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Préparation, caractérisation et étude de réactivité de complexes de nickel comportant un ligand de type « pincer »

par

Annie Castonguay

Département de Chimie

Faculté des Arts et des Sciences

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présentée par :
Annie Castonguay

a été évaluée par un jury composé des personnes suivantes :

Garry Hanan, président-rapporteur
Davit Zargarian, directeur de recherche
André L. Beauchamp, co-directeur
Frank Schaper, membre du jury
William D. Jones, examinateur externe
François Schiettekatte, représentant du doyen de la FES

Résumé

Une variété de complexes de nickel(II) et de nickel(III) a été préparée, la majorité d'entre eux étant composée de deux ou de trois ligands : un premier ligand anionique tridentate de type « pincer », lié au métal par deux atomes de phosphore ainsi que par un atome de carbone (PCP), de même que d'un second ligand (et dans quelques cas d'un troisième ligand), X, aussi anionique(s). À des fins de comparaison, certains des complexes (PCP)NiX préparés différaient seulement à des endroits spécifiques du ligand PCP (au niveau des substituents sur les atomes de phosphore, de la nature du carbone cyclométallé, etc.).

Les premiers complexes métalliques préparés comportent un ligand « pincer » doté d'un carbone cyclométallé d'hybridation sp^3 et des groupements *t*-Bu sur les atomes de phosphore (1,5-bis(di-*tert*-butylphosphino)pentane, $PC_{sp3}P^{t\text{-}Bu}$). La synthèse de ces composés $(PC_{sp3}P^{t\text{-}Bu})NiX$ menant à de faibles rendements ainsi qu'à la formation de sous-produits de protonation de type $(HPC_{sp3}P^{t\text{-}Bu})NiX_3$ et $(HPC_{sp3}PH^{t\text{-}Bu})NiX_4$ s'avérant difficile à éviter, la modification du ligand a été envisagée. La préparation d'une série de complexes $(PC_{sp3}P^{i\text{-}Pr})NiX$ comportant un ligand « pincer » similaire (1,5-bis(di-*iso*-propylphosphino)pentane) mais dont les phosphores sont substitués par des groupements moins encombrés mais aussi moins électrodonneurs, *i*-Pr, a alors été effectuée. Cette modification n'a pas mené à de meilleurs rendements pour les complexes cibles, mais le sous-produit bimétallique obtenu en parallèle de ces réactions, soit $(PC_{sp3}P^{i\text{-}Pr})_2Ni_2X_4$, s'est avéré un bon précurseur pour leur préparation.

Certaines différences de réactivité ont été notés en ce qui a trait aux tentatives de préparation de dérivés $(PC_{sp3}P)NiR$ (R = Me, Ph, Bu) par la réaction de métathèse des présurseurs $(PC_{sp3}P)NiBr$ et des réactifs MeMgCl, PhMgBr et *n*-BuLi,

respectivement. Par exemple, il fut noté que la préparation de $(\mathrm{PC_{sp3}P}^{i\text{-Pr}})$NiMe s'effectue instantanément à la température ambiante tandis que celle de $(\mathrm{PC_{sp3}P}^{t\text{-Bu}})$NiMe nécessite un chauffage de 80 °C durant 1 h. Le complexe $(\mathrm{PC_{sp3}P}^{i\text{-Pr}})$NiPh se prépare par chauffage durant 1 h tandis que l'espèce $(\mathrm{PC_{sp3}P}^{t\text{-Bu}})$NiPh ne se forme pas, même en chauffant les réactifs sur une longue période. Finalement, le complexe $(\mathrm{PC_{sp3}P}^{i\text{-Pr}})$NiBu se prépare sans complication à la température de la pièce tandis que le composé $(\mathrm{PC_{sp3}P}^{t\text{-Bu}})$NiBu n'est jamais observé et subit une élimination β-H pour donner lieu à la formation de l'espèce $(\mathrm{PC_{sp3}P}^{t\text{-Bu}})$NiH. Aussi, d'autres dérivés neutres ont été préparés, dont les composés alcynyles $(\mathrm{PC_{sp3}P}^{i\text{-Pr}})$NiX (X = C≡CMe, C≡CPh).

Des voies de synthèse pour une série d'espèces cationiques ont aussi été mises au point à partir des précurseurs (PCP)NiBr comportant les ligands $\mathrm{PC_{sp3}P}^{t\text{-Bu}}$, $\mathrm{PC_{sp3}P}^{i\text{-Pr}}$, $\mathrm{PC_{sp2}P}^{i\text{-Pr}}$ (1,3-bis{(di-*iso*-propylphosphino)méthyl}benzène) et $\mathrm{POC_{sp2}OP}^{i\text{-Pr}}$ (1,3-bis(di-*iso*-propylphosphinito)benzène), un ligand analogue à $\mathrm{PC_{sp2}P}^{i\text{-Pr}}$, où deux atomes de carbone ont été remplacés pas des atomes d'oxygène. La préparation d'un complexe cationique basé sur un nouveau ligand, analogue au dernier mais dont le cycle aromatique a été substitué par deux atomes de chlore, $\mathrm{POC_{sp2}OP}^{i\text{-Pr}}\text{-}\mathrm{Cl_2}$ (1,3-dichloro-4,6-bis(di-*iso*-propylphosphinito)benzène), a aussi été effectuée. Une voie synthétique pour la formation de composés cationiques possédant des ligands stabilisants faibles a aussi été établie, faisant usage du précurseur neutre $(\mathrm{PC_{sp3}P}^{i\text{-Pr}})\mathrm{NiBF_4}$, composé possédant de faibles intéractions Ni-F.

La plupart des complexes préparés ont été caractérisés, en solution, par spectroscopie RMN et à l'état solide, par analyse élémentaire et diffraction des rayons X. À des fins de comparaison de la richesse électronique du métal, certains composés ont aussi été étudiés par voltammétrie cyclique.

La préparation de composés de nickel(III), état d'oxidation plutôt rare pour ce métal, fut possible par la réaction du précurseur le plus riche en électron parmi ceux qui ont été synthétisés, $(\mathrm{PC_{sp3}P}^{i\text{-Pr}})$NiBr, et des agents oxydants $\mathrm{FeX_3}$ (X = Cl, Br).

L'activité catalytique de certains des complexes synthétisés a été sondée. Il fut démontré que les composés « pincer » $(\mathrm{PC_{sp3}P^{\mathit{i}\text{-}Pr}})\mathrm{NiBr}$ et $(\mathrm{PC_{sp3}P^{\mathit{t}\text{-}Bu}})\mathrm{NiBr}$ sont d'efficaces catalyseurs pour le couplage de chlorobenzène et de MeMgCl, bien connue sous le nom de couplage de Kumada-Corriu, tandis que leur analogue $(\mathrm{PC_{sp2}P^{\mathit{i}\text{-}Pr}})\mathrm{NiBr}$ est presque inactif pour cette dernière. Il a aussi été établi que les composés $(\mathrm{PC_{sp3}P^{\mathit{t}\text{-}Bu}})\mathrm{NiMe}$ et $(\mathrm{PC_{sp3}P^{\mathit{t}\text{-}Bu}})\mathrm{NiH}$ peuvent oligomériser le $\mathrm{PhSiH_3}$ à la température de la pièce. Finalement, les complexes cationiques de type $[(\mathrm{PCP})\mathrm{Ni(NCCH_3)}][\mathrm{BPh_4}]$ peuvent efficacement catalyser la réaction d'hydroamination régiosélective de l'acrylonitrile avec aniline, résultant en le produit d'addition anti-Markovnikov.

Mots-clés : nickel, complexe « pincer », activation C-H, couplage de Kumada-Corriu, hydroamination des oléfines, oligomérisation des silanes, diffraction des rayons X, RMN, voltammétrie cyclique.

Abstract

A variety of nickel(II) and nickel(III) complexes has been prepared, most of them consisting of two or three ligands : a tridentate pincer–type anionic ligand, linked to the metal by two phosphorus atoms as well as by a carbon atom (PCP), and a second ligand (and in some cases, a third ligand), X, also anionic. In order to allow comparisons, some of the (PCP)NiX complexes prepared were differed only at specific positions of the PCP ligand (the phosphorus atom substituents, the nature of the cyclometallated carbon, etc.).

The first metallic complexes prepared bore a pincer ligand having a sp^3-hybridized cyclometallated carbon and *t*-Bu groups on the phosphorus atoms (1,5-bis(di-*tert*-butylphosphino)pentane, $PC_{sp3}P^{t\text{-Bu}}$). The synthesis of these compounds $(PC_{sp3}P^{t\text{-Bu}})NiX$ leading to low yields and also to the formation of by-products of protonation of type $(HPC_{sp3}P^{t\text{-Bu}})NiX_3$ and $(HPC_{sp3}PH^{t\text{-Bu}})NiX_4$ difficult to avoid, the modification of the ligand has been considered. The preparation of a series of complexes $(PC_{sp3}P^{i\text{-Pr}})NiX$ bearing a similar pincer ligand (1,5-bis(di-*iso*-propylphosphino)pentane), but with their phosphorus being substituted by less sterically hindered and also less electrodonor groups, *i*-Pr, has been achieved. This modification did not lead to better yields for the target complexes, but the bimetallic by-product generated from these reactions, $(PC_{sp3}P^{i\text{-Pr}})_2Ni_2X_4$, was found to be a good precursor for their preparation.

Some differences in the reactivities have been noted for the preparation of the derivatives $(PC_{sp3}P)NiR$ (R = Me, Ph, Bu) by the metathesis of the precursors $(PC_{sp3}P)NiBr$ and the reactants MeMgCl, PhMgBr and *n*-BuLi, respectively. For example, it has been noted that the preparation of $(PC_{sp3}P^{i\text{-Pr}})NiMe$ occurs instantaneouly at room temperature while the one of $(PC_{sp3}P^{t\text{-Bu}})NiMe$ requires heating at 80 °C for 1 h. The complex $(PC_{sp3}P^{i\text{-Pr}})NiPh$ can be prepared by heating during 1 h

while the species $(PC_{sp3}P^{t\text{-}Bu})NiPh$ does not form, even by heating the reactants over a long period of time. Finally, the complex $(PC_{sp3}P^{i\text{-}Pr})NiBu$ can be prepared without any problem at room temperature while the compound $(PC_{sp3}P^{t\text{-}Bu})NiBu$ is never observed and undergoes a β-H elimination leading to the formation of the species $(PC_{sp3}P^{t\text{-}Bu})NiH$. Also, other neutral derivatives have been prepared, including the alkynyl complexes $(PC_{sp3}P^{i\text{-}Pr})NiX$ (X = C≡CMe, C≡CPh).

Synthetic routes for a series of cationic species have also been established using the precursors (PCP)NiBr bearing the ligands $PC_{sp3}P^{t\text{-}Bu}$, $PC_{sp3}P^{i\text{-}Pr}$, $PC_{sp2}P^{i\text{-}Pr}$ (1,3-bis{(di-*iso*-propylphosphino)methyl}benzene) and $POC_{sp2}OP^{i\text{-}Pr}$ (1,3-bis(di-*iso*-propylphosphinito)benzene), a ligand analogous to $PC_{sp2}P^{i\text{-}Pr}$, where two carbon atoms have been replaced by oxygen atoms. The preparation of a cationic complex based on a new ligand, analogous to the latter but where the aromatic cycle has been substituted by two chloride atoms, $POC_{sp2}OP^{i\text{-}Pr}\text{-}Cl_2$ (1,3-dichloro-4,6-bis(di-*iso*-propylphosphinito)benzene), has also been achieved. Another synthetic pathway for the formation of cationic complexes bearing weak stabilizing ligands has also been established, using the neutral precursor $(PC_{sp3}P^{i\text{-}Pr})NiBF_4$, compound possessing weak Ni-F interactions.

Most of the complexes have been characterized, in solution, by NMR spectroscopy and in the solid state, by elemental analysis and X-ray diffraction. In order to compare the electronic richness of the metal, some compounds have also been studied by cyclic voltammetry.

The preparation of a nickel(III) species, an oxidation state which is quite rare for this metal, was possible by the reaction of a more electron-rich precursor among those which have been synthesized, $(PC_{sp3}P^{i\text{-}Pr})NiBr$, and the oxidizing agents FeX_3 (X = Cl, Br).

The catalytic activity of some of the complexes prepared has been screened. It has been shown that the pincer compounds $(PC_{sp3}P^{i\text{-}Pr})NiBr$ et $(PC_{sp3}P^{t\text{-}Bu})NiBr$ are efficient catalysts for the coupling of chlorobenzene and MeMgCl, well known under

the name of Kumada-Corriu coupling, while their analogue $(PC_{sp2}P^{i\text{-}Pr})NiBr$ is almost inactive for the latter. It has also been established that the compounds $(PC_{sp3}P^{t\text{-}Bu})NiMe$ and $(PC_{sp3}P^{t\text{-}Bu})NiH$ can oligomerize $PhSiH_3$ at room temperature. Finally, the cationic complexes of the type $[(PCP)Ni(NCCH_3)][BPh_4]$ can efficiently catalyze the regioselective hydroamination reaction of acrylonitrile with aniline, resulting in the anti-Markovnikov product.

Key-words : nickel, pincer complexes, C-H activation, Kumada-Corriu coupling, olefin hydroamination, silanes oligomerization, X-ray diffraction, NMR, cyclic voltammetry.

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Liste des abréviations

Å	Angstrom
δ	déplacement chimique
br	*broad*
Bu	butyle
cif	*cristallographic information file*
COD	1,5-cyclooctadiène
COSY	*correlation spectroscopy*
CV	*cyclic voltammetry*
d	doublet
DEPT	*distortionless enhancement by polarization transfer*
deg	degrés
DMAP	diméthylaminopyridine
é	électron
equiv	équivalents
Et	éthyle
F	facteur de structure
GC	*gas chromatography*
h	heure
HMQC	*heteronuclear multiple-quantum correlation*
HOMO	highest occupied molecular orbital
i	ipso
IR	infrarouge
J	constante de couplage
L	ligand neutre
m	méta

M	métal
m	multiplet
m/z	masse/charge
min	minute
Me	méthyle
NMR	*nuclear magnetic resonance*
n-Bu	*n*-butyle
o	ortho
ORTEP	*Oak ridge thermal ellipsoid program*
p	para
i-Pr	isopropyle
Ph	phényle
ppm	parties par million
q	quadruplet
quin	quintuplet
RMN	résonance magnétique nucléaire
s	singulet
MS	*mass spectrometry*
t	triplet
t-Bu	*tert*-butyle
TBAH	tetrabutylhexafluorophosphate
THF	tétrahydrofurane
TOF	*turnover frequency*
TON	*turnover number*
X	ligand anionique

À ceux qui m'ont soutenu au cours de
cette déterminante étape de ma vie…

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Chapitre 1: Introduction

La recherche sur les composés organométalliques a pris beaucoup d'expansion au cours des dernières années étant donné les propriétés intéressantes qu'ils comportent. Plusieurs de ces complexes métalliques servent de catalyseurs pour un bon nombre de réactions organiques importantes et offrent une efficacité ainsi qu'une sélectivité intéressantes. Toutefois, plusieurs d'entre eux sont instables à l'air ou en milieu humide et se décomposent à la chaleur. Le développement de méthodes synthétiques pour de nouveaux catalyseurs capables de supporter des températures élevées et ne nécessitant pas un entreposage sous atmosphère inerte présente un défi intéressant et serait un réel atout. En plus de la possibilité de mener à une diminution des coûts ainsi que du temps requis pour la préparation de molécules organiques (médicaments, chimie de synthèse, etc.) et de certains polymères (applications électroniques et médicales, etc.), la préparation de nouveaux complexes organométalliques pourrait permettre la synthèse de nouveaux matériaux ayant des propriétés qui sortent de l'ordinaire.

Un sujet d'actualité en chimie organométallique est celui des complexes dits « pincer ». Ces composés, initialement introduits par Shaw dans les années 1970,[1] sont reconnus pour leur grande stabilité thermique ainsi que leurs propriétés inusuelles. Ils sont notamment d'excellents catalyseurs pour une variété de réactions organiques d'intérêt.[2] Ils sont malheureusement restés dans l'ombre durant près de vingt ans avant que la communauté scientifique décide de les scruter de plus près. La présente thèse traitera de la préparation et de l'étude de la réactivité de ce type de complexe organométallique, plus particulièrement de composés à base de nickel.

Ce premier chapitre consiste en une présentation bibliographique permettant de situer le travail effectué par rapport à ce qui est présentement connu dans le domaine. De façon à en connaître davantage sur le métal dont il sera question, la première partie de ce chapitre sera consacrée à l'importance de ce dernier en catalyse. Après une de ce que l'on entend par complexe « pincer » seront aussi présentés quelques exemples des principales applications de ce type de complexe. Comme la thèse traitera plus particulièrement d'un type spécifique de complexes «pincer», ceux de type dit « PCP », une description de ce qui est connu dans la littérature pour cette sous-catégorie de composés du nickel suivra. Pour terminer, les objectifs de recherche de même qu'une description des travaux seront présentés.

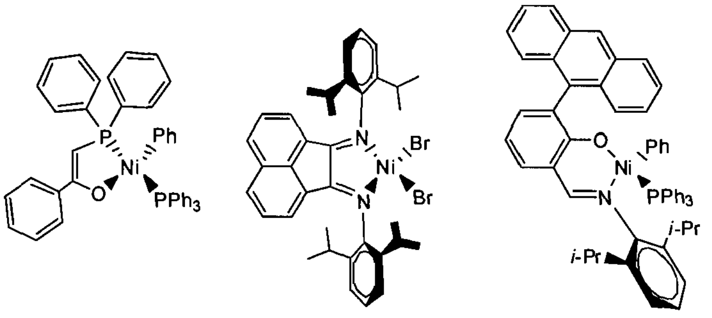
1.1 Potentiel catalytique du nickel

Le nickel est un métal relativement peu dispendieux et c'est l'une des raisons majeures pour laquelle l'étude de son potentiel en catalyse est très désirable. Ce métal s'est vu, jusqu'à ce jour, attribuer des propriétés surprenantes et certaines ont même été mises à profit par l'industrie où il se mérite maintenant une place importante. Parmi les nombreuses réactions catalysées par le nickel figurent l'hydrocyanation et l'hydrogénation hétérogène des oléfines, la polymérisation de l'éthylène ainsi que différentes réactions de couplage C-C.

1.1.1 La polymérisation de l'éthylène

La polymérisation de l'éthylène est efficacement effectuée par plusieurs catalyseurs de Ni^{II}, les plus importants étant présentés à la Figure 1.1. On y retrouve le complexe développé par Keim pour le procédé « SHOP » (« shell higher olefin process »),[3] celui de Brookhart[4] ainsi que celui de Grubbs.[5]

Ces complexes sont en fait des précatalyseurs puisque leur cycle catalytique respectif ne regénère pas le complexe initial. L'espèce active est habituellement un complexe hydrure ou bien alkyle. Un exemple de cycle catalytique pour la polymérisation de l'éthylène est illustré à la Figure 1.2.



Keim Brookhart Grubbs

Figure 1.1. Exemples de catalyseurs pour la polymérisation de l'éthylène.

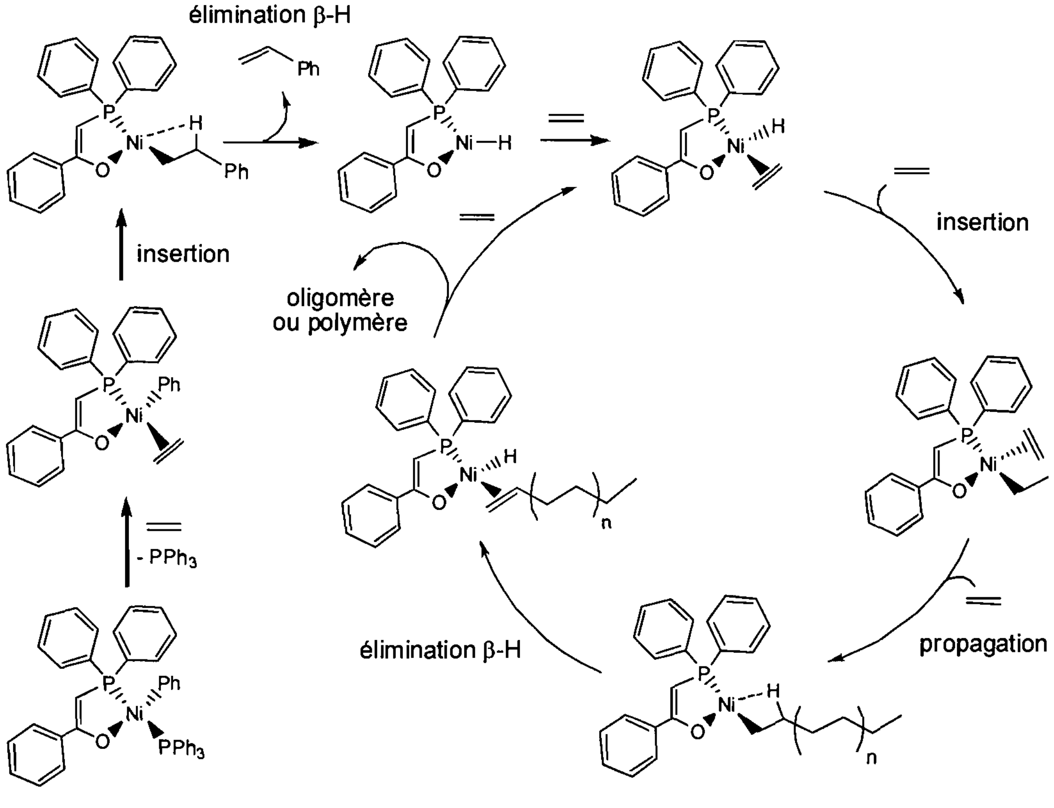


Figure 1.2. Exemple de cycle catalytique pour la polymérisation de l'éthylène.

1.1.1 Les réactions de couplage C-C

Le nickel est reconnu pour posséder une activité catalytique pour différentes réactions de couplage, menant à la formation de liaisons C-C, procédés qui sont vivement exploités en chimie organique de synthèse. Par exemple, tout comme le palladium, le nickel peut effectuer la réaction de couplage d'halogénures d'aryle ou de vinyle et de réactifs organométalliques des groupes principaux (Mg, Sn, B, Al, Li, etc) ou d'autres métaux de transition (Zn, Zr, etc).[6]

Un des premiers exemples de ce type de réaction de couplage fut la réaction de Kumada-Corriu,[7] qui consiste en le couplage d'un halogénure d'aryle, d'alkyle ou de vinyle (R'X), avec un réactif de Grignard (RMgX). Un complexe de Ni^{II} de la forme NiL_2X_2 (L = phosphine) est généralement utilisé et, par réaction avec le Grignard, forme un composé NiL_2R_2 qui, par élimination réductrice de R-R, génère le catalyseur. Le mécanisme généralement proposé (Figure 1.3) consiste en l'addition oxydante de l'halogénure d'aryle, d'alkyle ou de vinyle sur l'espèce de Ni^0 résultante, suivie de la transmétallation du réactif de Grignard avec le lien Ni-X nouvellement formé et de l'élimination réductrice subséquente du produit de couplage R-R'.

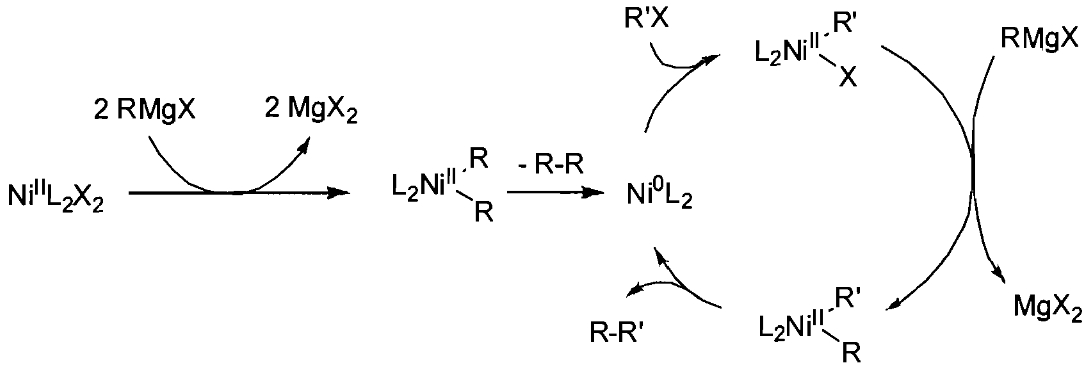


Figure 1.3. Mécanisme généralement accepté pour la réaction de couplage de Kumada-Corriu.

