A—C321—H32C	109.5

H32B—C321—H32C	109.5	C341—C340—H340	108.1
C320—C322—H32D	109.5	C342—C340—H340	108.1
C320—C322—H32E	109.5	C340—C341—H34A	109.5
H32D—C322—H32E	109.5	C340—C341—H34B	109.5
C320—C322—H32F	109.5	H34A—C341—H34B	109.5
H32D—C322—H32F	109.5	C340—C341—H34C	109.5
H32E—C322—H32F	109.5	H34A—C341—H34C	109.5
C42—N41—C45	110.60 (16)	H34B—C341—H34C	109.5
C42—N41—C411	119.47 (17)	C340—C342—H34D	109.5
C45—N41—C411	129.42 (16)	C340—C342—H34E	109.5
N43—C42—N41	108.22 (17)	H34D—C342—H34E	109.5
N43—C42—H42	125.9	C340—C342—H34F	109.5
N41—C42—H42	125.9	H34D—C342—H34F	109.5
C42—N43—C44	108.65 (16)	H34E—C342—H34F	109.5
C42—N43—C431	123.19 (17)	C416—C411—C412	123.43 (19)
C44—N43—C431	128.11 (17)	C416—C411—N41	117.17 (18)
C45—C44—N43	108.65 (18)	C412—C411—N41	119.09 (18)
C45—C44—H44	125.7	C413—C412—C411	116.9 (2)
N43—C44—H44	125.7	C413—C412—C420	119.6 (2)
C44—C45—N41	103.86 (16)	C411—C412—C420	123.42 (19)
C44—C45—PD3	126.39 (15)	C414—C413—C412	121.1 (2)
N41—C45—PD3	129.75 (14)	C414—C413—H413	119.4
C336—C331—C332	123.13 (19)	C412—C413—H413	119.4
C336—C331—N33	117.98 (18)	C415—C414—C413	120.4 (2)
C332—C331—N33	118.63 (17)	C415—C414—H414	119.8
C333—C332—C331	116.72 (19)	C413—C414—H414	119.8
C333—C332—C337	120.97 (19)	C414—C415—C416	121.3 (2)
C331—C332—C337	122.28 (18)	C414—C415—H415	119.3
C334—C333—C332	121.3 (2)	C416—C415—H415	119.3
C334—C333—H333	119.3	C415—C416—C411	116.7 (2)
C332—C333—H333	119.3	C415—C416—C417	119.7 (2)
C335—C334—C333	120.6 (2)	C411—C416—C417	123.48 (19)
C335—C334—H334	119.7	C416—C417—C419	111.87 (19)
C333—C334—H334	119.7	C416—C417—C418	110.3 (2)
C334—C335—C336	120.8 (2)	C419—C417—C418	111.0 (2)
C334—C335—H335	119.6	C416—C417—H417	107.8
C336—C335—H335	119.6	C419—C417—H417	107.8
C335—C336—C331	117.3 (2)	C418—C417—H417	107.8
C335—C336—C340	119.6 (2)	C417—C418—H41A	109.5
C331—C336—C340	122.95 (19)	C417—C418—H41B	109.5
C338—C337—C339	110.1 (3)	H41A—C418—H41B	109.5
C338—C337—C332	110.1 (2)	C417—C418—H41C	109.5
C339—C337—C332	112.1 (2)	H41A—C418—H41C	109.5
C338—C337—H337	108.2	H41B—C418—H41C	109.5
C339—C337—H337	108.2	C417—C419—H41D	109.5
C332—C337—H337	108.2	C417—C419—H41E	109.5
C337—C338—H33A	109.5	H41D—C419—H41E	109.5
C337—C338—H33B	109.5	C417—C419—H41F	109.5
H33A—C338—H33B	109.5	H41D—C419—H41F	109.5
C337—C338—H33C	109.5	H41E—C419—H41F	109.5
H33A—C338—H33C	109.5	C412—C420—C421	111.85 (19)
H33B—C338—H33C	109.5	C412—C420—C422	110.5 (2)
C337—C339—H33D	109.5	C421—C420—C422	109.97 (19)
C337—C339—H33E	109.5	C412—C420—H420	108.1
H33D—C339—H33E	109.5	C421—C420—H420	108.1
C337—C339—H33F	109.5	C422—C420—H420	108.1
H33D—C339—H33F	109.5	C420—C421—H42A	109.5
H33E—C339—H33F	109.5	C420—C421—H42B	109.5
C336—C340—C341	112.5 (2)	H42A—C421—H42B	109.5
C336—C340—C342	109.66 (18)	C420—C421—H42C	109.5
C341—C340—C342	110.11 (19)	H42A—C421—H42C	109.5
C336—C340—H340	108.1	H42B—C421—H42C	109.5

C420—C422—H42D	109.5	H44B—C441—H44C	109.5
C420—C422—H42E	109.5	C440—C442—H44D	109.5
H42D—C422—H42E	109.5	C440—C442—H44E	109.5
C420—C422—H42F	109.5	H44D—C442—H44E	109.5
H42D—C422—H42F	109.5	C440—C442—H44F	109.5
H42E—C422—H42F	109.5	H44D—C442—H44F	109.5
C432—C431—C436	123.91 (18)	H44E—C442—H44F	109.5
C432—C431—N43	118.01 (17)	O50—C51—C53	122.5 (3)
C436—C431—N43	118.03 (17)	O50—C51—C52	121.5 (3)
C431—C432—C433	116.93 (19)	C53—C51—C52	116.0 (2)
C431—C432—C437	122.62 (18)	C51—C52—H52A	109.5
C433—C432—C437	120.43 (19)	C51—C52—H52B	109.5
C434—C433—C432	120.8 (2)	H52A—C52—H52B	109.5
C434—C433—H433	119.6	C51—C52—H52C	109.5
C432—C433—H433	119.6	H52A—C52—H52C	109.5
C435—C434—C433	120.67 (19)	H52B—C52—H52C	109.5
C435—C434—H434	119.7	C51—C53—H53A	109.5
C433—C434—H434	119.7	C51—C53—H53B	109.5
C434—C435—C436	120.9 (2)	H53A—C53—H53B	109.5
C434—C435—H435	119.5	C51—C53—H53C	109.5
C436—C435—H435	119.5	H53A—C53—H53C	109.5
C435—C436—C431	116.69 (19)	H53B—C53—H53C	109.5
C435—C436—C440	120.90 (18)	O60—C61—C63	121.1 (3)
C431—C436—C440	122.40 (17)	O60—C61—C62	122.7 (3)
C438—C437—C432	110.86 (18)	C63—C61—C62	116.1 (3)
C438—C437—C439	110.2 (2)	C61—C62—H62A	109.5
C432—C437—C439	111.24 (19)	C61—C62—H62B	109.5
C438—C437—H437	108.2	H62A—C62—H62B	109.5
C432—C437—H437	108.2	C61—C62—H62C	109.5
C439—C437—H437	108.2	H62A—C62—H62C	109.5
C437—C438—H43A	109.5	H62B—C62—H62C	109.5
C437—C438—H43B	109.5	C61—C63—H63A	109.5
H43A—C438—H43B	109.5	C61—C63—H63B	109.5
C437—C438—H43C	109.5	H63A—C63—H63B	109.5
H43A—C438—H43C	109.5	C61—C63—H63C	109.5
H43B—C438—H43C	109.5	H63A—C63—H63C	109.5
C437—C439—H43D	109.5	H63B—C63—H63C	109.5
C437—C439—H43E	109.5	O70—C71—C73	122.1 (2)
H43D—C439—H43E	109.5	O70—C71—C72	122.4 (2)
C437—C439—H43F	109.5	C73—C71—C72	115.4 (2)
H43D—C439—H43F	109.5	C71—C72—H72A	109.5
H43E—C439—H43F	109.5	C71—C72—H72B	109.5
C436—C440—C441	111.60 (18)	H72A—C72—H72B	109.5
C436—C440—C442	110.92 (18)	C71—C72—H72C	109.5
C441—C440—C442	111.01 (18)	H72A—C72—H72C	109.5
C436—C440—H440	107.7	H72B—C72—H72C	109.5
C441—C440—H440	107.7	C71—C73—H73A	109.5
C442—C440—H440	107.7	C71—C73—H73B	109.5
C440—C441—H44A	109.5	H73A—C73—H73B	109.5
C440—C441—H44B	109.5	C71—C73—H73C	109.5
H44A—C441—H44B	109.5	H73A—C73—H73C	109.5
C440—C441—H44C	109.5	H73B—C73—H73C	109.5
H44A—C441—H44C	109.5		
C15—N11—C12—N13	−0.3 (2)	PD1—C12—N13—C14	−175.17 (15)
C111—N11—C12—N13	172.55 (18)	N11—C12—N13—C131	−170.38 (18)
C15—N11—C12—PD1	175.36 (15)	PD1—C12—N13—C131	13.8 (3)
C111—N11—C12—PD1	−11.8 (3)	C12—N13—C14—C15	−0.7 (2)
CL11—PD1—C12—N13	−74.65 (16)	C131—N13—C14—C15	170.78 (18)
CL12—PD1—C12—N13	104.38 (16)	N13—C14—C15—N11	0.5 (2)
CL11—PD1—C12—N11	110.63 (17)	C12—N11—C15—C14	−0.2 (2)
CL12—PD1—C12—N11	−70.33 (17)	C111—N11—C15—C14	−173.45 (19)
N11—C12—N13—C14	0.6 (2)	C12—N11—C111—C112	−76.8 (3)