Certains avantages sont reliés à l'utilisation du nickel par rapport à son voisin du bas dans le tableau périodique en ce qui a trait aux réactions de couplage. Le nickel est moins dispendieux que le palladium et il facilite l'addition oxydante d'halogénures d'aryle qui le sont aussi, tels que Ar-Cl ou Ar-Br. Un autre atout important du nickel est qu'il est moins disposé à l'élimination β-H, réaction qui peut faire compétition aux réactions de couplage désirées.[6]

Il est intéressant de noter que certaines études menées par Koshi[8] concernant la réaction de couplage d'halogénures d'aryle menant à la formation de biaryles catalysée par le nickel démontrent l'implication d'un processus radicalaire de réactions en chaîne où les étapes importantes du mécanisme sont l'addition oxydante de l'halogénure d'aryle sur une espèce de Ni^{I} et l'élimination réductrice subséquente du composé biaryle de Ni^{III} généré. Il faut alors rester vigilant avec le mécanisme présenté à la Figure 1.3 puisque l'implication d'un cycle de Ni^{I}/Ni^{III} n'est pas exclue en ce qui a trait aux réactions impliquant les réactifs de Grignard (Figure 1.4).[6]

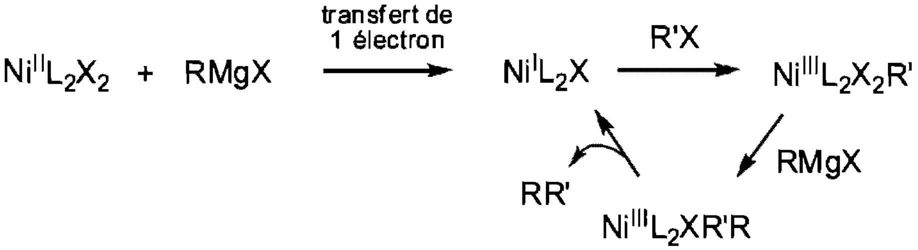


Figure 1.4. Mécanisme plausible pour le couplage de Kumada-Corriu basé sur certaines études effectuées par Koshi.

1.2 Les complexes « pincer »

Un complexe « pincer » est constitué d'un ligand tridentate, c'est-à-dire se liant aux métaux par trois de ses atomes. Il existe une grande variété de ligands « pincer » mais généralement, ils sont composés de deux atomes électrodonneurs **L** se coordonnant aux métaux (liaisons datives) en adoptant un arrangement *trans* et étant séparés par une chaîne alkyle ou aryle. Cette dernière comporte habituellement un atome anionique **X**, qui se lie lui aussi au métal (liaison σ) formant du même coup deux cycles intramoléculaires (Figure 1.5).

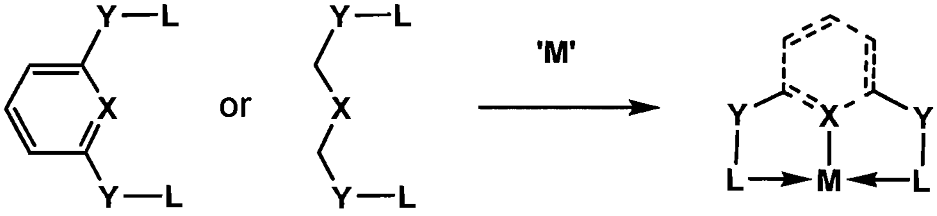
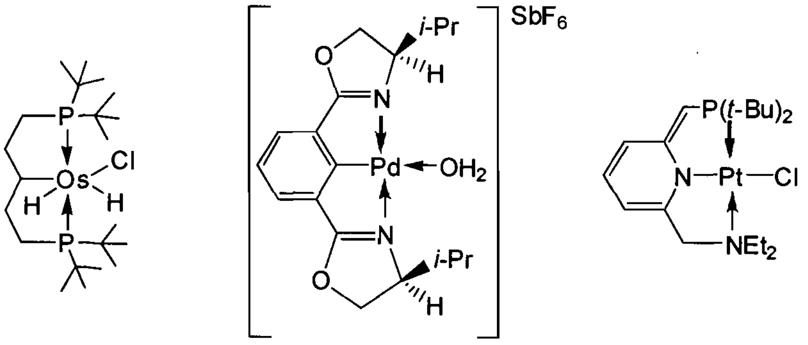


Figure 1.5. Allure des ligands et complexes « pincer ».

De façon systématique, on nomme ce type de complexe en énumérant les atomes du ligand qui sont liés au métal (**LXL**), mais il arrive que la notation soit quelque peu modifiée lorsque certains atomes de carbone de la chaîne alkyle ou aryle sont remplacés par des atomes de nature différente (**LYXYL**). On retrouve maintenant une série impressionnante de ce type de composés organométalliques dans la littérature (Figure 1.6).

La structure tridentate de ce type de ligand apporte une stabilisation additionnelle au lien métal-ligand σ. Par conséquent, cette rigidité mène à l'obtention de composés robustes qui sont bien souvent stables à l'oxygène, à l'humidité ainsi qu'à la chaleur, propriétés qui sont plus que convoitées dans le domaine de la catalyse.



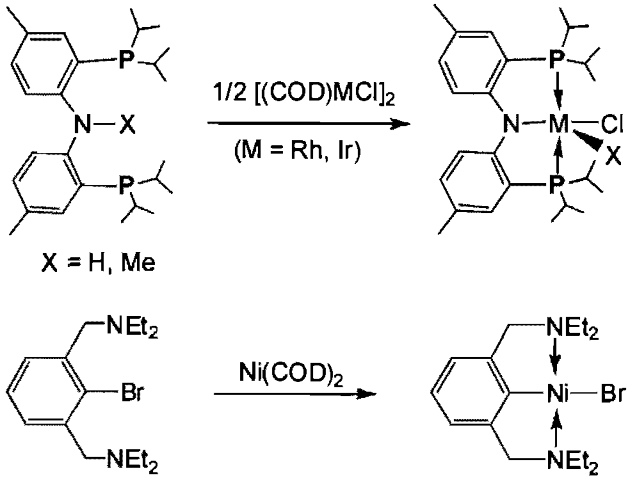
PCP **NCN** **PNN**

Figure 1.6. Exemples de complexes « pincer ».[9]

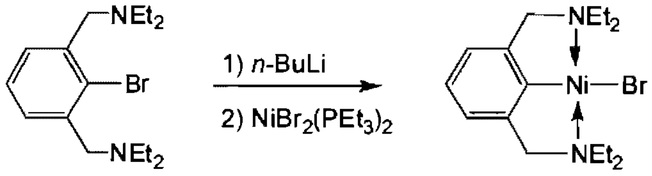
1.2.1 Leurs voies de synthèse

Certaines méthodes de préparation sont communément appliquées pour la formation de complexes « pincer ».[2a,10,11] La plus répandue est celle impliquant l'addition oxydante d'une liaison du ligand (Figure 1.7). Par cette méthode, le complexe est tout simplement formé par la réaction du ligand et du précurseur métallique; dans certains cas, la formation du complexe est favorisée par la libération d'un acide, d'un gaz, etc. Une deuxième voie de synthèse consiste en l'utilisation d'agents organométalliques (magnésiens ou lithiens) pour rehausser la réactivité du ligand avec le précurseur métallique (Figure 1.7). Une autre méthode importante de préparation, quoique plus rarement utilisée, consiste en la transcyclométallation d'un ligand. Il s'agit de faire réagir un complexe « pincer » avec un ligand générant des liens plus forts avec le métal que celui qui lui est initialement lié (Figure 1.7).

par addition oxydante du ligand[2a,10]



par transmétallation[2a]



par transcyclométallation[11]

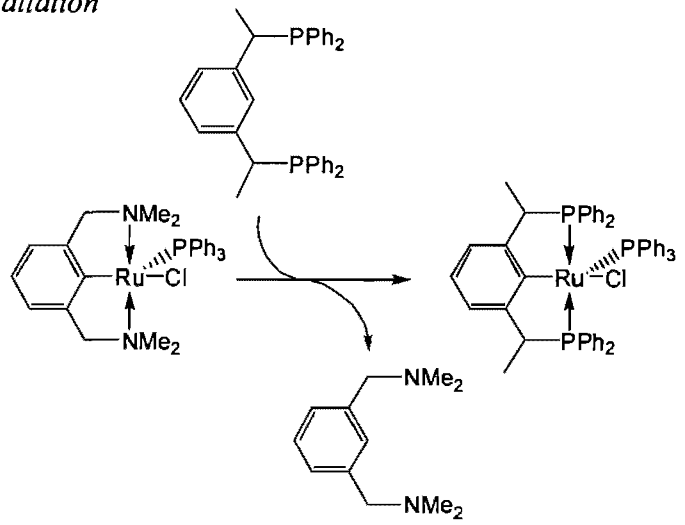


Figure 1.7. Exemples de voies de formation de complexes « pincer ».

1.2.2 Leurs principales applications en catalyse

Les complexes « pincer » sont reconnus pour être d'excellents catalyseurs pour plusieurs réactions organiques d'intérêt notamment pour le couplage de Heck, la déshydrogénation des alcanes de même que l'addition de Kharasch.

1.2.2.1 Le couplage de Heck

Différents complexes, particulièrement une variété d'espèces PCP et POCOP de palladium, se sont avérés très efficaces pour catalyser la réaction de couplage d'oléfines et d'halogénures d'aryle. Ces complexes « pincer » sont même parmi les plus actifs catalyseurs rapportés jusqu'à ce jour en ce qui a trait à cette réaction. Cette application étant de haute importance, plusieurs groupes de recherche se sont penchés sur l'étude de l'impact de la modification du ligand « pincer » sur la réactivité du métal.

Par exemple, Milstein[12] a démontré que, pour la réaction de couplage de l'iodobenzène et de l'acrylate de méthyle (Figure 1.8), changer la nature du carbone cyclométallé du ligand « pincer » d'hybridation sp^2 à sp^3 mène à une augmentation de la fréquence de cycles catalytiques (« TOF ») générés par le complexe (**A** et **B**, Figure 1.9). Dans la même publication, Milstein a aussi démontré qu'une catalyse moins efficace résulte lorsque les substituants des atomes de phosphore du ligand, *i*-Pr (**B**, Figure 1.9), sont remplacés par des groupements plus électrodonneurs mais aussi plus encombrés, *t*-Bu (**C**, Figure 1.9).

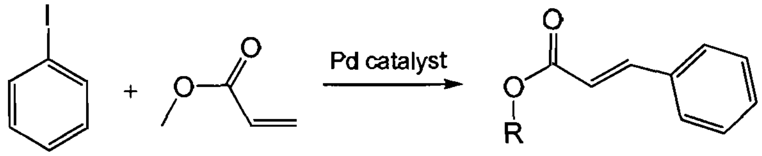
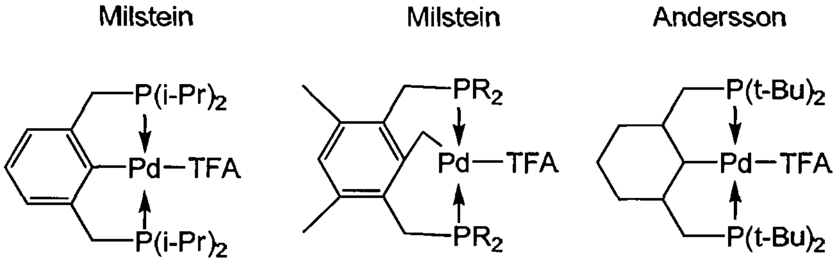


Figure 1.8. Réaction de couplage de l'iodobenzène et de l'acrylate de méthyle.

Andersson[13] a par la suite rapporté un nouveau catalyseur possédant aussi un carbone sp^3 mais impliquant un squelette plus électrodonneur, basé sur un cyclohexyle (**D**, Figure 1.9). Les résultats obtenus pour la réaction de couplage de Heck supportent l'hypothèse préalablement formulée concernant un bénéfique *effet* sp^3 du carbone cyclométallé du complexe sur la catalyse, étant donné que ce catalyseur mène à une fréquence plus élevée de cycles catalytiques effectués que son analogue aromatique **A** (Figure 1.9) et ce, malgré le fait que les substituants de ses atomes de phosphore soient des groupements *t*-Bu.



A
(TOF = 1487/h^{-1})

B
(R = *i*-Pr)
(TOF = 13218/h^{-1})

C
(R =*t*-Bu)
(TOF = 3573/h^{-1})

D
(TOF = 6935/h^{-1})

Figure 1.9. Comparaison de l'efficacité de différents complexes « pincer » pour la réaction de Heck (Figure 1.8).

Des études de réactivité, pour la réaction de Heck, d'une nouvelle gamme de composés « pincer », les complexes POCOP, ont été rapportées par Shibazaki[14] et Jensen[15] (Figure 1.10). Le complexe rapporté par Shibazaki mène à une efficacité impressionnante pour le couplage de l'iodobenzène et de l'acrylate de *n*-butyle (« TON » : 8 900 000; « TOF » : 400 000 TON/h), tandis que celui rapporté par Jensen s'avère efficace pour le couplage de chlorures d'aryle (« TON » : ~200). Récemment, Jensen[16] a rapporté un autre complexe POCOP où un atome de carbone a été inséré à chacun des endroits indiqués par les flèches en bleu de la Figure 1.10, ajoutant du coup un membre à chacun des deux cycles intramoléculaires formés par le ligand. Ce nouveau catalyseur s'est avéré ~100 fois plus actif en terme de « TON » que son analogue aux cycles à cinq membres pour l'usage de chlorures d'aryle.

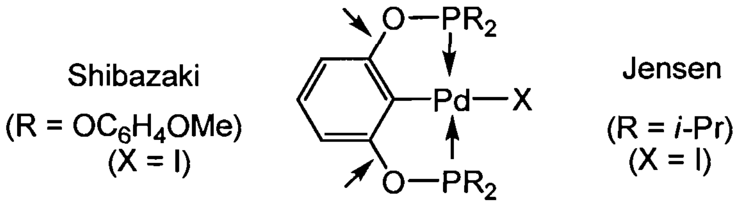


Figure 1.10. Complexes POCOP rapportés par Jensen et Shibazaki.

Le mécanisme généralement proposé pour ce type de réaction, qui utilise fréquemment un catalyseur de Pd^0 ou un complexe de Pd^{II} qui se réduit aisément dans le milieu pour générer l'espèce de Pd^0 active, est présenté à la Figure 1.11.[17] L'espèce active subit l'addition oxydante de l'halogénure d'aryle, étape habituellement favorisée par la présence de ligands qui rendent le métal assez riche en électrons, et l'oléfine s'insère ensuite dans le lien Pd-C nouvellement formé. L'intermédiaire alkyle subit ensuite une élimination β-hydrogène pour libérer le produit oléfinique désiré. Finalement, le catalyseur est régénéré par l'élimination réductrice de HX, favorisée par la présence de base dans le milieu réactionnel.

Le mécanisme emprunté par certains complexes « pincer » est le sujet d'un débat dans la littérature depuis un certain temps; quelques auteurs[15] ont proposé un cycle catalytique impliquant des espèces de Pd^{IV}. Le cycle catalytique proposé Jensen pour les composés POCOP est illustré à la Figure 1.12. Il propose l'addition oxydante de l'oléfine suivie de l'élimination de HCl. Le complexe résultant subirait l'addition oxydante de l'halogénure d'aryle pour ensuite, par élimination réductrice, libérer le produit de couplage désiré de même que regénérer le catalyseur.

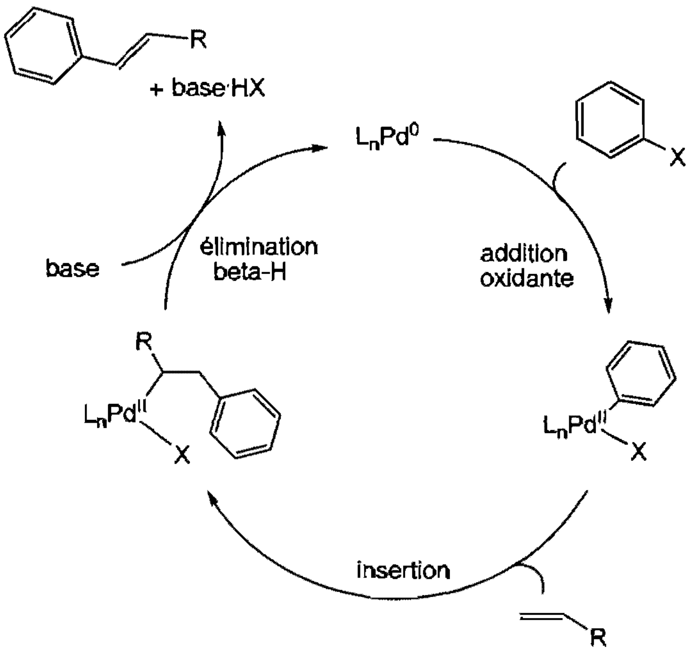


Figure 1.11 : Mécanisme généralement proposé pour le couplage de Heck.

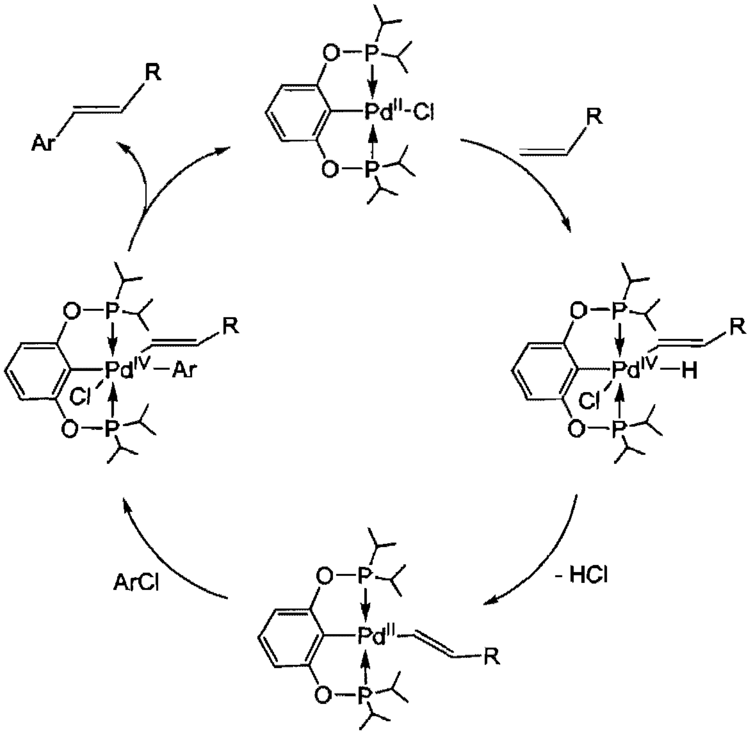


Figure 1.12. Cycle catalytique proposé par Jensen.

1.2.2.2 La déshydrogénation des alcanes

La transformation d'alcanes en alcènes communément appelée la déshydrogénation des alcanes est une réaction organique qui présente un défi intéressant. Comme il s'agit d'une réaction qui n'est pas thermodynamiquement favorisée, on doit soit l'effectuer photochimiquement, la chauffer à reflux ou l'effectuer en présence d'une oléfine « sacrifice » pour déplacer son équilibre vers les produits. Il fut démontré par Goldman que certains complexes « pincer », en particulier les dihydrures d'iridium, sont parmi les plus efficaces catalyseurs pour cette réaction et, quoique leur efficacité soit améliorée en leur présence, ils ne nécessitent pas une oléfine « sacrifice ». Le chauffage de la réaction à reflux est toutefois requis pour favoriser la libération d'hydrogène et générer l'espèce d'Ir^{I} qui subit l'addition oxydante de l'alcane. Le cycle catalytique proposé pour cette réaction de déshydrogénation des alcanes est illustré à la Figure 1.13. Un fait à noter est que la réaction est inhibée lorsqu'elle est effectuée sous atmosphère d'azote; ceci est dû à la formation d'une espèce dimérique dotée d'une molécule d'azote pontante (Figure 1.13).

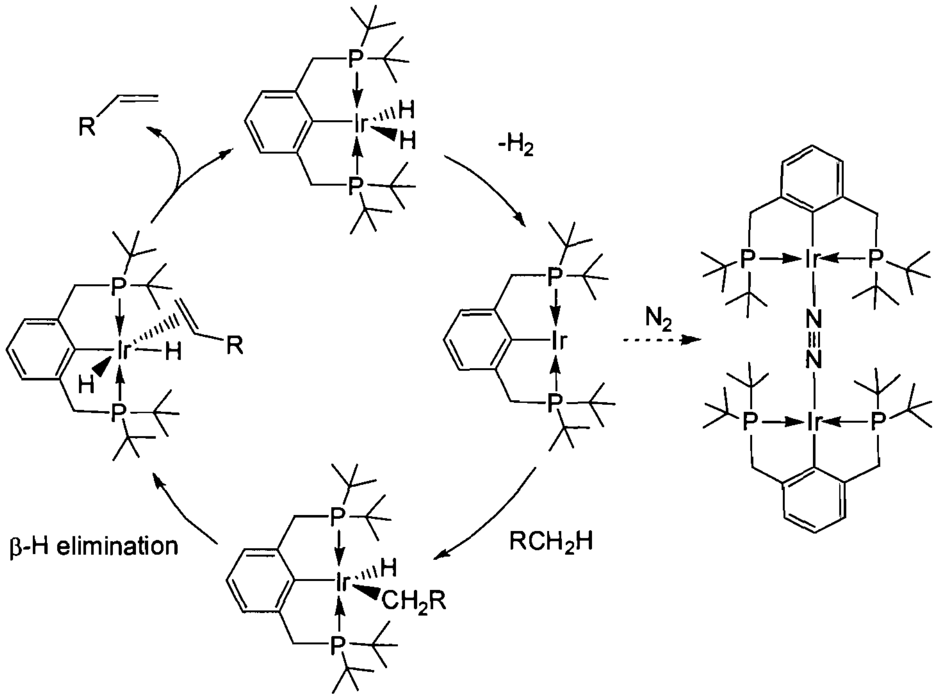


Figure 1.13 : Cycle catalytique proposé pour la déshydrogénation des alcanes.

Il est intéressant de noter qu'il est possible d'effectuer une réaction de déshydrogénation / métathèse d'oléfines « en cascade » en utilisant un complexe « pincer » d'iridium de ce type de même qu'un catalyseur de ruthénium. Cette application permet, de façon globale, de coupler un alcane avec lui-même et est alors une réaction ayant un énorme potentiel.[18]

1.2.2.3 L'addition de Kharasch

L'addition de Kharasch consiste en l'addition d'un lien carbone-halogène sur une double liaison. Certains complexes de métaux de transition se sont avérés efficaces pour agir en tant qu'initiateurs pour cette réaction, mais ces complexes requièrent habituellement des conditions assez dures. Par exemple, $NiCl_2(PR_3)_2$ nécessite de très hautes températures réactionnelles (~140 °C) et un des complexes les plus actifs pour cette réaction, $RuCl_2(PPh_3)_3$, est inactif en-dessous de 40 °C.[2c]

Il a été démontré par van Koten que certains complexes « pincer » de type NCN sont d'excellents catalyseurs pour l'addition de CCl_4 sur l'unité oléfinique de méthacrylate de méthyle : des rendements de 90% sont obtenus après 15 minutes à la température ambiante.[19] Le cycle catalytique proposé pour cette réaction est illustré à la Figure 1.14. Il s'avère que les complexes possédant un substituant R plus électrodonneur sur la chaîne aryle du ligand sont de meilleurs catalyseurs pour cette réaction, probablement à cause de la plus importante stabilisation de l'intermédiaire de Ni^{III} dans le cycle catalytique lorsque le métal est plus riche en électrons.