C15—N11—C111—C112	95.4 (2)	C211—N21—C25—PD1	−4.1 (3)
C12—N11—C111—C116	106.6 (2)	CL11—PD1—C25—C24	121.92 (18)
C15—N11—C111—C116	−79.1 (2)	CL12—PD1—C25—C24	−57.24 (18)
C116—C111—C112—C113	0.2 (3)	CL11—PD1—C25—N21	−58.14 (17)
N11—C111—C112—C113	−173.95 (18)	CL12—PD1—C25—N21	122.70 (17)
C116—C111—C112—C117	177.52 (19)	C22—N21—C211—C216	−72.7 (2)
N11—C111—C112—C117	3.3 (3)	C25—N21—C211—C216	112.3 (2)
C111—C112—C113—C114	0.6 (3)	C22—N21—C211—C212	103.1 (2)
C117—C112—C113—C114	−176.8 (2)	C25—N21—C211—C212	−72.0 (3)
C112—C113—C114—C115	−1.0 (3)	C216—C211—C212—C213	−0.5 (3)
C113—C114—C115—C116	0.6 (3)	N21—C211—C212—C213	−176.05 (18)
C114—C115—C116—C111	0.1 (3)	C216—C211—C212—C217	176.07 (19)
C114—C115—C116—C120	178.1 (2)	N21—C211—C212—C217	0.6 (3)
C112—C111—C116—C115	−0.6 (3)	C211—C212—C213—C214	1.3 (3)
N11—C111—C116—C115	173.58 (17)	C217—C212—C213—C214	−175.3 (2)
C112—C111—C116—C120	−178.48 (19)	C212—C213—C214—C215	−0.5 (4)
N11—C111—C116—C120	−4.3 (3)	C213—C214—C215—C216	−1.1 (3)
C113—C112—C117—C119	−44.6 (3)	C212—C211—C216—C215	−1.0 (3)
C111—C112—C117—C119	138.2 (2)	N21—C211—C216—C215	174.48 (18)
C113—C112—C117—C118	80.5 (3)	C212—C211—C216—C220	179.45 (19)
C111—C112—C117—C118	−96.7 (3)	N21—C211—C216—C220	−5.1 (3)
C115—C116—C120—C122	43.3 (3)	C214—C215—C216—C211	1.8 (3)
C111—C116—C120—C122	−136.9 (2)	C214—C215—C216—C220	−178.6 (2)
C115—C116—C120—C121	−80.3 (3)	C213—C212—C217—C219	−34.0 (3)
C111—C116—C120—C121	97.5 (2)	C211—C212—C217—C219	149.5 (2)
C12—N13—C131—C132	−86.7 (2)	C213—C212—C217—C218	89.8 (2)
C14—N13—C131—C132	103.2 (2)	C211—C212—C217—C218	−86.6 (2)
C12—N13—C131—C136	96.8 (2)	C211—C216—C220—C221	105.0 (2)
C14—N13—C131—C136	−73.4 (2)	C215—C216—C220—C221	−74.5 (2)
C136—C131—C132—C133	−0.3 (3)	C211—C216—C220—C222	−131.9 (2)
N13—C131—C132—C133	−176.66 (17)	C215—C216—C220—C222	48.5 (3)
C136—C131—C132—C137	176.47 (18)	C22—N23—C231—C236	−90.2 (2)
N13—C131—C132—C137	0.2 (3)	C24—N23—C231—C236	87.6 (2)
C131—C132—C133—C134	−1.1 (3)	C22—N23—C231—C232	88.8 (2)
C137—C132—C133—C134	−178.00 (19)	C24—N23—C231—C232	−93.4 (2)
C132—C133—C134—C135	1.6 (3)	C236—C231—C232—C233	2.2 (3)
C133—C134—C135—C136	−0.6 (3)	N23—C231—C232—C233	−176.67 (17)
C134—C135—C136—C131	−0.8 (3)	C236—C231—C232—C237	−177.83 (19)
C134—C135—C136—C140	177.4 (2)	N23—C231—C232—C237	3.3 (3)
C132—C131—C136—C135	1.3 (3)	C231—C232—C233—C234	−0.9 (3)
N13—C131—C136—C135	177.69 (17)	C237—C232—C233—C234	179.21 (19)
C132—C131—C136—C140	−176.86 (19)	C232—C233—C234—C235	−0.8 (3)
N13—C131—C136—C140	−0.5 (3)	C233—C234—C235—C236	1.2 (3)
C131—C132—C137—C139	140.0 (2)	C232—C231—C236—C235	−1.9 (3)
C133—C132—C137—C139	−43.3 (3)	N23—C231—C236—C235	177.03 (17)
C131—C132—C137—C138	−96.8 (3)	C232—C231—C236—C240	179.13 (18)
C133—C132—C137—C138	79.9 (3)	N23—C231—C236—C240	−2.0 (3)
C135—C136—C140—C142	48.0 (3)	C234—C235—C236—C231	0.1 (3)
C131—C136—C140—C142	−133.8 (2)	C234—C235—C236—C240	179.1 (2)
C135—C136—C140—C141	−75.5 (3)	C231—C232—C237—C239	122.6 (2)
C131—C136—C140—C141	102.7 (2)	C233—C232—C237—C239	−57.5 (2)
C25—N21—C22—N23	−0.7 (2)	C231—C232—C237—C238	−113.6 (2)
C211—N21—C22—N23	−176.51 (17)	C233—C232—C237—C238	66.4 (2)
N21—C22—N23—C24	0.6 (2)	C231—C236—C240—C242	−121.9 (2)
N21—C22—N23—C231	178.75 (17)	C235—C236—C240—C242	59.1 (3)
C22—N23—C24—C25	−0.4 (2)	C231—C236—C240—C241	114.3 (2)
C231—N23—C24—C25	−178.38 (18)	C235—C236—C240—C241	−64.6 (3)
N23—C24—C25—N21	0.0 (2)	C35—N31—C32—N33	0.0 (2)
N23—C24—C25—PD1	179.90 (14)	C311—N31—C32—N33	178.49 (18)
C22—N21—C25—C24	0.4 (2)	C35—N31—C32—PD3	175.23 (15)
C211—N21—C25—C24	175.90 (18)	C311—N31—C32—PD3	−5.3 (3)
C22—N21—C25—PD1	−179.50 (14)	CLS2—PD3—C32—N33	−76.34 (16)