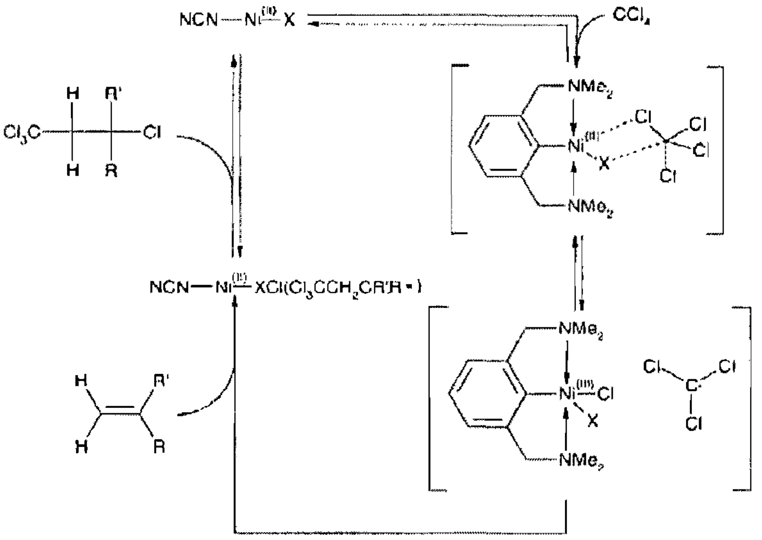
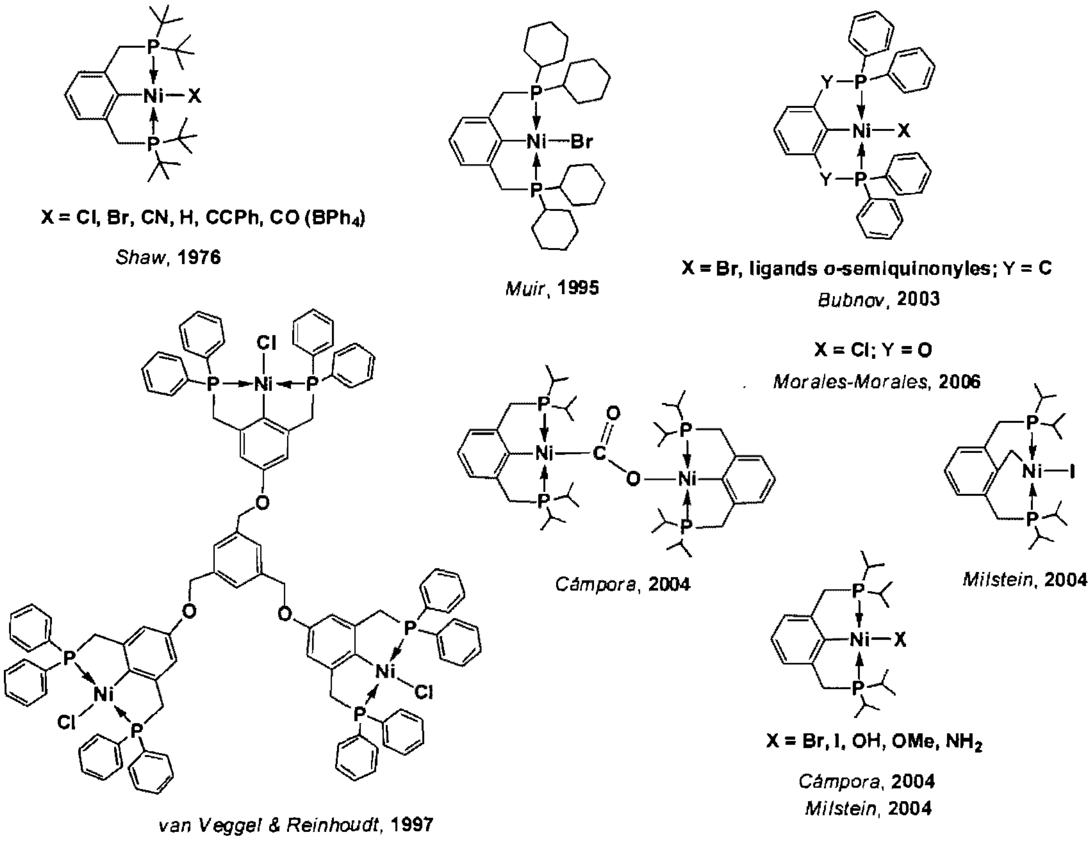


Figure 1.14. Cycle catalytique proposé pour l'addition de Kharasch.[2c]

1.3 Les composés PCP du nickel

La chimie des complexes « pincer » prend de plus en plus d'ampleur, mais la synthèse et la réactivité de tels composés avec certains métaux demeure une lacune dans la littérature. Jusqu'à ce jour, des complexes « pincer » PCP ont été préparés à partir d'une large variété de métaux de transition, mais plus particulièrement avec ceux des deuxième et troisième rangées, sans doute puisque leur formation implique l'activation d'un lien C-H qui est facilitée par les métaux plus lourds. Malgré le fait que les premiers complexes « pincer » aient été préparés à partir des trois métaux du groupe 10, les complexes de Pd et de Pt se sont avérés plus populaires dans la littérature et par conséquent, leur réactivité a été beaucoup plus étudiée au cours des années. Les complexes « pincer » PCP de nickel préparés par d'autres groupes de recherche se limitent, dans la littérature, à ceux qui sont présentés à la Figure 1.15.[20]

Les complexes publiés dans des articles dont les auteurs figurent en bleu étaient inexistants dans la littérature lorsque le projet de recherche a été mis en branle, ils sont apparus en cours de route. On constate aisément, en jetant un regard sur les complexes présentés à la Figure 1.15, que la plupart des complexes rapportés jusqu'à présent possède un lien C_{sp2}-M. C'est que la majorité d'entre eux a été préparée par la méthode de l'addition oxydante du ligand, plus spécifiquement par l'activation d'un lien C-H. Malgré le fait qu'une liaison C_{sp2}-H est reconnue pour être thermodynamiquement plus forte qu'une liaison C_{sp3}-H, l'activation de cette dernière est beaucoup plus difficile à effectuer. Par conséquent, plus rares sont les complexes possédant un lien C_{sp3}-M. En fait, le seul complexe de nickel de type $(PC_{sp3}P)$[a] qu'il fut possible de répertorier jusqu'à ce jour est celui rapporté par Milstein en 2004 (Figure 1.15), ce dernier possédant tout de même un squelette aromatique.


X = Cl, Br, CN, H, CCPh, CO (BPh_4)

Shaw, 1976

Muir, 1995

X = Br, ligands o-semiquinonyles; Y = C

Bubnov, 2003

X = Cl; Y = O

Morales-Morales, 2006

Cámpora, 2004

Milstein, 2004

X = Br, I, OH, OMe, NH_2

Cámpora, 2004

Milstein, 2004

van Veggel & Reinhoudt, 1997

Figure 1.15 : Les complexes PCP de nickel que l'on retrouve dans la littérature et qui ont été préparés par d'autres groupes de recherche.

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[a] La notation PC_xP^y sera adoptée tout au long de la thèse pour les composés de type PCP, « x » faisant référence au type d'hybridation du carbone cyclométallé et « y » faisant référence à la nature des substituants situés sur les atomes de phosphore.

1.4 Les débuts du présent projet

Dans le passé, aucun projet sur les complexes « pincer » n'avait été attribué à un étudiant dans les groupes de recherche des professeurs Davit Zargarian et André L. Beauchamp. Un certain intérêt s'est installé lorsque Frédéric-Georges Fontaine, en parallèle de son projet au sein du groupe du professeur Zargarian portant sur la polymérisation de silanes catalysée par des composés Ni-indényles, s'est voué à l'étude de la réactivité de complexes « pincer » d'osmium et de ruthénium de type $PC_{sp3}P$ avec des composés silylés. Des réactivités intéressantes ont découlé de cette étude qui a été effectuée en collaboration avec le professeur Dimitri Gusev de l'Université Wilfrid-Laurier (Waterloo, Ontario), dont la découverte d'un rare composé pentahydrure silyl-silylène d'osmium par la réaction d'un complexe « pincer » avec deux équivalents de phénylsilane (Figure 1.16).[21]

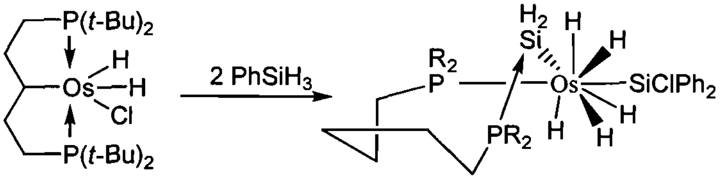

Figure 1.16 : Réactivité d'un complexe « pincer » d'osmium avec phénylsilane.

L'intérêt du groupe du professeur Zargarian ne s'est toutefois pas limité à ce composé. L'étude cristallographique du premier complexe « pincer » Ni-indényle (ayant été recristallisé par un étudiant stagiaire et analysé par une apprentie-cristallographe à la maîtrise) a suscité toute un étonnement au sein du groupe.[22] Laurent Groux, étudiant au doctorat, s'est intéressé de plus près à la préparation de ce composé surprise qui a ensuite fait l'objet d'une publication (Figure 1.17). Suite à l'obtention de ces résultats intéressants, le groupe s'est donné le défi d'en connaître davantage sur la préparation de ces composés ainsi que d'étudier leur réactivité.

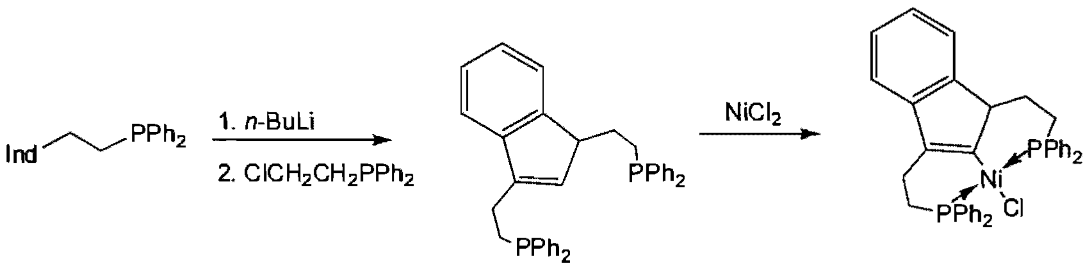

Figure 1.17 : Préparation du premier complexe « pincer » nickel-indényle.

1.5 Objectifs de recherche

L'objectif général de ce projet doctoral consistait en la préparation, la caractérisation et l'étude de la réactivité de nouveaux complexes organométalliques de type « pincer ». Étant donné qu'une panoplie de complexes de ce type se sont avérés de très bons catalyseurs pour plusieurs réactions organiques d'importance (Pd, Rh, Ru, Pt etc.) et ont mené à de surprenantes réactivités,[23] la préparation de tels complexes faisant usage d'un métal de transition peu dispendieux et dont l'activité catalytique soit peu connue dans le domaine des complexes « pincer » a été envisagée. Le nickel s'est alors avéré un métal de choix et c'est avec ce dernier que le présent projet a été mis en branle.

Comme il a été démontré que la plupart des composés « pincer » de nickel rapportés à date comportent un carbone cyclométallé d'hybridation sp^2, le premier objectif du projet fut de tenter la préparation de complexes en possédant un hybridé sp^3 ainsi que de déterminer les raisons pour lesquelles ces complexes étaient inexistants dans la littérature. Le deuxième objectif fixé fut de déterminer les différences électroniques et structurales engendrées par cette augmentation du caractère « p » du carbone cyclométallé par rapport aux complexes analogues $PC_{sp2}P$ connus ainsi que par l'apport d'autres modifications au ligand « pincer » tel que le changement des substituants sur les atomes de phosphore ou encore l'incorporation d'atomes électronégatifs dans le squelette PCP. Finalement, le troisième objectif fut de sonder la réactivité des complexes formés et d'évaluer l'impact des modifications apportées au ligand sur cette dernière.

1.6 Description des travaux

Le **chapitre 1** effectue, en premier lieu, un survol des principales applications du nickel en catalyse, métal dont il est question dans la présente thèse. Il présente ensuite une description détaillée de ce en quoi consistent les complexes « pincer », leurs voies synthétiques, de même qu'un survol des principales applications qui les caractérisent. Une brève revue de la littérature concernant les composés « pincer » PCP du nickel selon laquelle sont situés les objectifs du projet, est établie. Finalement, une vue d'ensemble des travaux figurant dans la thèse est présentée.

Dans le **chapitre 2** est rapportée une méthode synthétique menant à la préparation de nouveaux complexes « pincer » de nickel^{II} comportant le ligand $t\text{-Bu}_2\text{P}(\text{CH}_2)_5\text{P}(t\text{-Bu})_2$. En parallèle de ces complexes « pincer » $\{t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiX}$ (X = Cl, Br, I) fut obtenu, ce qui a été caractérisé comme étant un mélange d'espèces tétraédriques où un ou deux des atomes de phosphore du ligand ont été protonés. Les composés « pincer » qui ont été synthétisés ont servi de précurseurs pour la préparation de complexes hydrure $\{t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiH}$ et méthyle $\{t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiMe}$, dont les voies de synthèse de même que l'activité catalytique pour l'oligomérisation de phénylsilane sont rapportées. De plus, dans ce même chapitre, une méthode préparatoire pour la formation de certaines espèces cationiques est aussi décrite, $[\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(L)}][\text{BPh}_4]$ (L = NCCH_3, NCCH=CH_2).[b]

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[b] Suite à la parution de cet article s'est déroulé un projet de maîtrise mené par Valérica Pandarus qui a rencontré certains des objectifs fixés pour le présent projet, soit la préparation et l'étude de réactivité de complexes POC_xOP de nickel (x = sp^2, sp^3) comportant des atomes d'oxygène dans le squelette PCP. Ces résultats ont fait l'objet de publications qui seront citées au cours des chapitres subséquents.

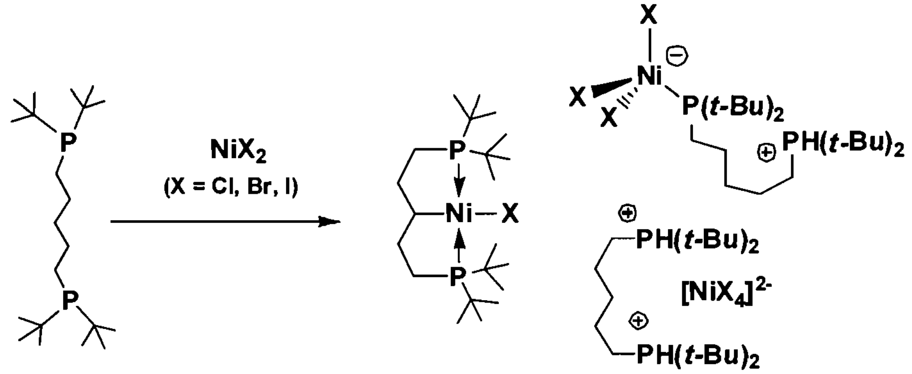


Figure 1.18 : Synthèse des complexes « pincer » rapportés au chapitre 2.

Le **chapitre 3** traite de la préparation d'un nouveau complexe « pincer » comportant un ligand analogue à celui présenté au chapitre 2, mais dont les atomes de phosphore sont substitués par des groupements *i*-Pr, $\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiBr$. Un sous-produit bimétallique est aussi obtenu lors de la synthèse du complexe cible et il fut démontré que ce complexe peut être reconverti en complexe « pincer ».

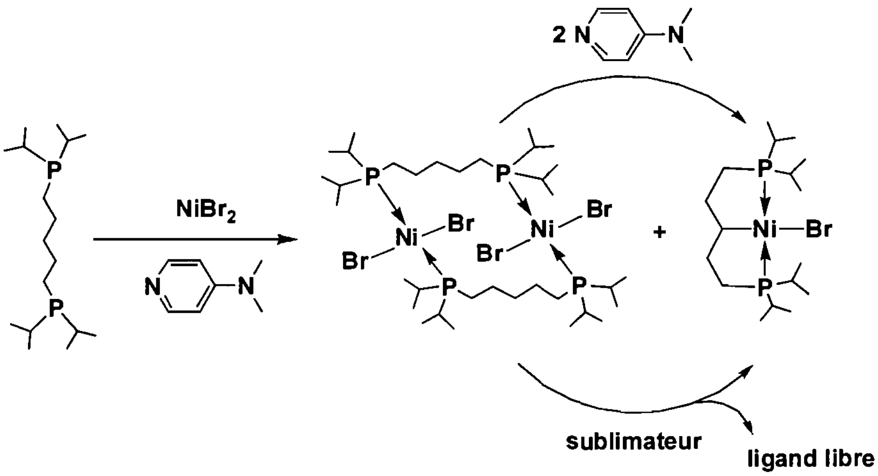


Figure 1.19 : Synthèse du complexe « pincer » rapporté au chapitre 3.

La métathèse du lien Ni-Br du complexe « pincer » avec différents réactifs organométalliques mène à la formation de complexes possédant deux liens Ni-C, $\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiR$ (R = Me, C≡CMe, Ph, *n*-Bu, C≡CPh) et les voies synthétiques conduisant à ces différents complexes sont présentées. Une autre voie de formation pour le composé $\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}Ni(C{\equiv}CPh)$, soit par la réaction des composés méthyle (R = Me), propynyle (R = $C{\equiv}CMe$) ou butyle (R = *n*-Bu) avec $PhC{\equiv}CH$ est aussi décrite.

Dans ce chapitre est aussi rapportée la réactivité du composé méthyle (R = Me) avec différents halogénures d'aryle, PhX (X = Cl, Br, I), pour former du toluène ainsi que les complexes halogénés correspondants, $\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiX$ (X = Cl, Br, I). Étant donné ces résultats, la réaction catalytique du couplage de Kumada-Corriu fut testée pour le complexe bromo (X = Br) et les résultats obtenus pour le couplage de PhCl et de MeMgCl ont été comparés avec ceux découlant de deux autres complexes analogues, $\{(t\text{-}Bu_2PCH_2CH_2)_2CH\}NiBr$ et $\{(i\text{-}Pr_2PCH_2)_2C_6H_3\}NiBr$, différant au niveau des substituants sur les phosphores ainsi qu'au niveau de la nature du carbone cyclométallé. La plupart des complexes préparés ont été caractérisés par spectroscopie RMN, diffraction des rayons X et analyse élémentaire. Des études électrochimiques ont aussi été effectuées pour certains de ces composés.

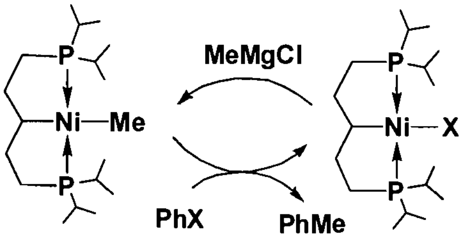


Figure 1.20 : Exemples de réactivités présentés au chapitre 3.

Il est aussi question dans ce chapitre de la préparation de rares complexes de Ni^{III},$\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiX_2$ (X = Cl, Br).

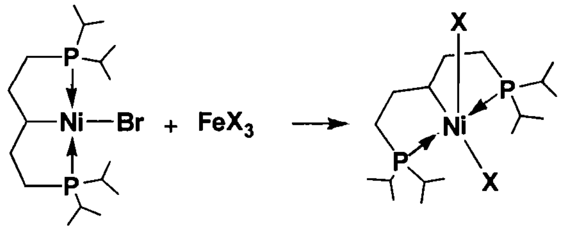
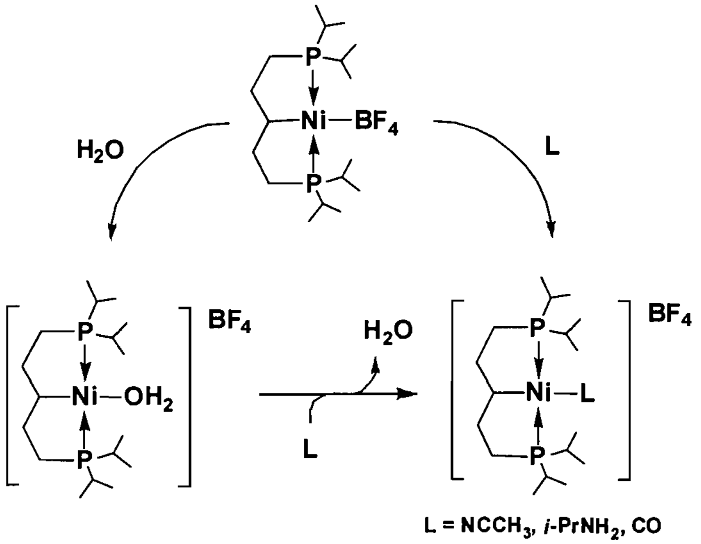


Figure 1.21 : Préparation des espèces de Ni^{III} rapportées dans le chapitre 3.

Dans le **chapitre 4** est présentée la synthèse du complexe $\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiBF_4$, composé comportant de faibles interactions Ni-F. Ce dernier a servi de précurseur pour la préparation de nouveaux complexes cationiques où différents ligands tels que H_2O, $i\text{-}PrNH_2$, CH_3CN et CO sont respectivement coordonnés. De plus, dans ce chapitre est rapportée la formation d'un complexe hydroxyde, obtenu par la déprotonation de la molécule d'H_2O coordonnée du complexe cationique (L = H_2O, Figure 1.22) à l'aide de la base $KN(SiMe_3)_2$.



L = $NCCH_3$, $i\text{-}PrNH_2$, CO

Figure 1.22 : Préparation des complexes cationiques présentés au chapitre 4.

Le **chapitre 5** présente la formation de divers complexes cationiques comportant des ligands PCP et POCOP et compare leurs caractéristiques structurales, électroniques ainsi que leur activité catalytique pour la réaction d'hydroamination de l'acrylonitrile avec aniline. À des fins de comparaison, la préparation d'un tout nouveau ligand POCOP possédant des atomes de chlore au niveau du cycle aromatique a été effectuée de façon à obtenir un complexe cationique plus pauvre en électrons.

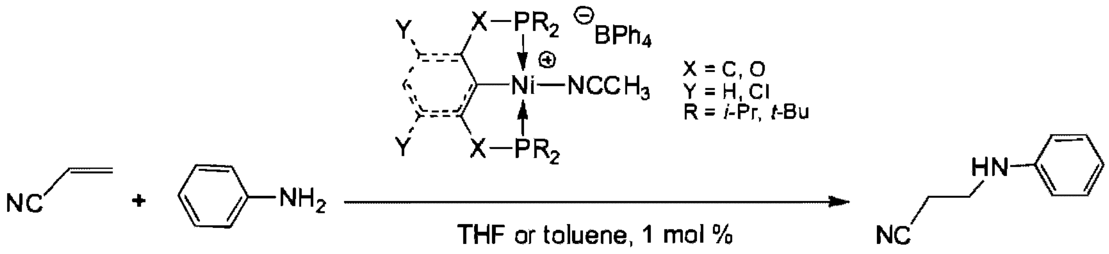


Figure 1.23 : Réaction d'hydroamination de l'acrylonitrile étudiée au chapitre 5.

Enfin, le **chapitre 6** présente une revue et une discussion des résultats de même que quelques perspectives concernant le projet.

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Chapitre 2: Syntheses and Reactivities of New $PC_{sp3}P$ Pincer Complexes of Nickel

Article 1

Organometallics **2006**, *25*, 602-608

Annie Castonguay, Christine Sui-Seng, Davit Zargarian,* and André L. Beauchamp*
Département de chimie, Université de Montréal, Montréal (Québec), Canada H3C 3J7

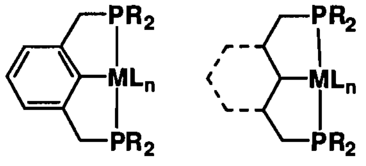
Abstract

Heating Ni(II) halides with one equivalent of $Bu^t_2P(CH_2)_5PBu^t_2$ gives the $PC_{sp3}P$ pincer complexes $[\{(Bu^t_2P(CH_2)_2)_2CH\}NiX]$ (X = Cl, **1a**; Br, **1b**; I, **1c**). These compounds react with MeMgCl or *n*-BuLi to give, respectively, the methyl species $\{(Bu^t_2P(CH_2)_2)_2CH\}NiMe$, **2**, or the hydride species $\{(Bu^t_2P(CH_2)_2)_2CH\}NiH$, **3**, while reaction with $NaBPh_4$ in a mixture of benzene/acetonitrile gives the cationic species $[\{(Bu^t_2P(CH_2)_2)_2CH\}Ni(N{\equiv}CCH_3)][BPh_4]$, **4**. Complexes **1-3** are inert toward olefins, but react with $PhSiH_3$ to give $(PhSiH)_n$. The cationic complex **4** is also inert toward most olefins, but its reaction with excess acrylonitrile results in displacement of coordinated acetonitrile to give $[\{(Bu^t_2P(CH_2)_2)_2CH\}Ni(N{\equiv}CCH{=}CH_2)][BPh_4]$, **5**. Complexes **1-5** have been characterized by NMR spectroscopy and, in the case of **1, 4** and **5**, by X-ray crystallography.

Introduction

The strongly chelating nature of PCP type pincer ligands and the rigid geometries they impose on transition metals bestow high thermal and oxidative stabilities to their complexes and facilitate novel reactivities.[1] Hence, PCP pincer complexes have been studied intensively during the past decade and a number of interesting reactivities[2] and highly efficient catalytic reactions[3] involving these complexes have been reported. The catalytic applications of pincer complexes have been reviewed recently.[4]

The most commonly investigated pincer complexes feature $PC_{sp2}P$ type ligands consisting of mutually *trans* PR_2 moieties linked by a *m*-xylyl group (Chart 2.1), but the analogous complexes featuring $PC_{sp3}P$ ligands are receiving increasing attention and have shown interesting reactivities in their own rights.[5] Noteworthy examples include Pd-$PC_{sp3}P$ complexes that promote the hydroamination of acrylonitrile[6] and the Heck vinylation of aryl halides;[7] for the latter reaction, the $PC_{sp3}P$ complexes are believed to be more active than their $PC_{sp2}P$ counterparts.[7,8] Furthermore, a number of spectacular transformations have been observed with Ru-, Os-, and Ir-$PC_{sp3}P$ complexes.[9]



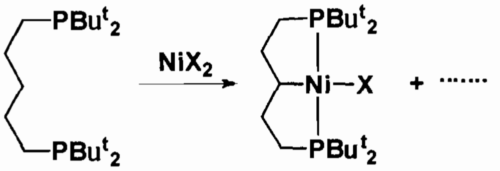
$PC_{sp2}P$ $PC_{sp3}P$

Chart 2.1

The interesting reactivities promoted by $PC_{sp3}P$ ligands and the virtually unexplored chemistry of their Ni derivatives[10] motivated us to prepare a series of Ni-$PC_{sp3}P$ complexes and study their reactivities.[11] Herein, we report convenient synthetic routes to a series of Ni-$PC_{sp3}P$ complexes based on the ligand 1,5-bis(di-tert-butylphosphino)pentane, and describe a preliminary account of their reactivities.

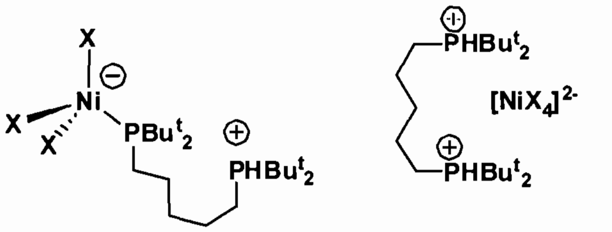
Results and Discussion

Synthesis, characterization, and reactivities of κ^P, κ^C, κ^P-[{(*t*-$Bu_2PCH_2CH_2)_2CH$}NiX], 1. Heating mixtures of 1,5-bis(di-*tert*-butylphosphino)pentane and different nickel halides gave 37-47% yields of orange solids that were identified readily as our target $PC_{sp3}P$ pincer complexes **1** (Scheme 2.1; X= Cl, **1a**; Br, **1b**; I, **1c**). These reactions also produced unexpected by-products that proved difficult to identify, because they were paramagnetic and only sparingly soluble in common solvents. The colors of these by-products, i.e., blue, green, and red for the Cl-, Br-, and I-derivatives, respectively, would be consistent with tetrahedral species of the type $[L_nNiX_{4-n}]^{n-2}$.[12] Indeed, repeated re-crystallizations of the by-product obtained from the $NiCl_2$ reaction yielded blue microcrystals that were identified as the tetrahedral, zwitterionic complex $[\{(t\text{-}Bu_2PH)(CH_2)_5(t\text{-}Bu_2P)\}NiCl_3]$, **A** (Chart 2.2).[13]



1a: X = Cl
1b: X = Br
1c: X = I

Scheme 2.1



A **B**

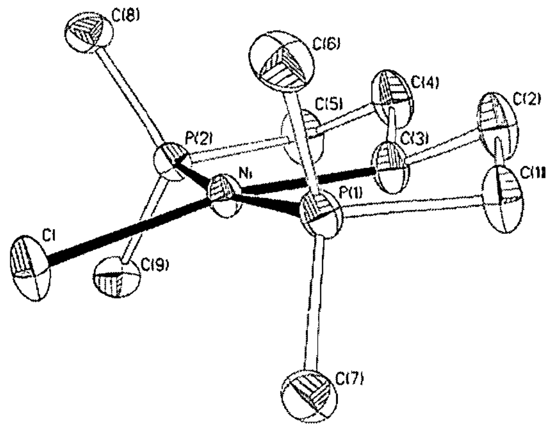
Chart 2.2

The formation of compound **A** likely arises from the reaction of **1a** with HCl, which is generated in-situ during the cyclometallation reaction; alternatively, protonation of the bis(phosphine) ligand might occur prior to its coordination to $NiCl_2$. Curiously, carrying out the cyclometallation reactions in the presence of NEt_3 did not circumvent the formation of by-products, implying that the phosphorous moieties are protonated in preference to the added base. Moreover, protonating isolated samples of **1a** with HCl (etherate) did not stop at the singly protonated product (complex **A**), proceeding instead to double protonation and formation of a blue solid that was identified as complex $[\{(t\text{-}Bu_2PH)(CH_2)_2\}_2CH_2][NiCl_4]$, **B** (Chart 2.2).[14] These observations indicate that the by-products formed during the syntheses of **1** are tetrahedral species analogous to **A** and **B**, but the available experimental evidence does not allow us to draw firm conclusions on their identities, structural details, or the pathways that lead to their formation.

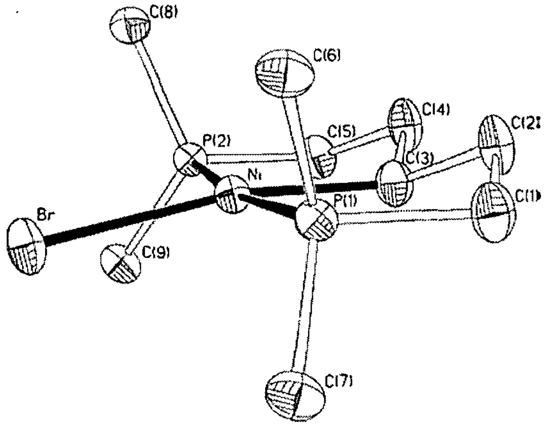
Complexes **1** are thermally stable and can be handled in air, both in the solid state and in solution, without noticeable decomposition even after weeks. Their $^{31}P\{^1H\}$ NMR spectra contain a sharp singlet resonance that confirms the equivalence of the phosphorus nuclei in accord with a *trans* geometry; the chemical shift of this signal (ca. 73-74 ppm) is very close to that of the analogous $PC_{sp2}P$ complex $\{2,6-(CH_2PBu^t_2)_2C_6H_3\}NiCl$ (ca. 74.7 ppm).[11a] The appearance in the ^1H NMR spectra of the characteristic pattern of virtual triplets for the *t*-Bu protons is also consistent with strong coupling of these nuclei to mutually *trans* phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectra also contained virtual triplets for *t*-Bu carbons in addition to low-field triplets (ca. 47-56 ppm; $^2J_{P-C} \sim 9$ Hz) attributed to the central carbon atom of the alkyl chain that is bonded to the nickel center.

X-Ray diffraction studies helped establish the solid state structures of **1a**, **1b**, and **1c**. The ORTEP views of these complexes are shown in Figure 2.1, the crystal data and collection details are listed in Table 2.I, and selected bond distances and angles are given in Table 2.II. The Ni center in all three structures adopts a distorted square-planar geometry defined by two phosphorus atoms, the central carbon atom of the $PC_{sp3}P$ ligand, and a halogen atom. All Ni-P bond lengths lie within the expected range for a *trans*-P-Ni-P arrangement, while the P(1)-Ni-P(2) angles of ca. 170° result from a slight tetrahedral distortion away from the ideal square-planar geometry expected for the d^8 centres. The Ni-C(3) distances of ca. 1.98 Å are comparable to the mean of all $Ni-C_{sp3}$ bond lengths reported to date (1.980 Å).[15]

1a



1b



1c

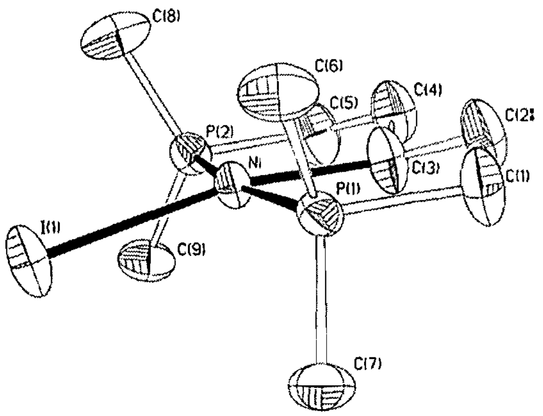


Figure 2.1. ORTEP diagrams for complexes **1a**, **1b** and **1c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl groups are omitted for clarity. The iodide atom in **1c** is disordered over two positions (54:46), only one of which is shown in the ORTEP.

Table 2.I. Crystal Data Collection and Refinement Parameters for Complexes **1a**, **1b**, **1c**, **4** and **5**.

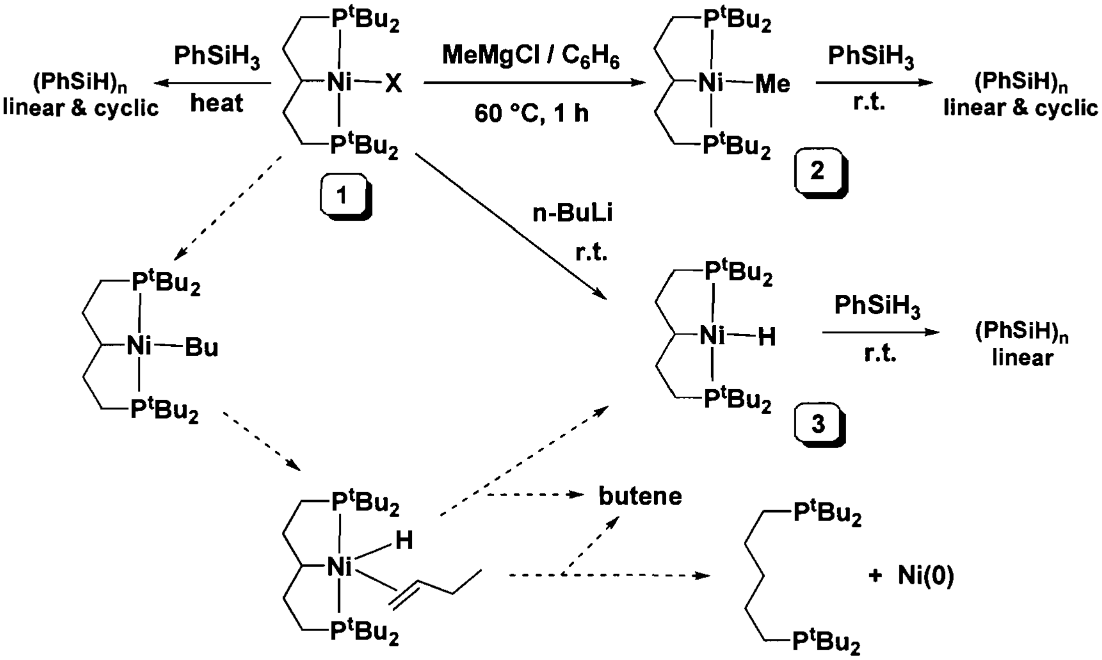
	1a	**1b**	**1c**	**4**	**5**
Chemical formula	$C_{21}H_{45}ClNiP_2$	$C_{21}H_{45}BrNiP_2$	$C_{21}H_{45}INiP_2$	$C_{47}H_{68}NBNiP_2$	$C_{48}H_{68}NBNiP_2$
Fw	453.67	498.13	545.12	778.48	790.49
T (K)	293 (2)	220 (2)	220 (2)	220 (2)	200 (2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a (Å)	12.1335 (2)	12.1501 (5)	11.8960 (5)	15.3450 (3)	14.3311(8)
b (Å)	14.2189 (2)	14.3036 (5)	14.1665 (5)	14.4944 (3)	18.2163(11)
c (Å)	14.8382 (2)	14.8142 (6)	15.1062 (6)	19.9357 (5)	17.4551(10)
α (deg)	90	90	90	90	90
β (deg)	104.4970 (10)	104.337 (3)	90	90.368 (2)	100.655(3)
γ (deg)	90	90	90	90	90
Z	4	4	4	4	4
V (Å^3)	2478.45 (6)	2494.38 (17)	2545.77 (17)	4433.94 (17)	4478.3(4)
ρ_{calcd} (g cm^{-3})	1.216	1.326	1.422	1.166	1.172
μ (cm^{-1})	33.37	42.07	118.06	15.34	15.27
Θ range (deg)	3.76-72.92	3.75-72.97	4.28-72.92	2.88-72.92	3.14-68.66
R1[a] [$I > 2\sigma(I)$]	0.0611	0.0688	0.0686	0.0639	0.0402
wR2[b] [$I > 2\sigma(I)$]	0.1838	0.2088	0.1720	0.1457	0.0860
R1 [all data]	0.0661	0.0888	0.0743	0.1134	0.0744
wR2 [all data]	0.1882	0.2940	0.1767	0.1641	0.0959
GOF	1.052	1.228	1.033	0.912	0.872

[a] $R1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ [b] $wR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table 2.II. Selected Bond Distances (Å) and Angles (deg) for Complexes **1a**, **1b**, **1c**, **4** and **5**.

	1a (X = Cl)	**1b** (X = Br)	**1c** (X = I)	**4** (X = N)	**5** (X = N)
Ni-C(3)	1.979(3)	1.971(4)	1.985(7)	1.969(3)	1.982(2)
Ni-P(1)	2.2079(8)	2.2182(12)	2.2353(17)	2.2154(10)	2.2261(7)
Ni-P(2)	2.2130(8)	2.2123(12)	2.2295(13)	2.2142(10)	2.2272(7)
Ni-X	2.2490(8)	2.3866(7)	2.561(3) 2.547(4)	1.908(3)	1.899(2)
C(3)-Ni-X	169.59(11)	169.89(13)	168.4(3) 178.1(5)	173.98(16)	173.81(9)
P(1)-Ni-P(2)	169.70(3)	170.16(5)	169.69(7)	169.31(4)	167.84(3)
P(1)-Ni-X	94.92(3)	94.48(3)	96.49(10) 94.93(13)	95.08(9)	96.34(6)
P(2)-Ni-X	94.95(3)	95.00(4)	93.75(10) 95.37(13)	95.56(8)	94.60(6)
P(1)-Ni-C(3)	85.24(9)	85.90(13)	84.5(3)	84.75(12)	84.64(7)
P(2)-Ni-C(3)	85.59(9)	85.22(13)	85.2(3)	84.79(12)	85.05(7)

We undertook to prepare alkyl derivatives of our pincer complexes in order to study their reactivities with olefins and hydrosilanes. Reaction of complex **1a** with one equivalent of MeMgCl gave the corresponding Ni-Me species **2**, whereas the reaction of **1** with BuLi led to the formation of the Ni-H derivative **3** (Scheme 2.2). The ^{1}H NMR spectra of the latter reaction mixture contained signals attributed to 1-butene, while a considerable amount of free ligand was detected in both the ^{1}H and ^{31}P NMR spectra. These observations imply that an initially formed Ni-Bu intermediate undergoes β-H elimination to give **3**, and that this Ni-H species is itself prone to reductive elimination and phosphine dissociation.



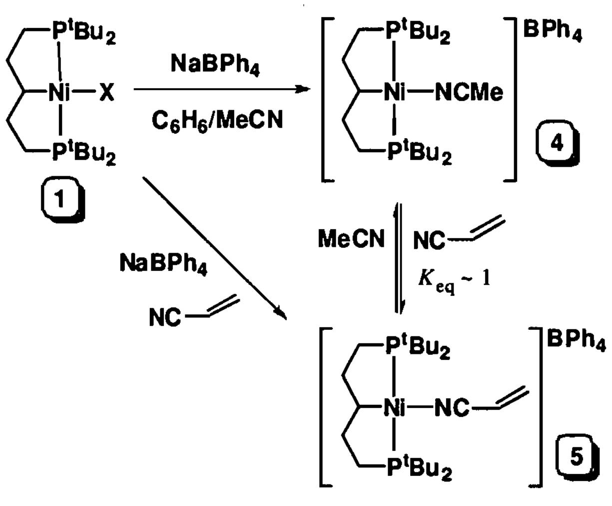
Scheme 2.2

The Ni-Me compound **2** and the Ni-H derivative **3** could not be isolated in analytically pure form,[16] but their NMR spectra provided sufficient evidence for a convincing characterization. For instance, the Ni-CH_3 moiety in **2** gave rise to triplet resonances in the ^{1}H and the $^{13}C\{^{1}H\}$ NMR spectra (^{1}H: –0.27 ppm, $^{3}J_{P-H} = 8$ Hz; ^{13}C:

–19.07 ppm, $^2J_{P\text{-}C} = 19$ Hz), whereas the $^{31}P\{^1H\}$ NMR spectrum showed a singlet resonance at 80 ppm. In the case of complex **3**, the appearance in the ^1H NMR spectrum of a triplet signal at ca. -10 ppm ($^2J_{P\text{-}H} = 53$ Hz) is characteristic of a hydride moiety. Moreover, the $^{31}P\{^1H\}$ NMR spectrum of **3** showed a singlet resonance at ca. 109 ppm, significantly downfield of the corresponding signals in the Ni-halide and Ni-Me derivatives, but fairly close to that of the analogous Pd-H complex reported by Trogler (ca. 106 ppm).[6a]

Our preliminary investigations of the reactivities of complexes **2** and **3** showed that these compounds are inert towards olefins, but they catalyze the oligomerization of $PhSiH_3$. Thus, reaction of excess $PhSiH_3$ (50-100 equivalents) with these complexes (ca. 0.05 M in C_6D_6) at room temperature for 24 h gave $(PhSiH)_n$ oligomers with ca. 50% conversion. The ^1H NMR spectra of these reaction mixtures indicated that the oligomers obtained from the reaction of the Ni-Me derivative **2** contained both cyclic and linear oligomers (Si-*H* signals at ca. 5.2-6.0 and ca. 4.4-4.8 ppm, respectively),[17] whereas those obtained from the reaction of the Ni-H derivative **3** showed only the signals characteristic of the linear oligomers. The halide derivatives reacted much more sluggishly with $PhSiH_3$; for instance, the reaction with the Ni-I analogue **1c** gave less than 5% conversion even after heating to ca. 100 °C for 24 h.

Synthesis, characterization, and reactivities of $\kappa^P,\kappa^C,\kappa^P$-[{(*t*-$Bu_2PCH_2CH_2)_2CH$}Ni(N≡CMe)][$BPh_4$], 4. Reacting complexes **1** with $NaBPh_4$ in a mixture of benzene and acetonitrile cleaved the Ni-X bond to form the pale yellow, cationic species **4** featuring a Ni-NCMe linkage (Scheme 2.3). The observation that halide abstraction does not take place in benzene or CH_2Cl_2 alone underscores the greater solubility of $NaBPh_4$ in MeCN and the latter's crucial role in stabilizing such cationic species. Solid samples of complex **4** can be handled in air indefinitely, but oxidation can occur if solutions of **4** are left exposed to air over several weeks. Gradual decomposition was also noticed by $^{31}P\{^1H\}$ NMR spectroscopy when C_6D_6 solutions of **4** were heated above 40 °C.



Scheme 2.3

The conversion of **1** to **4** was signalled by the disappearance of the $^{31}P\{^1H\}$ NMR signals for the precursors at ca. 74 ppm and the emergence of a new resonance at ca. 87 ppm. The formation of the $CH_3CN{\rightarrow}Ni$ moiety in **4** was also indicated by the presence in the ^1H NMR spectra of a new singlet at 0.70 ppm, indicating a significant upfield shift of this signal relative to free acetonitrile (ca. 2.1 ppm in $CDCl_3$). Comparison of the ^{13}C chemical shift for the nitrile carbon would have been very informative in this context, but this signal was not detected in the $^{13}C\{^1H\}$ NMR spectrum of complex **4**, presumably because of the coupling with the P nuclei that reduce the intensity of this signal. The IR spectrum of **4** shows a very weak band at 2270 cm^{-1}, which was assigned to $\nu_{C\equiv N}$.[18] Comparison to the corresponding band in free MeCN (2254 cm^{-1}) indicates that the N≡C bond order is reinforced upon coordination; we conclude, therefore, that the Ni-NCMe bond is dominated by ligand to metal σ-donation, which is known to diminish the anti-bonding character of the N lone pair with respect to the C-N bond.[19]

The spectral features of this complex are in agreement with its crystal structure (Figure 2.2, Table 2.I). The more or less unchanged Ni-P and Ni-C3 bond distances and P-Ni-P and P-Ni-C3 angles indicate that the slightly distorted square-planar geometry found for complexes **1** is largely maintained in **4** (Table 2.II). The end-bonded acetonitrile molecule has the expected attachment linearity

177°; N-C(10)-C(11) ~ 180°), whereas the Ni-N bond distance in **4** (1.908(3) Å) is significantly shorter than the mean value of Ni-NCMe bond lengths reported in the literature (2.068 Å).[20] The fairly short N-C distance (1.122(4) Å) points to a strong C≡N bond, as inferred from the IR data (vide supra).

The important reactivities of cationic species in catalytic settings prompted us to investigate the substitution lability of the acetonitrile moiety in **4** and its reactions with $PhSiH_3$ and a number of olefins, with the following results. No reaction was noted when **4** was allowed to react for ca. 18 h in $CDCl_3$ ([**4**] ~ 0.02 M) with 100 equivalents of $PhSiH_3$, isoprene, styrene, norbornene, COD, 4-vinylaniline, and methyl methacrylate. The target Ni-olefin cations were also inaccessible from the reaction of **1** with $NaBPh_4$ in neat olefin.[21] On the other hand, reaction of **4** with an excess of acrylonitrile led to the reversible exchange of MeCN (K_{eq} = 0.98 ± 0.07) to form complex **5** (Scheme 2.3). Complex **5** was also prepared directly via the reaction of **1** with $NaBPh_4$ in neat acrylonitrile, and was isolated in ca. 61% yield.