CL31—PD3—C32—N33	104.78 (16)		C331—C332—C333—C334	−0.2 (3)
CL32—PD3—C32—N31	108.21 (18)		C337—C332—C333—C334	−178.26 (19)
CL31—PD3—C32—N31	−70.67 (18)		C332—C333—C334—C335	0.2 (3)
N31—C32—N33—C34	0.4 (2)		C333—C334—C335—C336	0.4 (3)
PD3—C32—N33—C34	−176.04 (15)		C334—C335—C336—C331	−1.0 (3)
N31—C32—N33—C331	−175.55 (18)		C334—C335—C336—C340	176.2 (2)
PD3—C32—N33—C331	8.0 (3)		C332—C331—C336—C335	1.0 (3)
C32—N33—C34—C35	−0.7 (3)		N33—C331—C336—C335	175.01 (17)
C331—N33—C34—C35	175.61 (18)		C332—C331—C336—C340	−176.09 (19)
N33—C34—C35—N31	0.6 (3)		N33—C331—C336—C340	−2.1 (3)
C32—N31—C35—C34	−0.4 (3)		C333—C332—C337—C338	80.7 (3)
C311—N31—C35—C34	−179.02 (19)		C331—C332—C337—C338	−97.3 (3)
C32—N31—C311—C316	−78.0 (3)		C333—C332—C337—C339	−42.2 (3)
C35—N31—C311—C316	100.3 (2)		C331—C332—C337—C339	139.9 (3)
C32—N31—C311—C312	107.9 (2)		C335—C336—C340—C341	47.2 (3)
C35—N31—C311—C312	−73.8 (3)		C331—C336—C340—C341	−135.8 (2)
C316—C311—C312—C313	−0.9 (3)		C335—C336—C340—C342	−75.8 (3)
N31—C311—C312—C313	172.96 (19)		C331—C336—C340—C342	101.3 (2)
C316—C311—C312—C317	179.6 (2)		C42—N41—C411—C416	96.4 (2)
N31—C311—C312—C317	−6.5 (3)		C45—N41—C411—C416	−74.6 (3)
C311—C312—C313—C314	−0.9 (3)		C42—N41—C411—C412	−77.5 (2)
C317—C312—C313—C314	178.6 (2)		C45—N41—C411—C412	111.5 (2)
C312—C313—C314—C315	1.6 (4)		C416—C411—C412—C413	−1.2 (3)
C313—C314—C315—C316	−0.5 (4)		N41—C411—C412—C413	172.20 (18)
C314—C315—C316—C311	−1.2 (3)		C416—C411—C412—C420	−178.8 (2)
C314—C315—C316—C320	179.1 (2)		N41—C411—C412—C420	−5.4 (3)
C312—C311—C316—C315	1.9 (3)		C411—C412—C413—C414	−0.1 (3)
N31—C311—C316—C315	−171.89 (18)		C420—C412—C413—C414	177.6 (2)
C312—C311—C316—C320	−178.38 (19)		C412—C413—C414—C415	1.2 (4)
N31—C311—C316—C320	7.8 (3)		C413—C414—C415—C416	−0.9 (4)
C313—C312—C317—C318	48.8 (3)		C414—C415—C416—C411	−0.4 (8)
C311—C312—C317—C318	−131.7 (2)		C414—C415—C416—C417	−177.4 (2)
C313—C312—C317—C319	−74.6 (3)		C412—C411—C416—C415	1.5 (3)
C311—C312—C317—C319	104.8 (3)		N41—C411—C416—C415	−172.09 (18)
C315—C316—C320—C321	85.1 (3)		C412—C411—C416—C417	178.3 (2)
C311—C316—C320—C321	−94.6 (2)		N41—C411—C416—C417	4.8 (3)
C315—C316—C320—C322	−39.6 (3)		C415—C416—C417—C419	−58.4 (3)
C311—C316—C320—C322	140.7 (2)		C411—C416—C417—C419	124.8 (2)
C45—N41—C42—N43	−1.0 (2)		C415—C416—C417—C418	65.7 (3)
C411—N41—C42—N43	−173.61 (17)		C411—C416—C417—C418	−111.1 (3)
N41—C42—N43—C44	0.8 (2)		C413—C412—C420—C421	49.7 (3)
N41—C42—N43—C431	178.48 (17)		C411—C412—C420—C421	−132.8 (2)
C42—N43—C44—C45	−0.3 (2)		C413—C412—C420—C422	−73.2 (3)
C431—N43—C44—C45	−177.80 (18)		C411—C412—C420—C422	104.4 (2)
N43—C44—C45—N41	−0.4 (2)		C42—N43—C431—C432	−90.5 (2)
N43—C44—C45—PD3	179.84 (13)		C44—N43—C431—C432	86.8 (3)
C42—N41—C45—C44	0.8 (2)		C42—N43—C431—C436	87.2 (2)
C411—N41—C45—C44	172.47 (19)		C44—N43—C431—C436	−95.6 (2)
C42—N41—C45—PD3	−179.36 (15)		C436—C431—C432—C433	−1.7 (3)
C411—N41—C45—PD3	−7.7 (3)		N43—C431—C432—C433	175.77 (18)
CL32—PD3—C45—C44	124.96 (18)		C436—C431—C432—C437	180.0 (2)
CL31—PD3—C45—C44	−56.32 (18)		N43—C431—C432—C437	−2.5 (3)
CL32—PD3—C45—N41	−54.79 (17)		C431—C432—C433—C434	0.5 (3)
CL31—PD3—C45—N41	123.92 (18)		C437—C432—C433—C434	178.9 (2)
C32—N33—C331—C336	99.5 (2)		C432—C433—C434—C435	0.6 (3)
C34—N33—C331—C336	−76.2 (2)		C433—C434—C435—C436	−0.7 (3)
C32—N33—C331—C332	−86.3 (2)		C434—C435—C436—C431	−0.4 (3)
C34—N33—C331—C332	98.1 (2)		C434—C435—C436—C440	−179.8 (2)
C336—C331—C332—C333	−0.4 (3)		C432—C431—C436—C435	1.7 (3)
N33—C331—C332—C333	−174.40 (17)		N43—C431—C436—C435	−175.80 (18)
C336—C331—C332—C337	177.61 (18)		C432—C431—C436—C440	−179.0 (2)
N33—C331—C332—C337	3.6 (3)		N43—C431—C436—C440	3.5 (3)