The NMR features of **5** seem to indicate that the acrylonitrile molecule is linked to the Ni center by its nitrogen lone pair.[22] For example, very similar chemical shifts were observed for the ^{31}P signals in **5** (ca. 90 ppm) and **4** (ca. 88 ppm). In addition, the ^{1}H and ^{13}C signals for the vinyl moiety in **5** (ca. 4.8, 5.6, and 5.7 ppm for ^{1}H, and ca. 105 and 143 ppm for ^{13}C) are quite close to those of the corresponding signals in free acrylonitrile (ca. 5.6, 6.1, and 6.2 ppm for ^{1}H, and ca. 108 and 137 ppm for ^{13}C). As was the case for complex **4**, the ^{13}C signal for N*C* was not detected. These observations are consistent with an N-coordinated acrylonitrile moiety. On the other hand, the $\nu_{C\equiv N}$ band in the IR spectrum of **5** appears at ca. 2232 cm^{-1}, almost identical to that of free acrylonitrile (2231 cm^{-1} in CCl_4 solution). Since a shift to higher frequencies is normally expected for the $\nu_{C\equiv N}$ band in N-coordinated acrylonitrile complexes,[23] we invoke some Ni→acrylonitrile π–backdonation.[24]

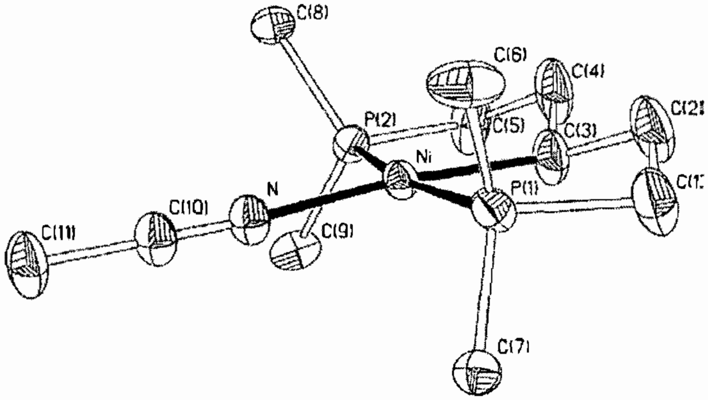


Figure 2.2. ORTEP diagram for complex **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl groups of the *t*-Bu substituents are omitted for clarity.

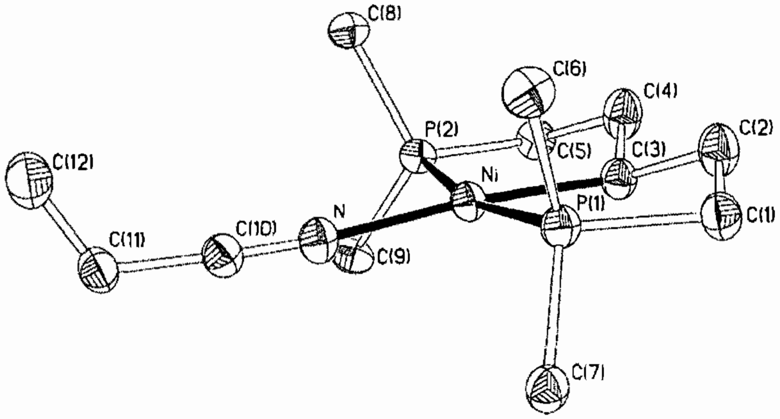


Figure 2.3. ORTEP diagram for complex **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl groups of the *t*-Bu substituents are omitted for clarity.

Nevertheless, an X-ray diffraction study carried out on a single crystal of **5** allowed us to establish that the acrylonitrile ligand is N-bound in the solid state (Figure 2.3, Table 2.I). The distorted square planar geometry around the nickel center resembles those of complexes **1** and **4** (Table 2.II). The Ni-N bond distance (ca. 1.90 Å) and the angles Ni-N-C (174°) and N-C-C (178°) in complex **5** are nearly equivalent to the corresponding values in complex **4**, while the C≡N (1.144(3) Å) and C=C (1.300(3) Å) bond distances are very similar to the corresponding bond lengths reported for a dicationic, N-bound methacrylonitrile-Ni complex (1.132(4) Å and 1.307(5) Å, respectively).[25]

Conclusion

Formation of the new Ni-$PC_{sp3}P$ pincer complexes **1** proceeds by an uncommon Ni-promoted C-H bond activation process. Access to complexes **1-5** should facilitate a systematic exploration of their reactivities. Our preliminary results show that the Ni-methyl (**2**) and Ni-hydride (**3**) species are, as expected, more reactive toward $PhSiH_3$ than the precursor Ni-halide complexes (**1**). The acetonitrile adduct (**4**) is surprisingly inert toward a range of olefins, but it does undergo reversible substitution of the acetonitrile moiety by acrylonitrile. Recent reports of successful Ni-promoted hydrophosphination[25] and hydroamination[26] reactions with methacrylonitrile and other activated olefins indicate that similar reactivities might be promoted by our cationic $PC_{sp3}P$-Ni compounds **4** and **5**. Studies are underway to probe such reactivities.

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and/or in nitrogen-filled glovebox, except where noted. Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received from commercial vendors. The diphosphine ligand $Bu^t_2P(CH_2)_5PBu^t_2$ was prepared according to a literature procedure[27] and distilled before use. The NMR spectra were recorded at ambient temperature on a Bruker ARX400 instrument. The ^1H and ^{13}C NMR spectra were referenced to solvent resonances, as follows: 7.26 and 77.16 ppm for $C\mathit{H}Cl_3$ and $\mathit{C}DCl_3$, respectively, and 7.15 and 128.06 ppm for $C_6D_5\mathit{H}$ and C_6D_6, respectively. The ^{31}P NMR spectra were referenced to an external 85% $H_3\mathit{P}O_4$ sample (0 ppm). The IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000-450 cm^{-1}) with samples prepared as KBr pellets. The ^{v}J term used refers to the apparent coupling constant of the virtual triplets. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montreal).

[{$Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2$}NiCl] (1a). 1,5-Bis(di-tert-butylphosphino)pentane (250 mg, 0.69 mmol) was added to a suspension of anhydrous nickel (II) chloride (90 mg, 0.69 mmol) in toluene (15 mL) and the reaction mixture was refluxed for 12h. Filtration of the final mixture in the air and evaporation of the filtrate gave complex **1a** as an orange solid (148 mg, 47%). ^1H NMR (C_6D_6): 1.07-1.85 (m, 9H), 1.41 (vt, ^{v}J = 5.7 Hz, $PC(C\mathit{H}_3)_3$, 18H), 1.46 (vt, ^{v}J = 6.4 Hz, $PC(C\mathit{H}_3)_3$, 18H); ^1H NMR ($CDCl_3$): 1.10-2.10 (m), 1.48 (vt, ^{v}J = 5.9 Hz, $PC(C\mathit{H}_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6): 23.44 (vt, ^{v}J = 9.0 Hz, $\mathit{C}H_2$, 2C), 29.46 (vt, ^{v}J = 2.4 Hz, $PC(\mathit{C}H_3)_3$, 6C), 30.19 (vt, ^{v}J = 2.8 Hz, $PC(\mathit{C}H_3)_3$, 6C), 34.63 (vt, ^{v}J = 6.9 Hz, $P\mathit{C}(CH_3)_3$, 2C), 35.43 (vt, ^{v}J = 5.2 Hz, $P\mathit{C}(CH_3)_3$, 2C), 39.43 (vt, ^{v}J = 10.0 Hz, $\mathit{C}H_2$, 2C), 46.86 (t, J = 9.7 Hz, $\mathit{C}H$, 1C); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 23.00 (vt, ^{v}J = 9.3 Hz, $\mathit{C}H_2$, 2C), 29.27 (vt, ^{v}J = 2.4 Hz, $PC(\mathit{C}H_3)_3$, 6C), 30.04 (vt, ^{v}J = 2.4 Hz, $PC(\mathit{C}H_3)_3$, 6C), 34.50 (vt, ^{v}J = 6.9 Hz, P*C*(CH$_3$)$_3$, 2C), 35.36 (vt, ^{v}J = 5.5 Hz, P*C*(CH$_3$)$_3$, 2C), 38.95 (vt, ^{v}J = 9.7 Hz, *C*H$_2$, 2C), 46.70 (t, *J* = 9.7 Hz, *C*H, 1C); ^{31}P{^{1}H} NMR (C$_6$D$_6$): 73.8 (s); ^{31}P{^{1}H} NMR (CDCl$_3$): 74.0 (s). Anal. Calcd for C$_{21}$H$_{45}$ClP$_2$Ni: C, 55.60; H, 10.00. Found: C, 55.43; H, 10.43.

[{Bu$^{t}_{2}$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^{t}_{2}$}NiBr] (1b). The procedure described for the preparation of complex **1a** was used with nickel (II) bromide to give complex **1b** as an orange solid (152 mg, 44%). ^{1}H NMR (C$_6$D$_6$): 0.90-1.85 (m, 9H), 1.42 (vt, ^{v}J = 6.4 Hz, PC(C*H*$_3$)$_3$, 18H), 1.47 (vt, ^{v}J = 6.4 Hz, PC(C*H*$_3$)$_3$, 18H); ^{13}C{^{1}H} NMR (C$_6$D$_6$): 23.89 (vt, ^{v}J = 8.6 Hz, *C*H2, 2C), 29.63 (s, PC(*C*H$_3$)$_3$, 6C), 30.54 (s, PC(*C*H$_3$)$_3$, 6C), 35.12 (vt, ^{v}J = 5.9 Hz, P*C*(CH$_3$)$_3$, 2C), 35.74 (vt, ^{v}J = 5.5 Hz, P*C*(CH$_3$)$_3$, 2C), 39.31 (vt, ^{v}J = 9.3 Hz, *C*H$_2$, 2C), 50.21 (t, *J* = 8.6 Hz, *C*H, 1C); ^{31}P{^{1}H} NMR (C$_6$D$_6$): 73.5 (s). Anal. Calcd for C$_{21}$H$_{45}$BrP$_2$Ni: C, 50.64; H, 9.11. Found: C, 50.67; H, 9.37 .

[{Bu$^{t}_{2}$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^{t}_{2}$}NiI] (1c). The procedure described for the preparation of complex **1a** was used with nickel (II) iodide to give complex **1c** as an orange solid (141 mg, 37%). ^{1}H NMR (C$_6$D$_6$): 0.80-1.85 (m, 9H), 1.43 (vt, ^{v}J = 5.1 Hz, PC(C*H*$_3$)$_3$, 18H), 1.49 (vt, ^{v}J = 5.1 Hz, PC(C*H*$_3$)$_3$, 18H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) 24.62 (vt, ^{v}J = 8.3 Hz, *C*H$_2$, 2C), 29.91 (s, PC(*C*H$_3$)$_3$, 6C), 31.19 (s, PC(*C*H$_3$)$_3$, 6C), 35.83 (vt, ^{v}J = 7.2 Hz, P*C*(CH$_3$)$_3$, 2C), 36.11 (vt, ^{v}J = 5.5 Hz, P*C*(CH$_3$)$_3$, 2C), 39.10 (vt, ^{v}J = 9.3 Hz, *C*H$_2$, 2C), 56.02 (t, *J* = 8.6 Hz, *C*H, 1C). ^{31}P{^{1}H} NMR (C$_6$D$_6$) 74.7 (s). Anal. Calcd for C$_{21}$H$_{45}$IP$_2$Ni: C, 46.27; H, 8.32. Found: C, 46.73; H, 8.66.

[{Bu$^{t}_{2}$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^{t}_{2}$}NiMe] (2). MeMgCl (0.20 mL of a 3.0 M solution in THF, 0.60 mmol) was added to a solution of complex **1a** (272 mg, 0.60 mmol) in benzene (10 mL) and the mixture was refluxed for 1 h. The solvent was then evaporated to dryness to give a crude sample of complex **2** as a yellow solid. This sample contained some in-situ formed MgCl$_2$, which could not be removed by washing with water or extraction into hexane. ^{1}H NMR (C$_6$D$_6$): –0.27 (t, *J* = 7.6 Hz, NiC*H*$_3$, 3H), 1.29 (vt, *J* = 6.4 Hz, PC(C*H*$_3$)$_3$, 18H), 1.30 (vt, *J* = 5.1 Hz, PC(C*H*$_3$)$_3$, 18H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) –19.07 (t, *J* = 19.0 Hz, Ni*C*H$_3$, 1C), 27.69 (vt, ^{v}J = 9.3 Hz, *C*H$_2$, 2C), 29.78 (vt, ^{v}J = 2.8 Hz, $PC(CH_3)_3$, 6C), 30.43 (vt, ^{v}J = 2.4 Hz, $PC(CH_3)_3$, 6C), 34.52 (vt, ^{v}J = 6.2 Hz, $PC(CH_3)_3$, 2C), 35.84 (vt, ^{v}J = 4.8 Hz, $PC(CH_3)_3$, 2C), 38.15 (vt, ^{v}J = 10.0 Hz, CH_2, 2C), 57.67 (t, J = 9.7 Hz, CH, 1C); $^{31}P\{^1H\}$ NMR (C_6D_6) 80.5 (s).

$[\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}NiH]$ (3). *n*-BuLi (0.05 mL of a 2.5 M solution in hexanes, 0.125 mmol) was added to a concentrated solution of **1a** (57 mg, 0.125 mmol) in benzene-d_6 (0,5 mL). Monitoring by NMR spectroscopy showed that the signals for **1a** were replaced over 30 min by new signals assigned to the hydride species **3**, 1-butene, and free ligand. Evaporation of the volatiles gave a mixture of complex **3** and the free ligand. ^1H NMR (C_6D_6): –10.14 (t, J = 53.4 Hz, NiH, 1H), 1.25 (vt, ^{v}J = 7.6 Hz, $PC(CH_3)_3$, 18H), 1.26 (vt, ^{v}J = 6.3 Hz, $PC(CH_3)_3$, 18H); $^{13}C\{^1H\}$ NMR (C_6D_6) 27.37 (vt, ^{v}J = 7.9 Hz, CH_2, 2C), 29.68 (vt, ^{v}J = 3.5 Hz, $PC(CH_3)_3$, 6C), 30.25 (vt, ^{v}J = 3.1 Hz, $PC(CH_3)_3$, 6C), 33.02 (vt, ^{v}J = 8.6 Hz, $PC(CH_3)_3$, 2C), 33.58 (vt, ^{v}J = 12.4 Hz, $PC(CH_3)_3$, 2C), 38.80 (vt, ^{v}J = 10.3 Hz, CH_2, 2C), 60.39 (t, J = 6.9 Hz, CH, 1C); $^{31}P\{^1H\}$ NMR (C_6D_6) 108.8 (s).

$[(Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2)Ni(N{\equiv}CCH_3)][BPh_4]$ (4). A solution of complex **1a** (345 mg, 0.813 mmol) in benzene (10 mL) was added to a solution of $NaBPh_4$ (293 mg, 0.813 mmol) in acetonitrile (15 mL) and the mixture was stirred at room temperature for 3h. Evaporation of the final mixture and extraction of the solid residues with CH_2Cl_2 (15 mL) gave a yellow solution, which was filtered and evaporated to give compound **4** as a pale yellow solid (373 mg, 63%). ^1H NMR ($CDCl_3$): 0.70 (s, CH_3CN, 3H), 0.90-2.25 (m, 9H), 1.29 (vt, ^{v}J = 7.6 Hz, $PC(CH_3)_3$, 18H), 1.34 (vt, ^{v}J = 6.4 Hz, $PC(CH_3)_3$, 18H), 6.88 (t, J = 7.6 Hz, Ar, 4H), 7.05 (t, J = 7.6 Hz, Ar, 8H), 7.47 (br s, Ar, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.32 (vt, ^{v}J = 11.0 Hz, CH_2, 2C), 29.38 (m, $PC(CH_3)_3$, 6C), 29.61 (m, $PC(CH_3)_3$, 6C), 34.94 (vt, ^{v}J = 7.2 Hz, $PC(CH_3)_3$, 2C), 36.21 (vt, ^{v}J = 6.2 Hz, $PC(CH_3)_3$, 2C), 39.07 (m, CH_2, 2C), 54.03 (m, CH, 1C), 121.82 (s, Ar, 4C), 125.88 (s, Ar, 8C), 136.10 (s, Ar, 8C), 164.40 (q, J = 49.0 Hz, Ar, 4C); $^{31}P\{^1H\}$ NMR ($CDCl_3$): 88.4 (s). IR (KBr) : 2270 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{47}H_{68}BNP_2Ni \cdot H_2O$: C, 70.87; H, 8.86; N, 1.76. Found: C, 70.73; H, 9.33; N, 1.54.

[(Bu$^t{}_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t{}_2$)Ni(N≡CCH=CH$_2$)][BPh$_4$] (5). NaBPh$_4$ (77 mg, 0.225 mmol) was added to a solution of complex **1a** (102 mg, 0.225 mmol) in neat acrylonitrile (4 mL). The reaction mixture was stirred for 16h at room temperature. Evaporation of the final mixture and extraction of the solid residues with CH$_2$Cl$_2$ (10 mL) gave a yellow solution, which was filtered and evaporated to give compound **5** as a pale yellow solid (109 mg, 61%). ^{1}H NMR (CDCl$_3$): 0.90-2.30 (m, 9H), 1.30 (vt, ^vJ = 6.7 Hz, PC(C*H*$_3$)$_3$, 18H), 1.34 (vt, ^vJ = 6.7 Hz, PC(C*H*$_3$)$_3$, 18H), 4.76 (dd, *J* = 17.2 Hz, 11.4 Hz, N≡CCH=CH$_2$, 1H), 5.57 (d, *J* = 11.4 Hz, N≡CCH=CH$_2$, 1H), 5.74 (d, *J* = 17.2 Hz, N≡CCH=CH$_2$, 1H), 6.87 (t, *J* = 6.7 Hz, Ar, 4H), 7.02 (t, *J* = 7.6 Hz, Ar, 8H), 7.42 (br s, Ar, 8H); ^{13}C{^{1}H} NMR (CDCl$_3$): 22.41 (vt, ^vJ = 11.0 Hz, *C*H$_2$, 2C), 29.38 (vt, ^vJ = 2.1 Hz, PC(*C*H$_3$)$_3$, 6C), 29.66 (vt, ^vJ = 2.1 Hz, PC(*C*H$_3$)$_3$, 6C), 35.25 (vt, ^vJ = 7.2 Hz, P*C*(CH$_3$)$_3$, 2C), 36.48 (vt, ^vJ = 6.6 Hz, P*C*(CH$_3$)$_3$, 2C), 39.21 (vt, ^vJ = 7.6 Hz, *C*H$_2$, 2C), 55.63 (m, *C*H, 1C), 105.06 (s, N≡CCH=CH$_2$, 1C), 121.73 (s, Ar, 4C), 125.66 (s, Ar, 8C), 136.35 (s, Ar, 8C), 142.57 (s, N≡CCH=CH$_2$, 1C), 164.39 (q, *J* = 48.9 Hz, Ar, 4C); ^{31}P{^{1}H} NMR (CDCl$_3$): 90.1 (s). IR (KBr) : 2232 cm^{-1}, $\nu_{C\equiv N}$. Anal. Calcd for C$_{48}$H$_{68}$BNP$_2$Ni·H$_2$O: C, 71.30; H, 8.73; N, 1.73. Found: C, 71.53; H, 8.86; N, 1.64.

Determination of K$_{eq}$ for the reaction of 4 with acrylonitrile. This experiment was performed by adding different amounts of acrylonitrile to an NMR sample containing a solution of **4** in CDCl$_3$ ([**4**] = 0.05M - 0.09M) and recording successive ^{1}H and ^{13}P{^{1}H} NMR spectra until the signal intensities were unchanged from one spectrum to the next. The K_{eq} values were determined on the basis of data obtained from 8 different experiments; the calculations were based on the relationship K_{eq} = [**5**][MeCN]/[**4**][acrylonitrile], using ratios of the NMR signal integrations for these species as approximation for concentration ratios. Since the ^{1}H NMR signals for **4** and MeCN were difficult to measure with precision, the K_{eq} was determined by combining ^{1}H and ^{31}P NMR data, as follows: the [**5**]/[**4**] ratio was determined from the integration values of the ^{31}P{^{1}H} signals for **5** and **4**, whereas the [MeCN]/[acrylonitrile] ratio was determined from the integration values of the ^{1}H signals for **5** and acrylonitrile, since the equilibrium mixture must contain equimolar quantities of **5** and MeCN.

X-Ray Crystal Structures of 1a, 1b, 1c, 4, and 5. Single crystals of these complexes were grown from : hexanes solutions at room temperature (**1a**, **1b**, **1c**); slow diffusion of hexanes into a saturated solution of the complex in benzene-d_6 (**4**); slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane (**5**). The crystallographic data (Table 2.1) was collected on a Bruker AXS diffractometer equipped with a SMART 2K CCD area detector with graphite monochromatic Cu K_α radiation using SMART. Cell refinement and data reduction were done using SAINT.[28] An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[29] The space group was confirmed by XPREP routine[30] in the program SHELXTL.[31] The absolute configuration of the non centrosymmetric crystal was determined using the Flack parameter.[32] The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97.[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. The autoindexing program for twinned crystals GEMINI[34] was used to resolve the molecular structure of complex **1b**. Some disorder was taken into account for two of the *t*-Bu groups of complex **1c**, as well as the iodine atom (two positions).

Supporting Information. Complete details of the X-ray analyses for complexes **1a**, **1b**, **1c**, **4**, and **5** have been deposited at The Cambridge Crystallographic Data Centre (CCDC 283327 – 283329 (**1**), 283330 (**4**), 284336 (**5**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Dalton Trans. **1975**, 1294) are green, and [$NiI_3(PPh_3)$][$AsPh_4$] is red (Taylor, R. P.; Templeton, D. H.; Zalkin, A.; Horrocks, W. *Inorg. Chem.* **1968**, *7*, 2629).

[13] X-ray diffraction studies carried out on the blue crystals of **A** and **B** have confirmed the empirical formulae and the connectivities in these compounds, but the poor quality of the data obtained does not allow firm commentary on the structural details.

[14] The ^{1}H NMR spectrum of this species contained poorly-defined, broad peaks, but its $^{31}P\{^1H\}$ NMR (CD_2Cl_2) spectrum showed only a singlet at 17.4 ppm, which is tentatively assigned to the phosphonium moiety.

[15] Cambridge Crystallographic Data Center, ConQuest 1.7 (2004).

[16] The Ni-Me derivative reverts to its precursor Ni-Cl species, partially or completely, during work-up, presumably because of the reverse metathesis reaction with in-situ generated $MgCl_2$. Attempts to remove $MgCl_2$ from samples of **2** by washing with water or extraction in hexanes were not successful. The Ni-H derivative is thermally unstable.

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[18] It is noteworthy that the IR spectrum also displayed two equally weak bands (ca. 2182 and 2304 cm^{-1}) that have not been assigned, but might arise from overtones of the BPh_4 anion or from a complex bearing two acetonitrile moieties, one engaging in π–backbonding and the other in σ–donation with the Ni center.

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[21] To be sure, the $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1a** with norbornene showed a small new peak (<5%), which might be the target olefin product, but isolation of this species was not pursued.

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[30] XPREP (**1997**) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program. Bruker AXS Inc., Madison, Wisconsin, USA.

[31] SHELXTL (**1997**) Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, Wisconsin, USA.

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Chapitre 3: Preparation and Reactivities of PCP-type Pincer Complexes of Nickel. Impact of Different Ligand Skeletons and Phosphine Substituents

Article 2

manuscrit accepté par *Organometallics*

Annie Castonguay, Davit Zargarian,* and André L. Beauchamp*
Département de chimie, Université de Montréal, Montréal (Québec), Canada H3C 3J7

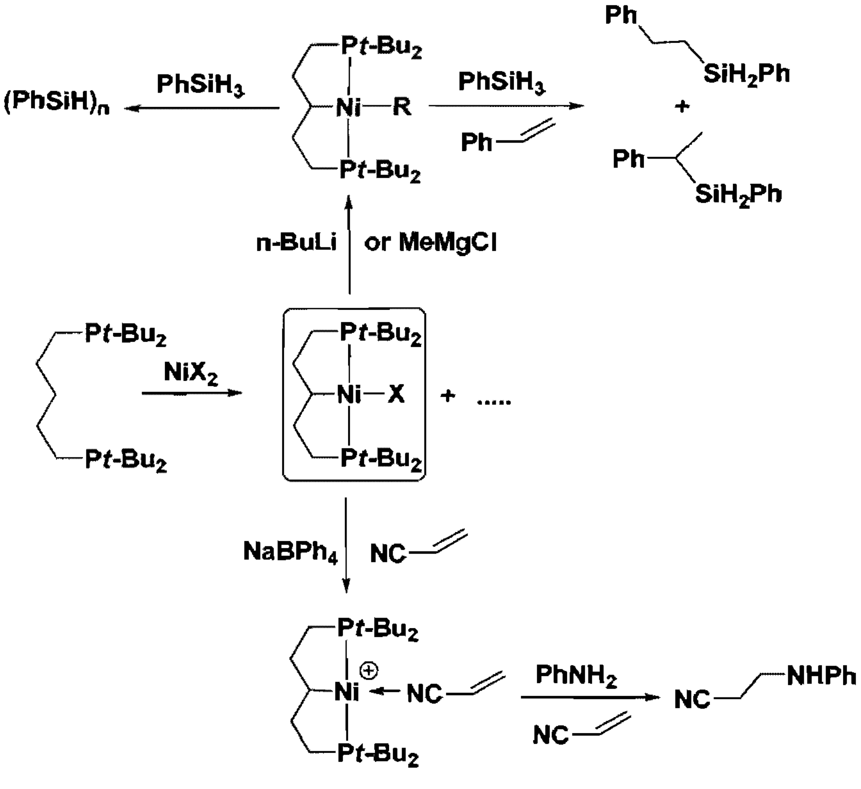
Abstract

Reaction of the diphosphine ligand $i\text{-Pr}_2\text{P}(\text{CH}_2)_5\text{P}(i\text{-Pr})_2$ with NiBr_2 at 110 °C gives a mixture of the 16-membered bimetallacycle $\{i\text{-Pr}_2\text{P}(\text{CH}_2)_5\text{P}(i\text{-Pr})_2\}_2\text{Ni}_2\text{Br}_4$, **1**, and the pincer-type complex $\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiBr}$, **2**; the latter can also be obtained by heating **1** in the presence of 4-(dimethylamino)pyridine or under vacuum. Complex **2** undergoes transmetallation with RMgCl or RLi to give $\{i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiR}$ (R= Me (**4**), C≡CMe (**5**), Ph (**6**), *n*-Bu (**7**), and C≡CPh (**8**)); the phenylacetylide derivative **8** was also obtained from the reaction of PhC≡CH with **4**, **5**, or **7**. The Ni-Me derivative **4** reacts with PhX (X= I, Br, Cl) to give the product of C-C coupling reaction (Ph-Me) and the Ni-X analogues of **2**, and tests have shown that **2** is a competent catalytic precursor for the coupling of PhCl and MeMgCl. The available evidence suggests that this catalytic process does not involve Ni^0 intermediates. Indeed, cyclic voltammetry measurements show that **2** can undergo two consecutive oxidations and attempts to generate isolable high-valent species yielded the 5-coordinate, 17-electron Ni^{III} species $\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiX}_2$, **9**, from the reaction of **2** with FeX_3 (X = Cl, Br). Characterization of all new complexes, including X-ray diffraction studies on single crystals of complexes **1-6** and **9**, are described.

Introduction

Many PCP-type pincer complexes[1] are efficient catalysts for a variety of organic transformations.[2,3] An important advantage of PCP ligands is that they can be modified easily at multiple sites, thus allowing control over the electronic and steric properties of their complexes. For example, it has been demonstrated that the catalytic efficiency of PCP-Pd complexes for the Heck coupling can be improved by changing the nature of the cyclometallated carbon from sp^2 to sp^3 hybridization, incorporating oxygens in the ligand skeleton, varying the phosphorus substituents from *t*-Bu to *i*-Pr or by increasing the size of the metallocycles from five to six-membered.[4]

Our long-standing interest in organonickel complexes[5] and the fairly unexplored chemistry of PCP-type pincer complexes of nickel[6] have prompted us to investigate the preparation of PCP-Ni complexes and their reactivities. Recent reports have described the results of our initial studies on the synthesis and reactivities of a new series of pincer complexes of nickel based on the PCP-type ligands 1,3-$(CH_2CH_2PPh_2)_2$-indenyl[7] and t-$Bu_2P(CH_2)_5P(t$-$Bu)_2$ ($PC_{sp3}P^{t\text{-}Bu}$).[8,9] We found, for example, that reacting the latter ligand with NiX_2 (X = Cl, Br, I) gives a mixture of the desired pincer-type complex $\{(t$-$Bu_2PCH_2CH_2)_2CH\}NiX$ along with paramagnetic species believed to be zwitterionic tetrahedral complexes featuring the unmetallated pincer ligand (Scheme 3.1). The $Ni(PC_{sp3}P^{t\text{-}Bu})X$ complexes (X= H, Me) promote the dehydrogenative oligomerization of $PhSiH_3$ and its addition to styrene, whereas their cationic NCR adducts (R= Me, CH=CH_2) promote the hydroamination of acrylonitrile with aniline (Scheme 3.1).



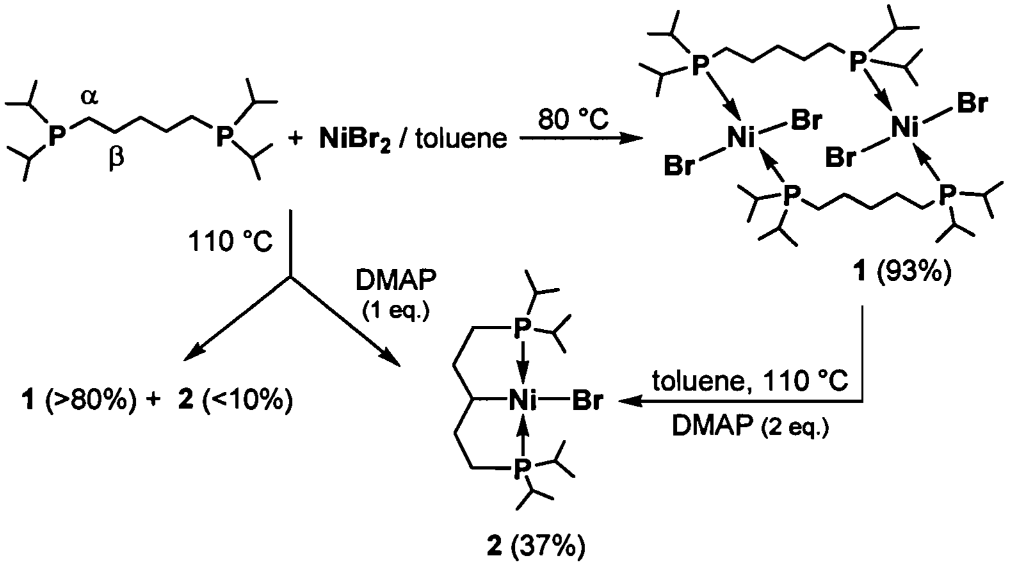
Scheme 3.1

Subsequent studies focused on modifying the $PC_{sp3}P$ ligand framework in order to evaluate the influence of ligand architecture on the reactivities of the resulting complexes. Thus, we found that some Ni pincer complexes based on the diphosphinito-type ligands ($(i\text{-}Pr_2POCH_2)_2CH_2$ ($POC_{sp3}OP^{i\text{-}Pr}$) or 1,3-$(i\text{-}Pr_2PO)_2C_6H_4$ ($POC_{sp2}OP^{i\text{-}Pr}$) are efficient catalysts for the hydroamination of acrylonitrile derivatives and the Kharasch addition of CCl_4 to olefins.[10]

As an extension of our initial studies, we have investigated the impact of phosphine substituents on the syntheses of pincer-type compounds and their reactivities. The present report describes the synthesis and reactivities of new Ni complexes based on the diphosphine ligand $i\text{-}Pr_2P(CH_2)_5P(i\text{-}Pr)_2$ ($PC_{sp3}P^{i\text{-}Pr}$), including the pincer-type Ni^{II} and Ni^{III} compounds ($PC_{sp3}P^{i\text{-}Pr}$)NiX (X= Br, Me, C≡CMe, Ph, *n*-Bu, and C≡CPh) and ($PC_{sp3}P^{i\text{-}Pr}$)NiX_2 (X= Br, Cl). Also reported is the synthesis and solid state structure of $\{i\text{-}Pr_2P(CH_2)_5P(i\text{-}Pr)_2\}_2Ni_2Br_4$, a dimeric species featuring the non-metallated ligand.

Results and Discussion

Synthesis of $\{i\text{-}Pr_2P(CH_2)_5P(i\text{-}Pr)_2\}_2Ni_2Br_4$, 1, and $\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiBr$, 2. Mixing the diphosphine ligand $PC_{sp3}P^{i\text{-}Pr}$ with $NiBr_2$ for 2 h at 80 °C gave 93% yield of a purple solid that was identified as the 16-membered bimetallacycle complex **1** (Scheme 3.2). Increasing the reaction temperature to 110 °C afforded, after 12 h, a mixture of products consisting of **1** as the major component (>80%) along with a small amount (<10%) of a golden-brown solid identified as the pincer-type complex **2** (Scheme 3.2). Carrying out the latter reaction in more dilute conditions did not lead to a better yield of the target complex **2**, but the presence of one equivalent of 4-(dimethylamino)pyridine (DMAP) in the reaction mixture gave a 37% yield of complex **2** (Scheme 3.2). Interestingly, heating a 1:2 mixture of pure **1** and DMAP gives **2** with a similar yield, which implies that **1** might be an intermediate in the formation of **2**. Finally, a small amount of **2** was also obtained (along with some free ligand) when a solid sample of complex **1** was heated to 200-220 °C under reduced pressure for a few hours; a similar transformation has been reported for $\{t\text{-Bu}_2P(CH_2)_5P(t\text{-Bu})_2\}_2Pd_2Cl_4$.[1b,11]



Scheme 3.2

Complexes **1** and **2** can be handled in air, both in the solid state and in solution, without noticeable decomposition even after weeks. The NMR spectra of these complexes were quite different from one another, showing that complex **1** adopts a fluxional structure in solution whereas **2** displays spectral patterns typical of pincer complexes. For instance, the room temperature $^{31}P\{^1H\}$ NMR spectrum of **1** showed no signal at all, while its room temperature ^1H and $^{13}C\{^1H\}$ NMR spectra displayed broad, featureless signals; interestingly, the $^{13}C\{^1H\}$ chemical shifts were quite similar for **1** and the uncoordinated ligand. Lowering the probe temperature to -15 °C led to the emergence of a broad $^{31}P\{^1H\}$ signal (17 ppm), but this and the ^1H and $^{13}C\{^1H\}$ signals did not sharpen appreciably even at -50 °C, thus providing little structural information for complex **1**.

In contrast, NMR spectroscopy was very helpful in establishing the solution structure of complex **2**, as follows. The equivalence of the phosphorus nuclei was confirmed by the presence of one singlet resonance (67.4 ppm) in the room temperature $^{31}P\{^{1}H\}$ NMR spectrum of **2**, while the *trans* disposition of the phosphorus atoms in this complex was suggested by the presence of virtual triplets in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for the methyl protons and carbons of the isopropyl groups. The $^{13}C\{^{1}H\}$ NMR spectrum also displayed virtual triplets for the α and β carbons of the alkyl chain of the ligand, and the cyclometallation of the central carbon atom was confirmed by the presence of a downfield-shifted triplet signal (52 ppm, $^{2}J_{PC}$ = 9 Hz; free ligand: 34 ppm).

The solid state structures of **1** and **2** were established by X-ray analyses of single crystals of these compounds.[12] The crystal data and collection details are listed in Table 3.I, whereas ORTEP views are shown in Figures 3.1 and 3.2. The nickel center in **1** adopts a slightly distorted square-planar geometry, the P-Ni-P and Br-Ni-Br angles varying between ~166° and ~173°. The Ni-Br bond lengths (2.30-2.32 Å) are within the expected range for *trans*-NiP_2Br_2 arrangements (ca. 2.30),[13] whereas the Ni-P bond lengths (2.25-2.27 Å) are similar to those of the analogous species $\{i\text{-}Pr_2P(CH_2)_5P(i\text{-}Pr)_2\}_2Ni_2Cl_4$ (2.24-2.26 Å).[12] The size of the macrocycle can be estimated from the distances between P1 and P3 (9.6 Å), P2 and P4 (9.1 Å), C3 and C8 (6.0 Å), and Ni1 and Ni2 (8.4 Å).

The Ni center in **2** adopts a square-planar geometry wherein all structural parameters (Table 3.II) are in the expected range. This solid state structure confirms the metallation of the ligand as inferred from the solution NMR spectra. Comparison of Ni-ligand bond lengths in **2** and its *t*-Bu analogue $\{(t\text{-}Bu_2PCH_2CH_2)_2CH\}NiBr$[8] (Table 3.II) shows that the main structural impact brought about by the change of the phosphorus substituents is on the Ni-P bond distances, that are significantly shorter in complex **2** (ca. 2.18 vs. 2.21 Å). We infer that the greater steric bulk of the *t*-Bu groups must prevent the phosphine moieties from approaching the metal center sufficiently to allow optimal orbital overlap.

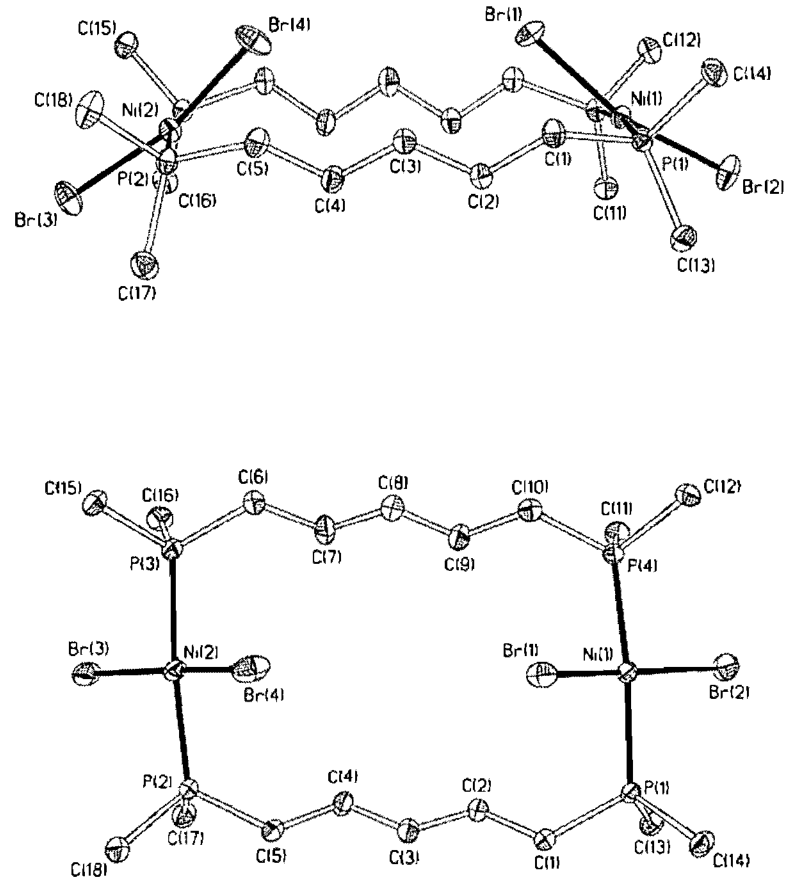


Figure 3.1. ORTEP diagrams for complex **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and isopropyl methyl carbons are omitted for clarity. Selected Bond Distances (Å) and Angles (deg) : Ni(1)-P(1) = 2.2494(10), Ni(1)-P(4) = 2.2466(10), Ni(2)-P(2) = 2.2680(10), Ni(2)-P(3) = 2.2704(10), Ni(1)-Br(1) = 2.3038(6), Ni(1)-Br(2) = 2.3125(7), Ni(2)-Br(3) = 2.3244(7), Ni(2)-Br(4) = 2.3013(7), P(1)-Ni(1)-P(4) = 171.85(4), P(2)-Ni(2)-P(3) = 173.36(4), Br(1)-Ni(1)-Br(2) = 165.99(3), Br(3)-Ni(2)-Br(4) = 167.83(4).

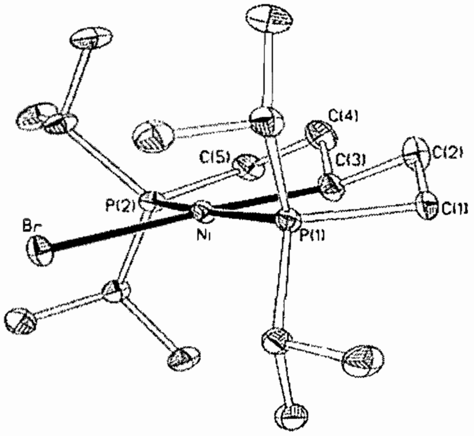


Figure 3.2. ORTEP diagram for complex **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens are omitted for clarity.

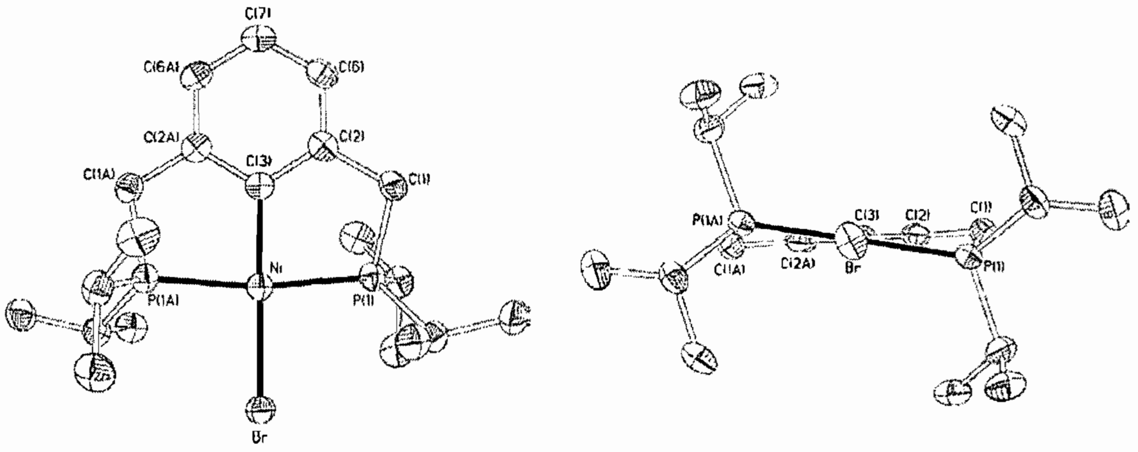


Figure 3.3. ORTEP diagrams for complex **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens are omitted for clarity.

Table 3.I. Crystal Data Collection and Refinement Parameters for Complexes **1**-**6** and **9**.

	1	**2**	**3**	**4**	**5**	**6**	**9b**
chemical formula	$C_{34}H_{76}Br_4Ni_2P_4$	$C_{17}H_{37}BrNiP_2$	$C_{20}H_{35}BrNiP_2$	$C_{18}H_{40}NiP_2$	$C_{20}H_{40}NiP_2$	$C_{23}H_{42}NiP_2$	$C_{17}H_{37}Br_2NiP_2$
Fw	1045.89	442.03	476.04	377.15	401.17	439.22	521.92
T (K)	220(2)	100(2)	150(2)	100(2)	220(2)	220(2)	150(2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178	1.54178	1.54178
space group	Pbca	$P2_1/n$	R-3c	$P2_1/c$	$P2_1/n$	$P2_1/n$	Pbca
a (Å)	23.6525 (13)	8.4858(2)	25.2547(3)	14.2542(6)	10.8603(6)	10.1898(9)	14.0098(16)
b (Å)	14.4554 (9)	11.8590(3)	25.2547(3)	13.7514(6)	14.5551(9)	12.5298(12)	16.2434(18)
c (Å)	27.6110 (16)	20.8903(5)	20.6154(5)	10.5561(4)	14.1473(8)	19.3011(16)	38.914(4)
α (deg)	90	90	90	90	90	90	90
β (deg)	90	90.7960(10)	90	95.091(2)	92.175(2)	97.936(4)	90
γ (deg)	90	90	120	90	90	90	90
Z	8	4	18	4	4	4	16
V (Å^3)	9440.4 (10)	2102.05(9)	11386.9(3)	2060.99(15)	2234.7(2)	2440.7(4)	8855.5(17)
ρ_{calcd} (g cm^{-3})	1.472	1.397	1.250	1.215	1.192	1.195	1.566
μ (cm^{-1})	63.85	49.23	41.32	27.49	25.68	23.95	68.07
θ range (deg)	3.20-73.04	4.23-68.81	3.50-68.45	3.11-68.87	4.36-72.03	4.22-72.00	2.27-65.85
R1[a] [$I > 2\sigma(I)$]	0.0615	0.0322	0.0436	0.0395	0.0410	0.0486	0.0328
wR2[b] [$I > 2\sigma(I)$]	0.1303	0.0811	0.1517	0.1019	0.1118	0.1264	0.0757
R1 [all data]	0.0704	0.0382	0.0517	0.0468	0.0427	0.0549	0.0520
wR2 [all data]	0.1360	0.0838	0.1518	0.1068	0.1134	0.1317	0.0812
GOF	1.079	1.021	1.186	1.003	1.084	1.023	0.963

[a] $R1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[b] $wR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

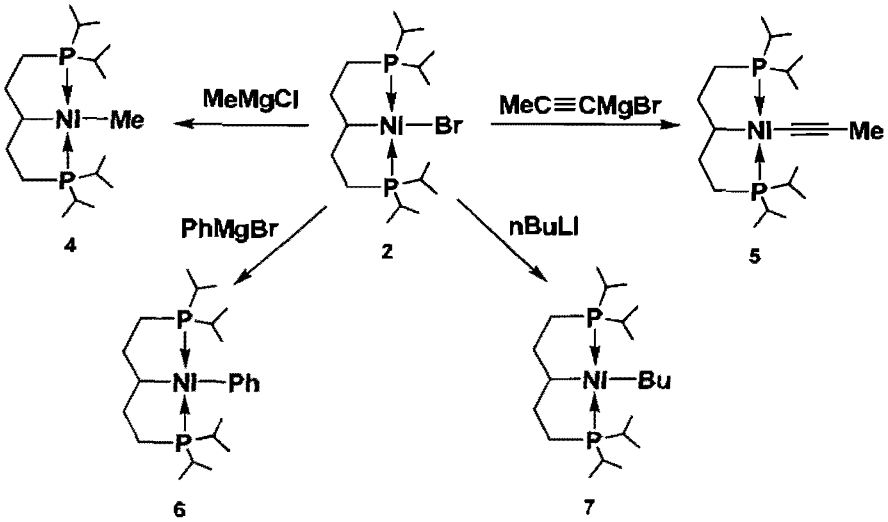
Table 3.II. Selected Bond Distances (Å) and Angles (deg) for Complexes **2**, **3** and **4-6**.