C431—C432—C437—C438	111.3 (2)		C435—C436—C440—C441	−57.7 (3)
C433—C432—C437—C438	−67.0 (3)		C431—C436—C440—C441	123.0 (2)
C431—C432—C437—C439	−125.8 (2)		C435—C436—C440—C442	66.6 (3)
C433—C432—C437—C439	56.0 (3)		C431—C436—C440—C442	−112.7 (2)

Annexe VIII - Analyse crystallographique complète pour IPr$_2$Pd$_2$Cl$_4$ normal

Structure of CHA106 (avec SQUEEZE)

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Abstract

To finish the structure, it was decided to use the *PLATON* (Spek, 2000) facility SQUEEZE to handle the disordered solvent. *PLATON* identified a remarkably large potential solvent volume of 415.4 Å^3, or 13.6% of the cell volume. The use of *PLATON*/SQUEEZE resulted in a 2.6% improvement in R1 while correcting for 99 electrons/cell. The reported structure is based on the *PLATON*/SQUEEZE corrected data. The actual solvent content is unknown, so several quantities reported in Table 1 [empirical formula, density, absorption coefficient, $F(000)$] are incorrect and should be indicated as such in future publications.

Comment

Here should be written the text of the article

Experimental

Small details about the preparation of the compound.

Crystal data

$C_{54}H_{72}Cl_4N_4Pd_2$

$M_r = 1131.80$

Monoclinic

$P2_1/n$

$a = 13.5150\,(3)$ Å

$b = 14.4146\,(3)$ Å

$c = 15.7738\,(4)$ Å

$\beta = 97.021\,(2)^\circ$

$V = 3049.90\,(12)$ Å^3

$Z = 2$

$D_x = 1.232$ Mg m^{-3}

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 19965 reflections

$\theta = 2.82$–72.94°

$\mu = 6.620$ mm^{-1}

$T = 220\,(2)$ K

Block

Orange

$0.50 \times 0.25 \times 0.25$ mm

Crystal source: synthesized by the authors.
  See text

Data collection

Bruker AXS Smart 2K/Platform diffractom-
  eter

ω scans

Absorption correction:
  multi-scan Sadabs (Sheldrick,1996)
  $T_{\min} = 0.1300$, $T_{\max} = 0.3700$

24717 measured reflections

5999 independent reflections

5480 reflections with
  $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 72.93^\circ$

$h = -16 \rightarrow 16$

$k = -17 \rightarrow 17$

$l = -18 \rightarrow 19$

288 standard reflections

every ? reflections
  intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0386$

$wR(F^2) = 0.1037$

$S = 1.036$

5999 reflections

297 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.850$ e Å^{-3}

$\Delta\rho_{\min} = -1.188$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables
  for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd—C2	1.965 (2)	C15—C16	1.392 (4)
Pd—Cl1	2.2668 (7)	C16—C161	1.524 (4)
Pd—Cl2	2.3154 (6)	C121—C122	1.531 (6)
Pd—Cl2^i	2.4070 (6)	C121—C123	1.534 (5)
Cl2—Pd^i	2.4070 (6)	C161—C163	1.520 (5)
N1—C2	1.353 (3)	C161—C162	1.538 (5)
N1—C5	1.384 (3)	C31—C32	1.393 (4)
N1—C11	1.449 (3)	C31—C36	1.398 (4)
C2—N3	1.348 (3)	C32—C33	1.404 (4)
N3—C4	1.393 (3)	C32—C321	1.507 (5)
N3—C31	1.451 (3)	C33—C34	1.373 (5)
C4—C5	1.336 (4)	C34—C35	1.369 (5)
C11—C16	1.388 (4)	C35—C36	1.397 (4)
C11—C12	1.395 (4)	C36—C361	1.514 (5)
C12—C13	1.394 (4)	C321—C323	1.503 (7)
C12—C121	1.521 (5)	C321—C322	1.536 (7)
C13—C14	1.360 (6)	C361—C363	1.524 (5)
C14—C15	1.380 (5)	C361—C362	1.536 (4)

C2—PD—CL1	89.57 (7)	C11—C16—C15	116.7 (3)
C2—PD—CL2	93.18 (7)	C11—C16—C161	123.6 (2)
CL1—PD—CL2	177.16 (2)	C15—C16—C161	119.7 (3)
C2—PD—CL2^i	177.98 (7)	C12—C121—C122	110.0 (3)
CL1—PD—CL2^i	91.61 (2)	C12—C121—C123	113.0 (3)
CL2—PD—CL2^i	85.66 (2)	C122—C121—C123	111.4 (3)
PD—CL2—PD^i	94.34 (2)	C163—C161—C16	113.3 (3)
C2—N1—C5	110.4 (2)	C163—C161—C162	109.9 (3)
C2—N1—C11	127.06 (19)	C16—C161—C162	109.7 (3)
C5—N1—C11	122.5 (2)	C32—C31—C36	123.8 (2)
N3—C2—N1	105.14 (19)	C32—C31—N3	118.0 (2)
N3—C2—PD	129.13 (17)	C36—C31—N3	117.8 (2)
N1—C2—PD	125.72 (16)	C31—C32—C33	116.9 (3)
C2—N3—C4	110.6 (2)	C31—C32—C321	123.9 (3)
C2—N3—C31	129.5 (2)	C33—C32—C321	119.1 (3)
C4—N3—C31	119.9 (2)	C34—C33—C32	120.5 (3)
C5—C4—N3	106.6 (2)	C35—C34—C33	121.1 (3)
C4—C5—N1	107.3 (2)	C34—C35—C36	121.5 (3)
C16—C11—C12	123.3 (2)	C35—C36—C31	116.2 (3)
C16—C11—N1	118.7 (2)	C35—C36—C361	120.0 (3)
C12—C11—N1	117.7 (2)	C31—C36—C361	123.8 (2)
C13—C12—C11	117.2 (3)	C323—C321—C32	112.5 (4)
C13—C12—C121	120.0 (3)	C323—C321—C322	112.0 (4)
C11—C12—C121	122.7 (3)	C32—C321—C322	110.0 (4)
C14—C13—C12	120.9 (3)	C36—C361—C363	110.6 (3)
C13—C14—C15	120.8 (3)	C36—C361—C362	113.1 (3)
C14—C15—C16	121.2 (3)	C363—C361—C362	109.5 (3)

Symmetry codes: (i) $-x, 1-y, -z$.

All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters. The H atoms were generated geometrically (C—H 0.93 to 0.99 Å) and were included in the refinement in the riding model approximation; their temperature factors were set to 1.5 times those of the equivalent isotropic temperature factors of the parent site (methyl) and 1.2 times for others. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 2000).

Data collection: SMART (Bruker, 1999). Cell refinement: SMART (Bruker, 1999). Data reduction: SAINT (Bruker, 1999). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: UdMX (local program).

Supplementary data for this paper are available from the IUCr electronic archives (Reference:). Services for accessing these data are described at the back of the journal.

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Fig 1 *ORTEP* view of the title compound. Thermal ellipsoids are shown at 30% probability levels.

Table 1. Selected geometric parameters (Å, °) for the title compound.

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

<div align="center">http://journals.iucr.org/c/journalhomepage.html</div>

Table S1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	0.080393 (11)	0.536934 (10)	0.087425 (10)	0.02752 (9)
Cl1	0.20557 (6)	0.46705 (4)	0.17294 (5)	0.04929 (18)
Cl2	−0.04712 (5)	0.60239 (4)	−0.00473 (4)	0.04208 (15)
N1	0.03745 (14)	0.68902 (13)	0.20423 (13)	0.0316 (4)
C2	0.10259 (16)	0.65078 (15)	0.15563 (14)	0.0279 (4)
N3	0.18357 (15)	0.70615 (13)	0.16648 (14)	0.0337 (4)
C4	0.1689 (2)	0.77913 (18)	0.2214 (2)	0.0439 (6)
H4	0.2142	0.8270	0.2387	0.053
C5	0.0780 (2)	0.76781 (18)	0.24488 (19)	0.0430 (6)
H5	0.0473	0.8062	0.2821	0.052
C11	−0.05949 (18)	0.65321 (17)	0.21801 (15)	0.0348 (5)
C12	−0.0624 (2)	0.57943 (19)	0.27488 (18)	0.0433 (6)
C13	−0.1560 (3)	0.5492 (2)	0.2916 (3)	0.0611 (9)
H13	−0.1609	0.4989	0.3287	0.073
C14	−0.2404 (3)	0.5916 (3)	0.2548 (3)	0.0705 (10)
H14	−0.3030	0.5702	0.2668	0.085
C15	−0.2354 (2)	0.6658 (3)	0.2002 (2)	0.0584 (8)
H15	−0.2946	0.6948	0.1762	0.070
C16	−0.1442 (2)	0.69843 (19)	0.18000 (18)	0.0417 (6)
C121	0.0313 (3)	0.5366 (2)	0.3224 (2)	0.0537 (8)
H121	0.0872	0.5508	0.2894	0.064
C122	0.0550 (4)	0.5821 (4)	0.4102 (3)	0.0859 (13)
H12A	0.0683	0.6476	0.4031	0.129
H12B	0.1133	0.5528	0.4410	0.129
H12C	−0.0014	0.5748	0.4423	0.129
C123	0.0250 (4)	0.4307 (3)	0.3299 (4)	0.0866 (14)
H12D	−0.0274	0.4145	0.3640	0.130
H12E	0.0882	0.4068	0.3569	0.130
H12F	0.0103	0.4039	0.2733	0.130
C161	−0.1414 (2)	0.7818 (2)	0.1208 (2)	0.0539 (8)
H161	−0.0754	0.7827	0.0997	0.065
C162	−0.1519 (4)	0.8718 (3)	0.1713 (4)	0.0843 (13)
H16A	−0.2117	0.8886	0.1996	0.126
H16B	−0.1566	0.9242	0.1324	0.126
H16C	−0.0942	0.8793	0.2137	0.126
C163	−0.2208 (3)	0.7782 (3)	0.0438 (3)	0.0761 (11)
H16D	−0.2181	0.7186	0.0156	0.114
H16E	−0.2089	0.8273	0.0043	0.114
H16F	−0.2861	0.7864	0.0624	0.114
C31	0.27598 (18)	0.69972 (17)	0.12871 (19)	0.0380 (5)
C32	0.2767 (2)	0.7324 (2)	0.0457 (2)	0.0507 (7)
C33	0.3697 (2)	0.7370 (3)	0.0147 (2)	0.0605 (8)
H33	0.3736	0.7587	−0.0409	0.073
C34	0.4548 (2)	0.7099 (2)	0.0652 (3)	0.0617 (9)
H34	0.5166	0.7146	0.0439	0.074
C35	0.4511 (2)	0.6762 (2)	0.1458 (2)	0.0552 (8)
H35	0.5103	0.6566	0.1783	0.066
C36	0.36127 (19)	0.67030 (18)	0.18096 (19)	0.0415 (6)
C321	0.1849 (3)	0.7642 (3)	−0.0107 (3)	0.0731 (11)
H321	0.1264	0.7443	0.0167	0.088
C322	0.1826 (4)	0.8706 (4)	−0.0155 (4)	0.111 (2)

H32A	0.2420	0.8927	−0.0380	0.166
H32B	0.1805	0.8959	0.0413	0.166
H32C	0.1239	0.8904	−0.0527	0.166
C323	0.1759 (4)	0.7206 (5)	−0.0979 (3)	0.111 (2)
H32D	0.2338	0.7368	−0.1256	0.167
H32E	0.1162	0.7434	−0.1319	0.167
H32F	0.1718	0.6537	−0.0925	0.167
C361	0.3608 (2)	0.6370 (2)	0.2719 (2)	0.0503 (7)
H361	0.2909	0.6228	0.2802	0.060
C362	0.4228 (3)	0.5487 (2)	0.2920 (3)	0.0690 (11)
H36A	0.4064	0.5036	0.2468	0.103
H36B	0.4082	0.5229	0.3459	0.103
H36C	0.4932	0.5639	0.2960	0.103
C363	0.3979 (3)	0.7131 (3)	0.3350 (3)	0.0717 (10)
H36D	0.4611	0.7367	0.3210	0.107
H36E	0.4067	0.6879	0.3925	0.107
H36F	0.3495	0.7631	0.3317	0.107