	$(PC_{sp3}P^{i\text{-}Pr})NiBr$ (**2**)	$(PC_{sp3}P^{t\text{-}Bu})NiBr^{8}$	$(PC_{sp2}P^{i\text{-}Pr})NiBr$ (**3**)	$(PC_{sp3}P^{i\text{-}Pr})NiMe$ (**4**)	$(PC_{sp3}P^{i\text{-}Pr})NiCCMe$ (**5**)	$(PC_{sp3}P^{i\text{-}Pr})NiPh$ (**6**)
Ni-C(3)	1.982(3)	1.971(4)	1.918(3)	2.004(2)	1.992(2)	2.006(2)
Ni-P(1)	2.1801(7)	2.218(1)	2.1645(6)	2.1535(6)	2.1491(5)	2.1479(6)
Ni-P(2)	2.1794(7)	2.212(1)	2.1645(6)*	2.1381(6)	2.1604(5)	2.1455(6)
Ni-X	2.3712(5)	2.3866(7)	2.3443(6)	2.016(2)	1.914(2)	1.944(2)
C(3)-Ni-X	177.22(8)	169.9(1)	180.0(2)	172.81(9)	174.28(8)	177.5(1)
P(1)-Ni-P(2)	171.13(3)	170.16(5)	170.60(4)*	170.05(3)	170.57(2)	170.24(2)
P(1)-Ni-X	94.76(2)	94.48(3)	94.70(2)	94.93(6)	91.74(5)	94.27(6)
P(2)-Ni-X	94.09(2)	95.00(4)	94.70(2)*	94.74(6)	97.64(5)	95.46(6)
P(1)-Ni-C(3)	86.08(8)	85.9(1)	85.30(2)	84.80(6)	85.42(5)	84.57(7)
P(2)-Ni-C(3)	85.05(8)	85.2(1)	85.30(2)*	85.91(6)	85.15(5)	85.68(7)

*Symmetry transformation used to generate equivalent atoms : y + 1/3, x – 1/3, -z + 1/6

In order to assess the structural differences in PCP-type pincer complexes featuring aliphatic vs. aromatic linkers, we have prepared complex $\{(i\text{-Pr}_2PCH_2)_2C_6H_3\}$NiBr, **3**, the previously reported[14] $PC_{sp2}P$ analogue of **2**, and examined its solid state structure. ORTEP views of **3** are shown in Figure 3.3 and crystal data are listed in Table 3.I. We found that the Ni-P and the Ni-Br bond lengths are approximately the same in both complexes, but that the Ni-C bond is shorter in **3** (1.92 vs. 1.98 Å), as expected for a M-C bond distance with greater s character (Table 3.II).

Reactivities of 2. Our interest in exploring the potential of PCP-Ni compounds as promoters of carbon-carbon bond formation reactions led us to prepare organonickel derivatives of complex **2** and compare their stabilities and reactivities as a function of phosphine substituents. We found that **2** reacts with MeMgCl or MeC≡CMgBr at room temperature to give the Ni-Me (**4**, ca. 71%) and Ni-C≡CMe (**5**, 79%) derivatives, respectively, whereas the reaction with PhMgBr required refluxing in THF for 1 h to give the Ni-Ph derivative (**6**, ca. 62% yield, Scheme 3.3). By comparison, preparation of the analogous Ni-Me derivative based on the $PC_{sp3}P^{t\text{-Bu}}$ ligand was less facile, requiring heating for at least 1 h for total conversion,[8] whereas the Ni-Ph derivative could not be prepared with this ligand even after extended heating. Phosphine substituents also influence the stability of the alkyl derivatives toward β-hydrogen elimination. Thus, solutions of the Ni-Bu derivative **7** obtained from the reaction of **2** with *n*-BuLi are stable for hours at room temperature (Scheme 3.3), whereas under the same conditions the analogous complex $(PC_{sp3}P^{t\text{-Bu}})$Ni-Bu undergoes β-hydrogen elimination within a few minutes to give the corresponding hydride complex (and a considerable amount of free ligand); this difference of reactivity likely arises from the steric blocking of the d_{z^2}-p_z hybrid orbital by the $(i\text{-Pr})_2P$ groups that are at a closer proximity to the Ni center in comparison to their $(t\text{-Bu})_2P$ analogues.[8]



Scheme 3.3

Spectroscopic characterization of complexes **4**-**7** was relatively straight forward. The appearance of a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum of each derivative (71.4, 76.1, 68.1, and 68.1 ppm for **4**, **5**, **6** and **7**, respectively) demonstrated the equivalence of the phosphine moieties, while the maintenance of their *trans* arrangement was reflected in the presence of virtual triplets in their respective ^1H and $^{13}C\{^1H\}$ NMR spectra. The metallated nature of the central CH group was evident from a slightly downfield-shifted triplet (56-59 ppm, $^2J_{PC} \sim$ 9-10 Hz; free ligand: 34 ppm) in the $^{13}C\{^1H\}$ NMR spectrum for each of these complexes.

The Ni-Me moiety in complex **4** was represented by high-field triplet resonances in its ^1H (–0.50 ppm, $^3J_{P\text{-}H} = 7.7$ Hz) and $^{13}C\{^1H\}$ (–18.64 ppm, $^2J_{PC} = 19.9$ Hz) NMR spectra. The $^{13}C\{^1H\}$ NMR spectrum of complex **5** exhibited three resonances for the propynyl moiety: a triplet at 98.44 ppm ($^2J_{PC}$ = 30.8 Hz, Ni-*C*≡CCH$_3$), a singlet at 115.74 ppm (Ni-C≡*C*CH$_3$), and a singlet at 7.61 ppm (Ni-C≡C*C*H$_3$). The ^1H NMR spectrum of this complex showed a singlet at 2.13 ppm corresponding to the methyl protons of the propynyl moiety, while the IR spectrum showed a sharp band at 2100 cm^{-1}, which was assigned to $\nu_{C\equiv C}$. The Ni-Ph moiety of complex **6** was identified by the appearance in the ^1H and $^{13}C\{^1H\}$ NMR spectra of signals corresponding to the five non-equivalent aromatic protons and carbon nuclei, in addition to a low-field triplet resonance assigned to the *ipso*-C (168.77 ppm, ${}^2J_{PC}$ = 24.0 Hz). The non-equivalence of the carbons and protons of the Ni-Ph moiety implies that the phenyl ring does not undergo rapid rotation in solution and does not lie in the coordination plane of the molecule; the solid state structure of this complex confirms a non-planar conformation for the Ph ring (*vide infra*). The ${}^{13}C\{{}^1H\}$ NMR spectrum of complex **7** showed two triplet resonances assigned to Ni-CH_2 (0.51 ppm, ${}^2J_{PC}$= 19.0 Hz) and Ni-CH_2CH_2 (36.41 ppm, ${}^3J_{PC}$ = 2.3 Hz) and two singlets assigned to Ni-$CH_2CH_2CH_2$ (31.02 ppm) and Ni-$CH_2CH_2CH_2CH_3$ (14.46 ppm) while its ${}^1H$ NMR spectrum displayed a multiplet at 0.50 ppm which was assigned to NiCH_2.

The solid state structures of **4-6** were studied by X-ray analyses performed on single crystals of these compounds. The ORTEP views of the three complexes are shown in Figure 3.4, the crystal data and collection details are listed in Table 3.I, and selected bond distances and angles are given in Table 3.II. The nickel center maintains a distorted square-planar geometry in all three structures. In comparison to the corresponding distances in the Ni-Br derivative **2**, the Ni-P bonds are shorter (~2.14-2.16 Å vs. 2.18 Å) and the Ni-C(3) bonds longer (~1.99-2.00 Å vs. 1.98 Å) in **4-6**. The mean plane defined by the phenyl ring in complex **6** makes an angle of ca. 75° with the NiP_2C plane.[15] The alkynyl moiety in **5** is slightly tilted at C10 (Ni-C(10)-C(11) ~172°) but is otherwise linear (C(10)-C(11)-C(12) ~176°).

Inspection of the Ni-R bond lengths found in these pincer species shows their anticipated dependence on the hybridization of the carbon atom in each case (i.e., Ni-C_{sp} < Ni-C_{sp2} < Ni-C_{sp3}). We note also that these Ni-R bonds are significantly longer than the mean value for the corresponding bond distances found in the literature:[13] 2.02 Å in **4** vs. 1.96 Å for other Ni-Me distances; 1.91 Å in **5** vs. 1.87 Å for other Ni-C≡CR distances;[16] 1.94 Å in **6** vs. 1.90 Å for other Ni-Ph distances. The longer Ni-C bonds in these complexes can be explained by the high *trans* influence exerted by the sp^3-hybridized central carbon atom of the $PC_{sp3}P^{i\text{-}Pr}$ ligand.

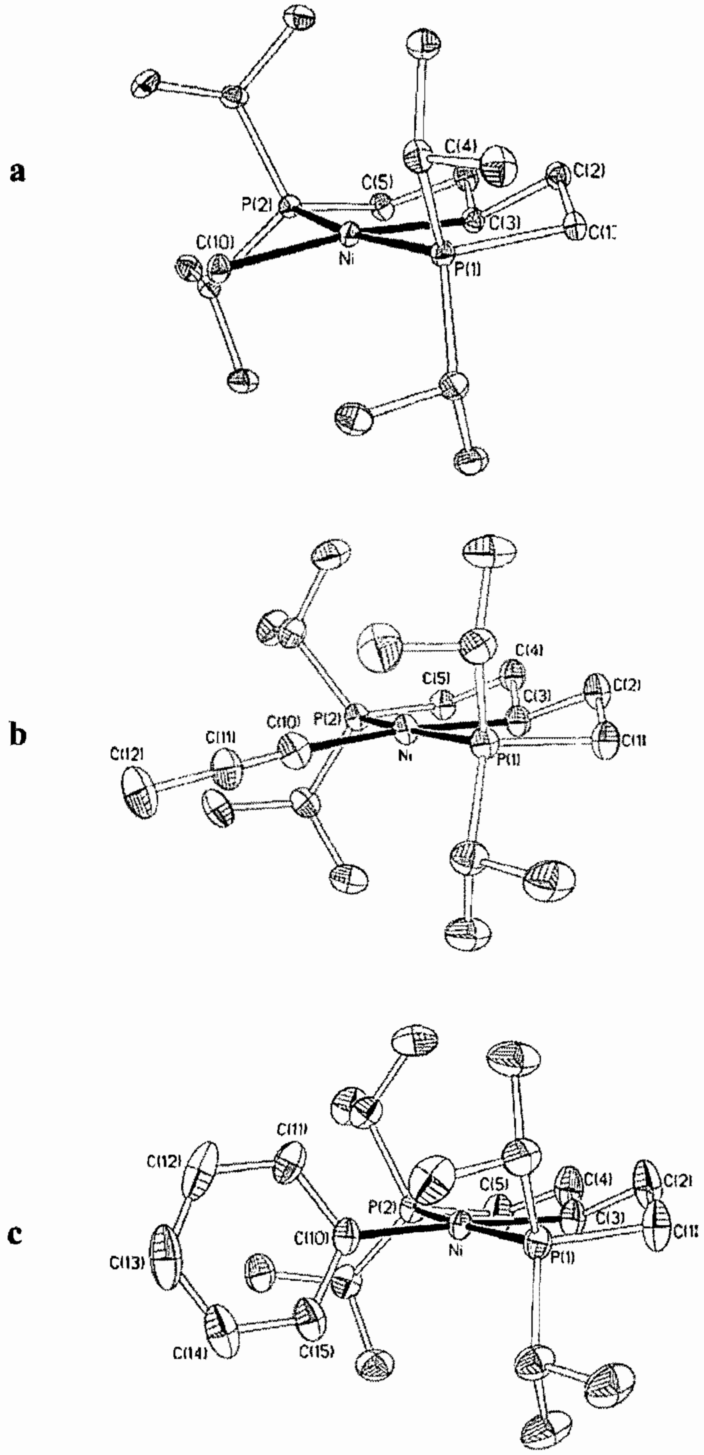
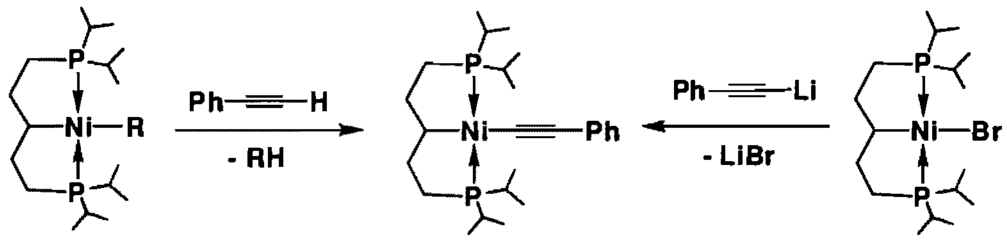


Figure 3.4. ORTEP diagram for complexes **4** (a), **5** (b) and **6** (c). Thermal ellipsoids are shown at the 30% probability level. Hydrogens are omitted for clarity.



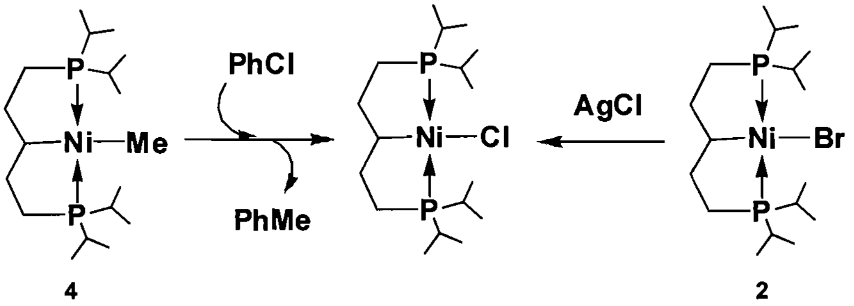
R = Me (4), CCMe (5), Bu (7) 8 2

Scheme 3.4

Reaction of phenylacetylene with ($PC_{sp3}P^{i\text{-}Pr}$)Ni-R. The relative strengths of M-C bonds usually follow the order M-C_{sp} > M-C_{sp2} > M-C_{sp3} such that converting M-C_{sp3} bonds to the stronger M-C_{sp2} or M-C_{sp} bonds should be thermodynamically favorable. Accordingly, we have found that the Ni-Me complex **4** and the Ni-Bu **7** react with PhC≡CH at room temperature to give the corresponding Ni-C≡CPh derivative **8** (Scheme 3.4). The corresponding reaction also proceeds with the Ni-C≡CMe derivative **5**, but this reaction required heating to go to completion, whereas the Ni-Ph complex **6** did not lead to **8** even with extended heating in the presence of PhC≡CH.[17] The Ni-C≡CPh complex **8**, which was also prepared by reacting **2** with LiC≡CPh (Scheme 3.4), was obtained as an oily solid that could not be isolated in pure form, but its identity has been confirmed by NMR spectroscopy.

The conversion of **4**, **5**, and **7** to **8** raises the question of whether these reactions proceed by a sequence of oxidative addition and reductive elimination, or via a concerted process involving σ-bond metathesis. NMR monitoring of the reaction of **5** with PhC≡CH did not reveal any intermediates, precluding any direct evidence in favor of a mechanism involving discrete addition/elimination steps. In an effort to determine whether or not the "protonolysis" of the Ni-R moiety by PhC≡CH involves oxidative addition of the C_{sp}-H bond, we investigated the kinetic isotope effects (KIE) for the reaction of **5** with PhC≡CH/D. These studies have shown that the KIE values, which cover a relatively wide range (0.1-12), are strongly dependent on solvent polarity and reaction temperature; unfortunately, however, the results were not reproducible, precluding any reliable conclusions at this point on the question of whether these reactions are concerted processes or involve discrete addition/elimination steps.

Kumada coupling. Recent reports have shown that the coupling of Grignard reagents and aryl halides, first reported independently by the groups of Kumada[18] and Corriu,[19] can be efficiently catalyzed by PNP, PNN and NNN-type pincer complexes of Ni^{II}.[20] Since Grignard reagents readily transform our Ni-Br complex **2** to the corresponding Ni-R derivatives, we set out to test if $(PC_{sp3}P^{i\text{-}Pr})NiR$ would react with phenyl halides to give coupling products. Heating the Ni-Me complex **4** with excess PhX (X= I, Br, Cl; C_6D_6 solutions at 60 °C) produced toluene, as detected by GC/MS; analysis of the final mixtures by $^{31}P\{^1H\}$ NMR spectroscopy showed the conversion of **4** to the Ni-X derivatives.[21] The observed degrees of conversion indicated that the coupling reaction is more facile in the order PhI > PhBr > PhCl; nevertheless, refluxing **4** in neat PhCl for 1 hour gave complete conversion to the Ni-Cl derivative and toluene (Scheme 3.5).



Scheme 3.5

Table 3.III. Kumada coupling reactions catalyzed by (PCP)NiX[a]

$$\text{MeMgCl} + \text{Ph—Cl} \xrightarrow[\substack{\text{THF}\\ \text{reflux}\\ \text{20 h}}]{\text{catalyst}} \text{Ph—Me} + \text{Ph—Ph}$$

Run	Catalyst (mol%)	Yield (%)[b]	
		Ph-Me	Ph-Ph
1	**2** (2.0)	67	2
2	**2** (1.0)	57	3
3	**2** (0.5)	42	4
4	Ni(PC$_{sp3}$P$^{t\text{-Bu}}$)Br (1.0)	34	3
5	**3** (1.0)	1	0

[a] Reaction conditions : 2 mmol of chlorobenzene, 3 mmol of MeMgCl, 0.5 mmol of p-xylene (used as an internal standard), 1.0 mL of THF (conditions not optimized). [b] Yields were determined by GC/MS and are the average of three experiments.

Having established that **4** can promote the C-C bond formation reaction, we examined the competence of complex **2** for catalyzing the Kumada-Corriu coupling reaction between MeMgCl and chlorobenzene. The organic products of these reactions were identified by GC/MS analyses and the catalysis yields were determined from independently prepared calibration curves using authentic samples. As can be seen from Table 3.III, **2** catalyzes the desired heterocoupling reaction in refluxing THF with up to 84 turnovers; minor amounts of the homocoupling product are also produced (runs 1-3). Preliminary results have also shown that under similar conditions, **2** also couples chlorobenzene and *n*-BuMgCl, an alkyl chain bearing hydrogens in the β position.

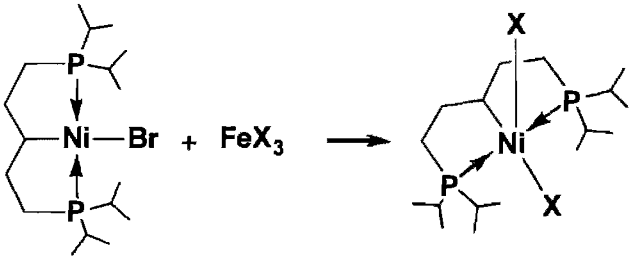
Tests showed that the catalysis proceeds less efficiently with the closely related species (PC$_{sp3}$P$^{t\text{-Bu}}$)NiBr[8] (run 4), whereas complex **3** is nearly inactive for this reaction (run 5). Combining these results with our observations from cyclic voltammetry measurements (*vide infra*) suggests a direct correlation between the catalytic efficiency of these PCP systems and the respective electron richness of their Ni centers (**2** > ($PC_{sp3}P^{t\text{-}Bu}$)NiBr > **3**).

The coupling reaction catalyzed by **2** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy in order to gain some insight into the mechanism of this process in our system. This experiment showed that the only P-containing (and diamagnetic) species present during the course of the catalysis is the Ni-Me complex **4** (a singlet observed at 71.4 ppm), which implies that this species is the resting state of the catalysis. Furthermore, this observation strongly suggests that, contrary to the commonly proposed mechanism for Ni-catalyzed Kumada coupling reactions,[22] the coupling reaction catalyzed by **2** does not involve any Ni^0 intermediate because formation of Ni^0 species by reductive elimination from **4** would deplete the concentration of this compound irreversibly.[23]

The observation of small amounts of the homo-coupling product biphenyl in the coupling reaction can signal the involvement of an electron transfer process.[24] We have also considered the alternative possibility that the reaction of the in-situ generated Ni-Me derivative with PhCl might produce MeCl and a Ni-Ph intermediate instead of the anticipated products PhMe and the Ni-Cl complex; the Ni-Ph derivative could then react with PhCl to produce Ph-Ph and regenerate the Ni-Cl species. We found, however, that refluxing mixtures of the independently prepared Ni-Ph derivative **6** (0.01 M) and 100 equivalents of PhCl in THF for 20 h did not give any biphenyl or Ni-Cl complex, thus ruling out the involvement of a Ni-Ph intermediate in the formation of biphenyl. Studies are underway to glean more information about the mechanism of this reaction.

Oxidation of 2. In order to assess the extent of electron donation from the various ligands to the nickel center, we subjected the PCP compounds **2**, ($PC_{sp3}P^{t\text{-}Bu}$)NiBr, and **3** to electrochemical experiments. The results of cyclic voltammetry measurements (Figure 3.5) indicate that the ease of $Ni^{II} \rightarrow Ni^{III}$ oxidation[25] follows the order **2** > ($PC_{sp3}P^{t\text{-}Bu}$)NiBr > **3**, which is consistent with the greater net donation of electron density by $PC_{sp3}P$ vs. $PC_{sp2}P$ and $PC_{sp3}P^{i\text{-}Pr}$ vs. $PC_{sp3}P^{t\text{-}Bu}$ ligands. It is particularly noteworthy that the most electron-rich compound, **2**, appears to be undergoing a second oxidation step, presumably generating a Ni^{IV} species.[26]

The ease of oxidation of **2** prompted us to attempt its chemical oxidation and isolation of high-valent species. We did not succeed in generating Ni^{IV} species, but reaction of **2** with FeX_3 (X = Cl, Br) formed reddish species identified by X-ray crystallography as the trivalent complexes $(PC_{sp3}P^{i\text{-}Pr})NiX_2$, **9** (Scheme 3.6). The solid state structure of complex **9a** (X= Cl) could not be determined accurately due to a complex disorder present in its crystalline structure,[27] but the structure of **9b** (X= Br) was resolved successfully; the ORTEP view for **9b** is shown in Figure 3.6 and the crystal data and collection details are listed in Table 3.I. This paramagnetic 17-electron species adopts a distorted square-pyramidal geometry wherein the nickel center is displaced out from the P(1)-C(3)-P(2)-Br(1) plane toward the Br(2) atom by 0.354 Å.[28] There was only a very slight deviation from a square-pyramidal geometry of **2**, as reflected in the small value of the τ parameter for this complex (0.03);[29] a similarly negligible trigonal distortion was found in the analogous Ni^{III} complex $(POC_{sp3}OP^{i\text{-}Pr})NiBr_2$ ($\tau = 0.05$).[10a]



2

9a (X = Br, Cl)
9b (X = Br)

Scheme 3.6

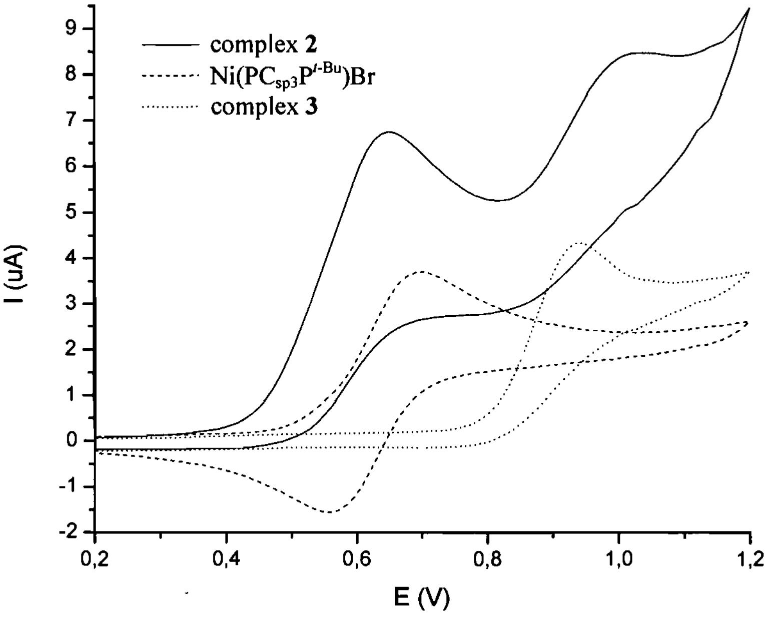


Figure 3.5. Cyclic voltammograms of complexes **2**, **3**, and Ni($PC_{sp3}P^{t\text{-}Bu}$)Br in CH_2Cl_2 (1 mM solutions) measured at 298K with 0.1 M of TBAH as electrolyte (scan rate 100 mV s^{-1}).