Table 52. *Anisotropic displacement parameters* (Å^2)

|	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.02770 (12)	0.02185 (12)	0.03239 (12)	0.00157 (5)	0.00116 (8)	−0.00231 (5)
Cl1	0.0492 (4)	0.0312 (3)	0.0614 (4)	0.0067 (2)	−0.0175 (3)	0.0003 (3)
Cl2	0.0473 (3)	0.0281 (3)	0.0466 (3)	0.0110 (2)	−0.0117 (3)	−0.0091 (2)
N1	0.0314 (9)	0.0230 (8)	0.0412 (10)	−0.0017 (7)	0.0076 (8)	−0.0042 (8)
C2	0.0274 (10)	0.0223 (9)	0.0337 (10)	−0.0001 (8)	0.0019 (8)	0.0011 (8)
N3	0.0277 (9)	0.0251 (9)	0.0484 (11)	−0.0021 (7)	0.0045 (8)	−0.0005 (8)
C4	0.0387 (13)	0.0296 (12)	0.0631 (16)	−0.0059 (10)	0.0056 (12)	−0.0128 (12)
C5	0.0436 (14)	0.0295 (12)	0.0571 (15)	−0.0027 (10)	0.0114 (12)	−0.0134 (11)
C11	0.0342 (12)	0.0305 (11)	0.0416 (12)	−0.0054 (9)	0.0126 (10)	−0.0063 (10)
C12	0.0510 (15)	0.0369 (13)	0.0439 (13)	−0.0070 (11)	0.0130 (12)	−0.0009 (11)
C13	0.061 (2)	0.0584 (18)	0.068 (2)	−0.0176 (16)	0.0245 (17)	0.0096 (16)
C14	0.0463 (18)	0.082 (2)	0.088 (3)	−0.0151 (17)	0.0291 (18)	0.011 (2)
C15	0.0365 (14)	0.065 (2)	0.075 (2)	0.0010 (14)	0.0166 (14)	−0.0019 (17)
C16	0.0361 (13)	0.0397 (13)	0.0520 (14)	0.0012 (10)	0.0158 (11)	−0.0051 (12)
C121	0.061 (2)	0.0504 (18)	0.0511 (17)	−0.0009 (13)	0.0120 (15)	0.0132 (13)
C122	0.098 (3)	0.096 (3)	0.060 (2)	0.002 (3)	−0.006 (2)	0.005 (2)
C123	0.106 (3)	0.049 (2)	0.107 (3)	0.008 (2)	0.021 (3)	0.029 (2)
C161	0.0410 (15)	0.0426 (15)	0.080 (2)	0.0148 (12)	0.0167 (14)	0.0108 (15)
C162	0.084 (3)	0.0416 (18)	0.128 (4)	0.0170 (18)	0.017 (3)	−0.005 (2)
C163	0.058 (2)	0.083 (3)	0.086 (3)	0.026 (2)	0.0057 (19)	0.022 (2)
C31	0.0263 (11)	0.0301 (11)	0.0587 (15)	−0.0049 (9)	0.0099 (10)	−0.0046 (11)
C32	0.0386 (14)	0.0526 (16)	0.0624 (17)	−0.0082 (12)	0.0122 (13)	0.0023 (14)
C33	0.0515 (18)	0.066 (2)	0.0676 (19)	−0.0146 (15)	0.0225 (16)	−0.0011 (17)
C34	0.0372 (15)	0.0635 (19)	0.089 (2)	−0.0089 (14)	0.0249 (16)	−0.0161 (18)
C35	0.0282 (13)	0.0506 (16)	0.087 (2)	−0.0002 (12)	0.0069 (14)	−0.0134 (16)
C36	0.0297 (12)	0.0315 (12)	0.0623 (16)	−0.0031 (9)	0.0021 (11)	−0.0105 (11)
C321	0.0485 (18)	0.102 (3)	0.069 (2)	−0.0041 (19)	0.0093 (16)	0.035 (2)
C322	0.093 (4)	0.106 (4)	0.132 (5)	0.023 (3)	0.010 (3)	0.055 (4)
C323	0.076 (3)	0.185 (6)	0.069 (3)	−0.007 (4)	−0.006 (2)	0.013 (3)
C361	0.0419 (14)	0.0422 (15)	0.0635 (18)	0.0010 (12)	−0.0064 (13)	−0.0015 (14)
C362	0.058 (2)	0.0529 (19)	0.089 (3)	0.0073 (15)	−0.021 (2)	0.0023 (18)
C363	0.084 (3)	0.058 (2)	0.068 (2)	0.0012 (19)	−0.0098 (19)	−0.0107 (18)

Table S3. Geometric parameters ($\mathring{A}$, °)

Pd—C2	1.965 (2)	C161—H161	0.99
Pd—Cl1	2.2668 (7)	C162—H16a	0.97
Pd—Cl2	2.3154 (6)	C162—H16b	0.97
Pd—Cl2^i	2.4070 (6)	C162—H16c	0.97
Cl2—Pd^i	2.4070 (6)	C163—H16d	0.97
N1—C2	1.353 (3)	C163—H16e	0.97
N1—C5	1.384 (3)	C163—H16f	0.97
N1—C11	1.449 (3)	C31—C32	1.393 (4)
C2—N3	1.348 (3)	C31—C36	1.398 (4)
N3—C4	1.393 (3)	C32—C33	1.404 (4)
N3—C31	1.451 (3)	C32—C321	1.507 (5)
C4—C5	1.336 (4)	C33—C34	1.373 (5)
C4—H4	0.94	C33—H33	0.94
C5—H5	0.94	C34—C35	1.369 (5)
C11—C16	1.388 (4)	C34—H34	0.94
C11—C12	1.395 (4)	C35—C36	1.397 (4)
C12—C13	1.394 (4)	C35—H35	0.94
C12—C121	1.521 (5)	C36—C361	1.514 (5)
C13—C14	1.360 (6)	C321—C323	1.503 (7)
C13—H13	0.94	C321—C322	1.536 (7)
C14—C15	1.380 (5)	C321—H321	0.99
C14—H14	0.94	C322—H32a	0.97
C15—C16	1.392 (4)	C322—H32b	0.97
C15—H15	0.94	C322—H32c	0.97
C16—C161	1.524 (4)	C323—H32d	0.97
C121—C122	1.531 (6)	C323—H32e	0.97
C121—C123	1.534 (5)	C323—H32f	0.97
C121—H121	0.99	C361—C363	1.524 (5)
C122—H12a	0.97	C361—C362	1.536 (4)
C122—H12b	0.97	C361—H361	0.99
C122—H12c	0.97	C362—H36a	0.97
C123—H12d	0.97	C362—H36b	0.97
C123—H12e	0.97	C362—H36c	0.97
C123—H12f	0.97	C363—H36d	0.97
C161—C163	1.520 (5)	C363—H36e	0.97
C161—C162	1.538 (5)	C363—H36f	0.97
C2—PD—CL1	89.57 (7)	C13—C12—C11	117.2 (3)
C2—PD—CL2	93.18 (7)	C13—C12—C121	120.0 (3)
CL1—PD—CL2	177.16 (2)	C11—C12—C121	122.7 (3)
C2—PD—CL2^i	177.98 (7)	C14—C13—C12	120.9 (3)
CL1—PD—CL2^i	91.61 (2)	C14—C13—H13	119.6
CL2—PD—CL2^i	85.66 (2)	C12—C13—H13	119.6
PD—CL2—PD^i	94.34 (2)	C13—C14—C15	120.8 (3)
C2—N1—C5	110.4 (2)	C13—C14—H14	119.6
C2—N1—C11	127.06 (19)	C15—C14—H14	119.6
C5—N1—C11	122.5 (2)	C14—C15—C16	121.2 (3)
N3—C2—N1	105.14 (19)	C14—C15—H15	119.4
N3—C2—PD	129.13 (17)	C16—C15—H15	119.4
N1—C2—PD	125.72 (16)	C11—C16—C15	116.7 (3)
C2—N3—C4	110.6 (2)	C11—C16—C161	123.6 (2)
C2—N3—C31	129.5 (2)	C15—C16—C161	119.7 (3)
C4—N3—C31	119.9 (2)	C12—C121—C122	110.0 (3)
C5—C4—N3	106.6 (2)	C12—C121—C123	113.0 (3)
C5—C4—H4	126.7	C122—C121—C123	111.4 (3)
N3—C4—H4	126.7	C12—C121—H121	107.4
C4—C5—N1	107.3 (2)	C122—C121—H121	107.4
C4—C5—H5	126.3	C123—C121—H121	107.4
N1—C5—H5	126.3	C121—C122—H12A	109.5
C16—C11—C12	123.3 (2)	C121—C122—H12B	109.5
C16—C11—N1	118.7 (2)	H12A—C122—H12B	109.5
C12—C11—N1	117.7 (2)	C121—C122—H12C	109.5

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H12A—C122—H12C	109.5	C36—C35—H35	119.3
H12B—C122—H12C	109.5	C35—C36—C31	116.2 (3)
C121—C123—H12D	109.5	C35—C36—C361	120.0 (3)
C121—C123—H12E	109.5	C31—C36—C361	123.8 (2)
H12D—C123—H12E	109.5	C323—C321—C32	112.5 (4)
C121—C123—H12F	109.5	C323—C321—C322	112.0 (4)
H12D—C123—H12F	109.5	C32—C321—C322	110.0 (4)
H12E—C123—H12F	109.5	C323—C321—H321	107.4
C163—C161—C16	113.3 (3)	C32—C321—H321	107.4
C163—C161—C162	109.9 (3)	C322—C321—H321	107.4
C16—C161—C162	109.7 (3)	C321—C322—H32A	109.5
C163—C161—H161	107.9	C321—C322—H32B	109.5
C16—C161—H161	107.9	H32A—C322—H32B	109.5
C162—C161—H161	107.9	C321—C322—H32C	109.5
C161—C162—H16A	109.5	H32A—C322—H32C	109.5
C161—C162—H16B	109.5	H32B—C322—H32C	109.5
H16A—C162—H16B	109.5	C321—C323—H32D	109.5
C161—C162—H16C	109.5	C321—C323—H32E	109.5
H16A—C162—H16C	109.5	H32D—C323—H32E	109.5
H16B—C162—H16C	109.5	C321—C323—H32F	109.5
C161—C163—H16D	109.5	H32D—C323—H32F	109.5
C161—C163—H16E	109.5	H32E—C323—H32F	109.5
H16D—C163—H16E	109.5	C36—C361—C363	110.6 (3)
C161—C163—H16F	109.5	C36—C361—C362	113.1 (3)
H16D—C163—H16F	109.5	C363—C361—C362	109.5 (3)
H16E—C163—H16F	109.5	C36—C361—H361	107.8
C32—C31—C36	123.8 (2)	C363—C361—H361	107.8
C32—C31—N3	118.0 (2)	C362—C361—H361	107.8
C36—C31—N3	117.8 (2)	C361—C362—H36A	109.5
C31—C32—C33	116.9 (3)	C361—C362—H36B	109.5
C31—C32—C321	123.9 (3)	H36A—C362—H36B	109.5
C33—C32—C321	119.1 (3)	C361—C362—H36C	109.5
C34—C33—C32	120.5 (3)	H36A—C362—H36C	109.5
C34—C33—H33	119.8	H36B—C362—H36C	109.5
C32—C33—H33	119.8	C361—C363—H36D	109.5
C35—C34—C33	121.1 (3)	C361—C363—H36E	109.5
C35—C34—H34	119.5	H36D—C363—H36E	109.5
C33—C34—H34	119.5	C361—C363—H36F	109.5
C34—C35—C36	121.5 (3)	H36D—C363—H36F	109.5
C34—C35—H35	119.3	H36E—C363—H36F	109.5

C2—PD—CL2—PD[i]	−178.34 (6)		C14—C15—C16—C161	−178.8 (3)
CL2[i]—PD—CL2—PD[i]	0		C13—C12—C121—C122	−82.0 (4)
C5—N1—C2—N3	0.1 (3)		C11—C12—C121—C122	93.7 (4)
C11—N1—C2—N3	−176.7 (2)		C13—C12—C121—C123	43.2 (4)
C5—N1—C2—PD	178.78 (18)		C11—C12—C121—C123	−141.1 (3)
C11—N1—C2—PD	2.0 (3)		C11—C16—C161—C163	138.7 (3)
CL1—PD—C2—N3	63.8 (2)		C15—C16—C161—C163	−43.2 (4)
CL2—PD—C2—N3	−115.5 (2)		C11—C16—C161—C162	−98.0 (3)
CL1—PD—C2—N1	−114.62 (19)		C15—C16—C161—C162	80.1 (4)
CL2—PD—C2—N1	66.1 (2)		C2—N3—C31—C32	80.0 (3)
N1—C2—N3—C4	−0.3 (3)		C4—N3—C31—C32	−98.5 (3)
PD—C2—N3—C4	−178.93 (19)		C2—N3—C31—C36	−106.7 (3)
N1—C2—N3—C31	−178.8 (2)		C4—N3—C31—C36	74.8 (3)
PD—C2—N3—C31	2.5 (4)		C36—C31—C32—C33	−1.1 (4)
C2—N3—C4—C5	0.4 (3)		N3—C31—C32—C33	171.7 (3)
C31—N3—C4—C5	179.1 (3)		C36—C31—C32—C321	−180.0 (3)
N3—C4—C5—N1	−0.3 (3)		N3—C31—C32—C321	−7.1 (5)
C2—N1—C5—C4	0.2 (3)		C31—C32—C33—C34	0.1 (5)
C11—N1—C5—C4	177.2 (2)		C321—C32—C33—C34	179.0 (4)
C2—N1—C11—C16	−108.0 (3)		C32—C33—C34—C35	1.4 (6)
C5—N1—C11—C16	75.6 (3)		C33—C34—C35—C36	−1.8 (5)
C2—N1—C11—C12	77.3 (3)		C34—C35—C36—C31	0.7 (4)
C5—N1—C11—C12	−99.1 (3)		C34—C35—C36—C361	−177.0 (3)
C16—C11—C12—C13	1.8 (4)		C32—C31—C36—C35	0.8 (4)
N1—C11—C12—C13	176.2 (3)		N3—C31—C36—C35	−172.1 (2)
C16—C11—C12—C121	−174.0 (3)		C32—C31—C36—C361	178.4 (3)
N1—C11—C12—C121	0.4 (4)		N3—C31—C36—C361	5.5 (4)
C11—C12—C13—C14	−1.2 (5)		C31—C32—C321—C323	−130.3 (4)
C121—C12—C13—C14	174.7 (3)		C33—C32—C321—C323	50.9 (5)
C12—C13—C14—C15	−0.1 (6)		C31—C32—C321—C322	104.1 (4)
C13—C14—C15—C16	1.1 (6)		C33—C32—C321—C322	−74.7 (5)
C12—C11—C16—C15	−0.9 (4)		C35—C36—C361—C363	76.2 (4)
N1—C11—C16—C15	−175.3 (2)		C31—C36—C361—C363	−101.3 (3)
C12—C11—C16—C161	177.2 (3)		C35—C36—C361—C362	−47.0 (4)
N1—C11—C16—C161	2.8 (4)		C31—C36—C361—C362	135.4 (3)
C14—C15—C16—C11	−0.5 (5)			

Symmetry codes: (i) $-x, 1-y, -z$.

ANNEXE IX – Analyse crystallographique complète pour la coumarine cyclopropane
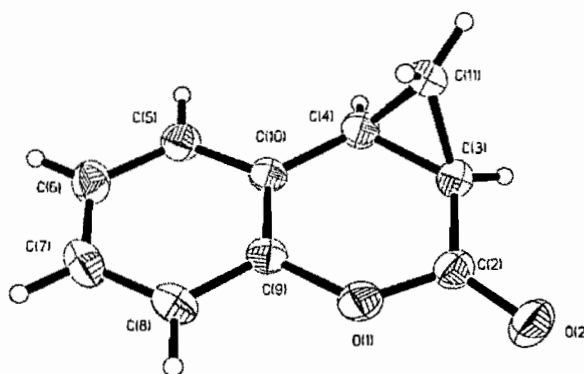
ANNEXE IX – Analyse crystallographique complète pour la coumarine cyclopropane
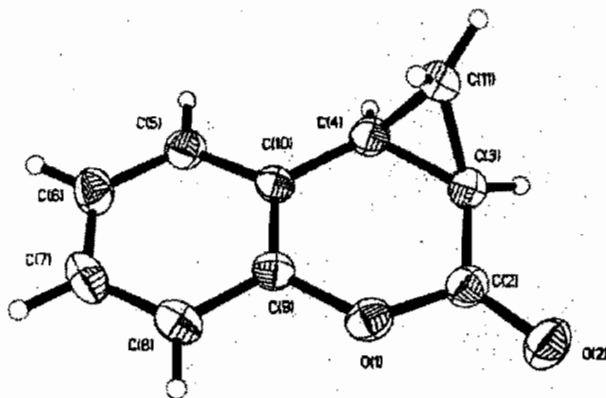
29 Jul 2005

Structure of CHA130

ANDR B. CHARETTE, MARC JANES AND FRANCINE BÉLANGER-GARIÉPY

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Abstract

Here should be written a short abstract

Comment

Here should be written the text of the article

Experimental

Small details about the preparation of the compound.

Crystal data

$C_{10}H_8O_2$

$M_r = 160.16$

Orthorhombic

$P2_12_12_1$

$a = 5.2410\,(10)$ Å

$b = 11.806\,(6)$ Å

$c = 12.403\,(7)$ Å

$V = 767.4\,(6)$ Å^3

$Z = 4$

$D_x = 1.386$ Mg m^{-3}

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 25 reflections

$\theta = 20.00–24.00°$

$\mu = 0.788$ mm^{-1}

$T = 293\,(2)$ K

Block

Colourless

$0.35 \times 0.26 \times 0.24$ mm

Crystal source: synthesized by the authors.

See text

Data collection
Enraf–Nonius–CAD-4 diffractometer
ω scans
Absorption correction:
  by integration Integration from crystal
  shape
  $T_{min} = 0.80$, $T_{max} = 0.85$
11630 measured reflections
1457 independent reflections

1286 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 69.92°$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
5 standard reflections
  frequency: 60 min
  intensity decay: 11.00%

Refinement
Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0270$
$wR(F^2) = 0.0724$
$S = 0.994$
1457 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.000$

$\Delta\rho_{max} = 0.091$ e Å^{-3}
$\Delta\rho_{min} = -0.102$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.052 (2)
Scattering factors from *International Tables*
  for Crystallography (Vol. C)
Absolute structure: Flack H D (1983), XXXX
  Friedel Pairs
Flack parameter = 0.0 (3)

Table 1. *Selected geometric parameters* (Å, °)

O1—C2	1.3642 (19)	C4—C11	1.499 (2)
O1—C9	1.3983 (16)	C5—C6	1.382 (2)
C2—O2	1.2042 (16)	C5—C10	1.3873 (19)
C2—C3	1.460 (2)	C6—C7	1.381 (2)
C3—C4	1.503 (2)	C7—C8	1.371 (2)
C3—C11	1.511 (2)	C8—C9	1.3771 (19)
C4—C10	1.4748 (18)	C9—C10	1.3780 (18)
C2—O1—C9	122.17 (10)	C7—C6—C5	119.69 (16)
O2—C2—O1	116.94 (14)	C8—C7—C6	120.42 (15)
O2—C2—C3	124.20 (15)	C7—C8—C9	119.00 (14)
O1—C2—C3	118.85 (13)	C8—C9—C10	122.27 (13)
C2—C3—C4	119.63 (13)	C8—C9—O1	115.28 (12)
C2—C3—C11	117.89 (14)	C10—C9—O1	122.44 (12)
C4—C3—C11	59.65 (10)	C9—C10—C5	117.73 (13)
C10—C4—C11	117.61 (13)	C9—C10—C4	120.03 (12)
C10—C4—C3	115.78 (11)	C5—C10—C4	122.18 (12)
C11—C4—C3	60.45 (10)	C4—C11—C3	59.91 (10)
C6—C5—C10	120.86 (14)		

C9—O1—C2—O2	−169.27 (12)	C2—O1—C9—C8	172.73 (13)
C9—O1—C2—C3	11.95 (18)	C2—O1—C9—C10	−6.85 (18)
O2—C2—C3—C4	173.82 (14)	C8—C9—C10—C5	0.0 (2)
O1—C2—C3—C4	−7.49 (19)	O1—C9—C10—C5	179.60 (13)
O2—C2—C3—C11	−117.07 (17)	C8—C9—C10—C4	177.38 (13)
O1—C2—C3—C11	61.62 (17)	O1—C9—C10—C4	−3.06 (19)
C2—C3—C4—C10	−1.64 (19)	C6—C5—C10—C9	1.3 (2)
C11—C3—C4—C10	−108.53 (16)	C6—C5—C10—C4	−176.02 (14)
C2—C3—C4—C11	106.89 (16)	C11—C4—C10—C9	−61.77 (18)
C10—C5—C6—C7	−1.1 (2)	C3—C4—C10—C9	6.79 (19)
C5—C6—C7—C8	−0.3 (2)	C11—C4—C10—C5	115.45 (16)
C6—C7—C8—C9	1.6 (2)	C3—C4—C10—C5	−175.99 (13)
C7—C8—C9—C10	−1.4 (2)	C10—C4—C11—C3	105.52 (14)
C7—C8—C9—O1	178.96 (13)	C2—C3—C11—C4	−109.78 (15)

All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters. The H atoms were generated geometrically (C—H 0.93 to 0.98 Å) and were included in the refinement in the riding model approximation; their temperature factors were set to 1.2 times those of the equivalent isotropic temperature factors of the parent site. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 2000).

Data collection: CAD-4 Program (Nonius 1989). Cell refinement: CAD-4 Program (Nonius 1989). Data reduction: Local Program. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: UdMX (local program).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: PREVIEW). Services for accessing these data are described at the back of the journal.

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Fig 1 *ORTEP* view of the title compound. Thermal ellipsoids are shown at 30% probability levels.

Table 1. Selected geometric parameters (Å, °) for the title compound.