Conclusion

A combination of crystallographic and reactivity studies as well as electrochemical measurements have revealed interesting differences in the structures, electronic properties, and reactivities of PCP pincer complexes of nickel. Both the phosphorus substituents of the PCP ligand and the hybridization of the cyclometallated carbon atom have significant influence on the chemistry of these complexes. For instance, the $PC_{sp3}P^{i\text{-}Pr}$ ligand stabilizes the Ni-Bu derivative toward β-H elimination; in contrast, the Ni-Bu derivative is unstable with the $PC_{sp3}P^{t\text{-}Bu}$ system under the same conditions.[30] Similarly, ($PC_{sp3}P^{i\text{-}Pr}$)NiBr was found to be a better catalyst than its $PC_{sp2}P^{i\text{-}Pr}$ and $PC_{sp3}P^{t\text{-}Bu}$ analogues for Kumada coupling; studies are underway to determine the scope of this and other coupling reactions.

The electrochemical measurements have hinted that Ni^{III} and Ni^{IV} species can be generated in-situ. Although the isolation of a stable Ni^{IV} species was not achieved, the preparation of a trivalent Ni complex has been possible and future efforts will be directed toward finding new pincer ligands that can allow the isolation of high-valent Ni complexes.

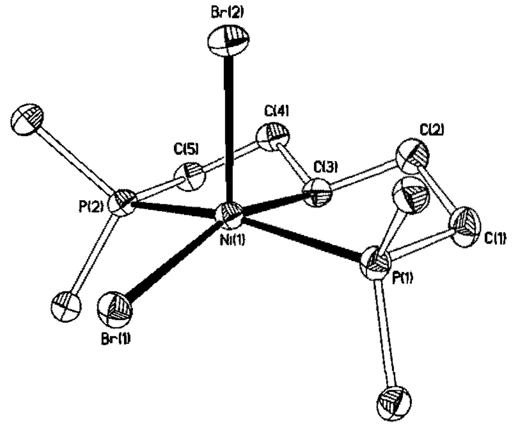


Figure 3.6. ORTEP diagram for one of the two molecules in the asymmetric unit of complex **9b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl carbons of the isopropyl groups are omitted for clarity. Selected Bond Distances (Å) and Angles (deg) for the molecule shown : Ni(1)-C(3) = 2.039(3), Ni(1)-P(1) = 2.2719(10), Ni(1)-P(2) = 2.2762(10), Ni(1)-Br(1) = 2.4144(6), Ni(1)-Br(2) = 2.4735(7), C(3)-Ni(1)-Br(1) = 159.41(10), C(3)-Ni(1)-Br(2) = 95.96(10), P(1)-Ni(1)-P(2) = 161.11(4), P(1)-Ni(1)-Br(1) = 93.88(3), P(1)-Ni(1)-Br(2) = 95.42(3), P(2)-Ni(1)-Br(1) = 93.71(3), P(2)-Ni(1)-Br(2) = 99.35(3), P(1)-Ni(1)-C(3) = 83.37(10), P(2)-Ni(1)-C(3) = 83.46(10).

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and/or in a nitrogen-filled glove box, except where noted. Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received from commercial vendors. LiC≡CPh was synthesized from the reaction of HC≡CPh with *n*-BuLi. All the NMR spectra were recorded at ambient temperature on Bruker instruments : AV400 ($^{1}\mathrm{H}$, $^{1}\mathrm{H}\{^{31}\mathrm{P}\}$, $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$) and ARX400 ($^{13}\mathrm{C}\{^{1}\mathrm{H}\}$). The ^{1}H and ^{13}C NMR spectra were referenced to solvent resonances, as follows: 7.26 and 77.16 ppm for $\mathrm{C}\mathit{H}\mathrm{Cl_3}$ and $\mathit{C}\mathrm{DCl_3}$, respectively, and 7.15 and 128.06 ppm for $\mathrm{C_6D_5}\mathit{H}$ and $\mathit{C}_6\mathrm{D_6}$, respectively. Assignments were confirmed by DEPT135, COSY and HMQC experiments. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra were referenced to an external 85% $\mathrm{H_3}\mathit{P}\mathrm{O_4}$ sample (0 ppm). The IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000-450 $\mathrm{cm^{-1}}$) with samples prepared as KBr pellets. The GC/MS analyses were done using a Agilent Technologies 6890 Network GC system equipped with a HP-5MS capillary column and a 5973 MS selective detector. The ^{v}J term used refers to the apparent coupling constant of the virtual triplets. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal).

***i*-Pr$_2$P(CH$_2$)$_5$P(*i*-Pr)$_2$.** A procedure for the preparation of this ligand has been published elsewhere,[31] but we describe here a more detailed and higher-yielding protocol.[32] Lithium wire (8.000 g, 1152.57 mmol) was washed with hexanes right before use to remove the mineral oil in which it is stored, cut into thin pieces, and quickly added to a solution of chlorodiisopropylphosphine (8.0 mL, 50.27 mmol) in THF (80 mL). This mixture was cooled immediately with an ice bath and then allowed to warm slowly to room temperature. After 16 h, the mixture was cooled again to 0 °C and 1,5-dibromopentane (3.43 mL, 25.18 mmol) was added drop-wise. The solvent was evaporated after 1 h, hexanes (80 mL) added with stirring, and the resulting mixture was filtered. The filtrate was washed with degassed water and evaporated to give the desired ligand as an oil (6.657 g, 87%) which was used without further purification. ^{1}H NMR ($\mathrm{CDCl_3}$): 0.82 (dd, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, $^{3}J_{\mathrm{PH}} = 9.7$ Hz, $\mathrm{CH(C}\mathit{H}_3)_2$, 12 H), 0.85 (dd, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, $^{3}J_{\mathrm{PH}} = 13.6$ Hz $\mathrm{CH(C}\mathit{H}_3)_2$, 12 H), 1.11 (m, $\mathrm{C}\mathit{H}_2\mathrm{P}$, 4H), 1.25 (m, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2P}$, 6H), 1.47 (m, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$, 4H); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): 18.69 (d, $^{2}J_{\mathrm{PC}} = 9.7$ Hz, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$, 4C), 20.00 (d, $^{2}J_{\mathrm{PC}} = 15.2$ Hz, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$, 4C), 21.33 (d, $^{1}J_{\mathrm{PC}} = 16.5$ Hz, $\mathit{C}\mathrm{H_2P}$, 2C), 23.13 (d, $^{1}J_{\mathrm{PC}} = 11.7$ Hz, $\mathit{C}\mathrm{H(CH_3)_2}$, 4C), 27.83 (d, $^{2}J_{\mathrm{PC}} = 17.9$ Hz, $\mathit{C}\mathrm{H_2CH_2P}$, 2C), 33.30 (t, $^{3}J_{\mathrm{PC}} = 11.4$ Hz, $\mathit{C}\mathrm{H_2CH_2CH_2P}$, 1C); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR

$(CDCl_3)$: 3.9 (s); ^1H NMR (C_6D_6): 1.01 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 10.4 Hz, $CH(CH_3)_2$, 12 H), 1.05 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 13.3 Hz, $CH(CH_3)_2$, 12 H), 1.30 (m, CH_2P, 4H), 1.45-1.65 ($CH_2CH_2CH_2P$ and $CH(CH_3)_2$, 10H). $^{13}C\{^1H\}$ NMR (C_6D_6): 19.08 (d, $^2J_{PC}$ = 10.3 Hz, $CH(CH_3)_2$, 4C), 20.42 (d, $^2J_{PC}$ = 16.5 Hz, $CH(CH_3)_2$, 4C), 22.20 (d, $^1J_{PC}$ = 19.3 Hz, CH_2P, 2C), 23.80 (d, $^1J_{PC}$ = 13.8 Hz, $CH(CH_3)_2$, 4C), 28.55 (d, $^2J_{PC}$ = 19.3 Hz, CH_2CH_2P, 2C), 33.81 (t, $^3J_{PC}$ = 11.7 Hz, $CH_2CH_2CH_2P$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 2.9 (s).

i-$Pr_2PCH_2C_6H_4CH_2P(i$-$Pr)_2$. A synthesis of this ligand has already been published elsewhere,[33] but we describe here a higher-yielding and faster protocol. Lithium wire (6.000 g, 864.43 mmol) was washed with hexanes right before use to remove the mineral oil in which it is stored, cut into thin pieces, and quickly added to a solution of chlorodiisopropylphosphine (6.0 mL, 37.70 mmol) in THF (60 mL). This mixture was cooled immediately with an ice bath and then allowed to warm slowly to room temperature. After 16 h, the mixture was cooled again to 0 °C and a solution of α,α'-dichloro-m-xylene (3.300 g, 18.85 mmol) in THF (20 mL) was added drop-wise. The solvent was evaporated after 1 h, hexanes (100 mL) added with stirring, and the resulting mixture was filtered. The filtrate was washed with degassed water and evaporated to give the desired ligand as an oil (4.280 g, 67 %) which was used without further purification. For NMR details, see reference 33.

$\{i$-$Pr_2P(CH_2)_5P(i$-$Pr)_2\}_2Ni_2Br_4$ (1). i-$Pr_2P(CH_2)_5P(i$-$Pr)_2$ (0.200 g, 0.66 mmol) was added to a suspension of anhydrous $NiBr_2$ (0.144 g, 0.66 mmol) in toluene (10 mL) and the mixture was brought to 80 °C for 2 h. The solvent was then removed under reduced pressure to give complex **1** as a dark purple solid (0.320 g, 93%). ^1H NMR $(CDCl_3)$: 1.39 (d, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$, 24H), 1.64 (d, $^3J_{HH}$ = 7.2 Hz, $CH(CH_3)_2$, 24H), 1.35-1.95 ($CH_2CH_2CH_2P$, 20H), 2.47 (m, $CH(CH_3)_2$, 8H). $^{13}C\{^1H\}$ NMR $(CDCl_3)$: 18.81 (s, $CH(CH_3)_2$, 8C), 20.20 (s, CH_2P, 4C), 20.54 (s, $CH(CH_3)_2$, 8C), 24.69 (s, $CH(CH_3)_2$, 8C), 26.50 (s, CH_2CH_2P, 4C), 35.03 (s, $CH_2CH_2CH_2P$, 2C). Anal. Calcd for $C_{34}H_{76}Br_4P_4Ni_2$: C, 39.05; H, 7.32. Found: C, 38.74; H, 7.54.

{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}NiBr (2). *i*-Pr$_2$P(CH$_2$)$_5$P(*i*-Pr)$_2$ (2.000 g, 6.57 mmol) was added to a suspension of anhydrous NiBr$_2$ (1.722 g, 7.88 mmol) and DMAP (0.803 g, 6.57 mmol) in toluene (40 mL) and the reaction mixture was refluxed for 12 h. The solvent was then evaporated to dryness, hexanes (40 mL) added and the resultant mixture was filtered in the air on a glass frit. The filtrate was washed with water and concentrated until a minimum of hexanes was left. Golden-brown crystals of **2** formed by keeping the solution at -14 °C for 1 h (1.065 g, 37%). ^{1}H NMR (C$_6$D$_6$): 0.97 (dvt, $^{3}J_{HH} \sim {}^{v}J_{PH} =$ 5.8-6.6 Hz, CH(C*H*$_3$)$_2$, 6H), 1.13 (dvt, $^{3}J_{HH} \sim {}^{v}J_{PH} =$ 6.6-6.8 Hz, CH(C*H*$_3$)$_2$, 6H), 1.46 (dvt, $^{3}J_{HH} \sim {}^{v}J_{PH} =$ 7.5-7.7 Hz, CH(C*H*$_3$)$_2$, 12H), 1.00-1.70 (C*H*$_2$C*H*$_2$P, 8H), 1.78 (m, C*H*Ni, 1H), 2.06-2.24 (C*H*(CH$_3$)$_2$, 4H); ^{1}H{^{31}P} NMR (C$_6$D$_6$): 0.97 (d, $^{3}J_{HH} =$ 7.1 Hz, CH(C*H*$_3$)$_2$, 6H), 1.13 (d, $^{3}J_{HH} =$ 7.0 Hz, CH(C*H*$_3$)$_2$, 6H), 1.46 (d, $^{3}J_{HH} =$ 7.1 Hz, CH(C*H*$_3$)$_2$, 12H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 17.56 (s, CH(*C*H$_3$)$_2$, 2C), 18.61 (s, CH(*C*H$_3$)$_2$, 2C), 19.36 (vt, $^{v}J_{PC} =$ 2.8 Hz, CH(*C*H$_3$)$_2$, 2C), 19.94 (vt, $^{v}J_{PC} =$ 1.7 Hz, CH(*C*H$_3$)$_2$, 2C), 22.12 (vt, $^{v}J_{PC} =$ 10.3 Hz, *C*H$_2$P, 2C), 23.38 (vt, $^{v}J_{PC} =$ 10.7 Hz, *C*H(CH$_3$)$_2$, 2C), 25.46 (vt, $^{v}J_{PC} =$ 9.7 Hz, *C*H(CH$_3$)$_2$, 2C), 38.94 (vt, $^{v}J_{PC} =$ 10.3 Hz, *C*H$_2$CH$_2$P, 2C), 52.30 (t, $^{2}J_{PC} =$ 9.0 Hz, *C*HNi, 1C). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 67.4. Anal. Calcd for C$_{17}$H$_{37}$BrNiP$_2$: C, 46.19; H, 8.44. Found: C, 45.97; H, 8.83.

{(*i*-Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}NiBr (3). The preparation of this complex from Ni(cod)$_2$ and the corresponding brominated ligand has already been reported;[6g] we report here another synthetic pathway. *i*-Pr$_2$PCH$_2$C$_6$H$_4$CH$_2$P(*i*-Pr)$_2$ (0.500 g, 1.48 mmol) was added to a solution of anhydrous NiBr$_2$ (0.387 g, 1.77 mmol) and DMAP (0.180 g, 1.48 mmol) in ethanol (10 mL), and the reaction mixture was refluxed for 1.5 h. The solvent was then evaporated to dryness, the schlenk was opened to air, and hexanes (40 mL) was added. The resultant mixture was filtered in the air on a glass frit and the filtrate evaporated to give complex **3** as a yellow solid (0.281 g, 40%). ^{1}H NMR (CDCl$_3$): 1.17 (dvt, $^{3}J_{HH} \sim {}^{v}J_{PH} =$ 6.7 -7.0 Hz, CH(C*H*$_3$)$_2$,12H), 1.45 (dvt, $^{3}J_{HH} \sim {}^{v}J_{PH} =$ 7.4-8.4 Hz, CH(C*H*$_3$)$_2$, 12H), 2.38 (m, C*H*(CH$_3$)$_2$, 4H), 3.08 (vt, $^{v}J_{PH} =$ 3.7 Hz, PCH$_2$, 4H), 6.91 (s, Ar*H*, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): 18.31 (s, PCH(*C*H$_3$)$_2$, 4C), 19.12 (s, PCH(*C*H$_3$)$_2$, 4C), 24.01 (vt, $^{v}J_{PC} =$ 11.0 Hz, P*C*H(CH$_3$)$_2$, 4C), 32.83 (vt, $^{v}J_{PC} =$ 12.8 Hz, P*C*H$_2$, 2C), 122.26 (vt, $^{v}J_{PC} =$ 9.0 Hz, *Ar*H, 2C), 125.35 (s, *Ar*H, 1C), 152.46 (t, $J_{PC} =$ 13.1 Hz, *Ar*CH$_2$, 2C), 159.13 (t, $^2J_{PC}$ =15.9 Hz, *Ar*$_{ipso}$, 1C). ^{31}P{^{1}H} NMR (CDCl$_3$): 61.8 (s). Anal. Calcd for $C_{20}H_{35}BrNiP_2$: C, 50.46; H, 7.41. Found: C, 49.94; H, 7.53.

{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}NiMe (4). MeMgCl (0.15 mL of a 3M solution in THF, 0.45 mmol) was added to a solution of **2** (0.200 g, 0.45 mmol) in toluene (2.5 mL). After 5 min, the solvents were evaporated, hexanes (20 mL) added, and the resultant suspension filtered. The filtrate was washed with degassed water (3 x 20 mL) and evaporated to dryness to give complex **4** as a yellow powder (0.121 g, 71%). ^{1}H NMR (C_6D_6): -0.50 (t, $^3J_{PH}$ = 7.7 Hz, NiC*H*$_3$, 3H), 0.96 (dvt, $^3J_{HH}$ ~ $^vJ_{PH}$ = 5.5-6.3 Hz, CH(C*H*$_3$)$_2$, 6H), 1.12 (dvt, $^3J_{HH}$ ~ $^vJ_{PH}$ = 6.2-6.5 Hz, CH(C*H*$_3$)$_2$, 6H), 1.21 (m, CH(C*H*$_3$)$_2$, 12H), 0.80-2.20 (C*H*(CH$_3$)$_2$, C*H*$_2$C*H*$_2$P, C*H*Ni, 13H). ^{13}C{^{1}H} NMR (C_6D_6): -18.64 (t, $^2J_{PC}$ = 19.9 Hz, Ni*C*H$_3$, 1C), 17.55 (s, CH(*C*H$_3$)$_2$, 2C), 19.01 (s, CH(*C*H$_3$)$_2$, 2C), 19.46 (vt, $^vJ_{PC}$ = 3.3 Hz, CH(*C*H$_3$)$_2$, 2C), 19.63 (vt, $^vJ_{PC}$ = 2.4 Hz, CH(*C*H$_3$)$_2$, 2C), 22.68 (vt, $^vJ_{PC}$ = 9.5 Hz, *C*H(CH$_3$)$_2$, 2C), 25.81 (vt, $^vJ_{PC}$ = 10.4 Hz, *C*H$_2$P, 2C), 25.85 (vt, $^vJ_{PC}$ = 9.0 Hz, *C*H(CH$_3$)$_2$, 2C), 37.70 (vt, $^vJ_{PC}$ = 10.9 Hz, *C*H$_2$CH$_2$P, 2C), 58.56 (t, $^2J_{PC}$ = 9.5 Hz, *C*HNi, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 71.4. Anal. Calcd for $C_{18}H_{40}NiP_2{\cdot}H_2O$: C, 54.71; H, 10.71. Found: C, 54.39; H, 10.48.

{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}NiC≡CMe (5). To complex **2** (1.000 g, 2.26 mmol) was added MeC≡CMgBr (4.52 mL of a 0.5 M solution in THF, 2.26 mmol) and the mixture stirred. After five minutes, the solvent was evaporated, hexanes (40 mL) added, and the resultant suspension was filtered. The filtrate was washed with degassed water (3 x 20 mL) and the solvent evaporated to dryness to give complex **5** as a yellow powder (0.716 g, 79%). ^{1}H NMR (C_6D_6): 1.02 (m, CH(C*H*$_3$)$_2$, 6H), 1.14 (m, CH(C*H*$_3$)$_2$, 6H), 1.25-1.50 (m, CH(C*H*$_3$)$_2$, 12H), 0.80-2.20 (C*H*(CH$_3$)$_2$, C*H*$_2$C*H*$_2$P, C*H*Ni, 13H), 2.13 (s, C≡CC*H*$_3$, 3H). ^{13}C{^{1}H} NMR (C_6D_6): 7.61 (s, C≡C*C*H$_3$, 1C), 17.81 (s, CH(*C*H$_3$)$_2$, 2C), 18.74 (s, CH(*C*H$_3$)$_2$, 2C), 19.40 (vt, $^vJ_{PC}$ = 2.5 Hz, CH(*C*H$_3$)$_2$, 2C), 19.68 (s, CH(*C*H$_3$)$_2$, 2C), 23.93 (vt, $^vJ_{PC}$ = 11.1 Hz, *C*H(CH$_3$)$_2$, 2C), 24.76 (vt, $^vJ_{PC}$ = 9.6 Hz, *C*H$_2$P, 2C), 25.90 (vt, $^vJ_{PC}$ = 10.6 Hz, *C*H(CH$_3$)$_2$, 2C), 38.41 (vt, $^vJ_{PC}$ = 10.6 Hz, *C*H$_2$CH$_2$P, 2C), 56.38 (t, $^2J_{PC}$ = 10.1 Hz, *C*HNi, 1C), 98.44 (t, $^2J_{PC}$ = 30.8 Hz, *C*≡CCH$_3$, 1C) 115.74 (s, C≡*C*CH$_3$, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 76.1; ^{31}P{^{1}H} NMR (CDCl$_3$): 76.0. IR (KBr) :

2100 cm^{-1} ($\mu_{C\equiv C}$). Anal. Calcd for $C_{20}H_{40}NiP_2$: C, 59.88; H, 10.05. Found: C, 60.12; H, 10.33.

{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}NiPh (6). PhMgBr (0.90 mL of a 1M solution in THF, 0.90 mmol) was added to a solution of **2** (0.400 g, 0.90 mmol) in toluene (5.0 mL) and the mixture was stirred and refluxed for 1 h. The solvent was then evaporated, hexanes (20 mL) added, and the resultant suspension was filtered. The filtrate was washed with degassed water (3 x 20 mL) and evaporated to dryness to give complex **6** as a yellow-brown powder (0.245 g, 62%). ^{1}H NMR (C_6D_6): 0.87-1.05 (m, CH(C*H*$_3$)$_2$, 24H), 0.85-2.50 (C*H*(CH$_3$)$_2$, C*H*$_2$C*H*$_2$P, C*H*Ni, 13H), 6.90-7.80 (Ph, 5H). ^{13}C{^{1}H} NMR (C_6D_6): 17.64 (s, CH(*C*H$_3$)$_2$, 2C), 17.79 (s, CH(*C*H$_3$)$_2$, 2C), 18.53 (s, CH(*C*H$_3$)$_2$, 2C), 18.97 (s, CH(*C*H$_3$)$_2$, 2C), 22.84 (vt, $^{v}J_{PC}$ = 10.7 Hz, *C*H(CH$_3$)$_2$, 2C), 24.44 (vt, $^{v}J_{PC}$ = 10.1 Hz, *C*H(CH$_3$)$_2$, 2C), 25.84 (vt, $^{v}J_{PC}$ = 10.7 Hz, *C*H$_2$P, 2C), 37.98 (vt, $^{v}J_{PC}$ = 10.7 Hz, *C*H$_2$CH$_2$P, 2C), 56.81 (t, $^2J_{PC}$ = 8.9 Hz, *C*HNi, 1C), 120.78 (s, *Ph*, 1C), 125.80 (s, *Ph*, 1C), 127.49 (s, *Ph*, 1C), 129.06 (s, *Ph*, 1C), 140.55 (s, *Ph*, 1C), 168.77 (t, $^2J_{PC}$ = 24.0 Hz, *Ph* (C_{ipso}), 1C). ^{31}P{^{1}H} NMR (C_6D_6): 68.1. Anal. Calcd for $C_{23}H_{42}NiP_2{\cdot}H_2O$: C, 60.42; H, 9.70. Found: C, 60.89; H, 9.73.

{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}NiBu (7). Addition of *n*-BuLi (52 μL of a 2.5 M solution in hexanes, 0.131 mmol) to a concentrated solution of **2** (0.058 g, 0.131 mmol) in benzene-d_6 (0.6 mL) resulted in the instantaneous formation of the butyl species **7**, as observed by NMR spectroscopy. ^{1}H NMR (C_6D_6): 0.50 (m, C*H*$_2$(CH$_2$)$_2$CH$_3$, 2H). ^{13}C{^{1}H} NMR (C_6D_6): 0.51 (t, $^2J_{PC}$ = 19.0 Hz, *C*H$_2$(CH$_2$)$_2$CH$_3$, 1C), 14.46 (s, CH$_2$(CH$_2$)$_2$*C*H$_3$, 1C), 17.91 (s, CH(*C*H$_3$)$_2$, 2C), 18.74 (s, CH(*C*H$_3$)$_2$, 2C), 19.52 (vt, $^{v}J_{PC}$ = 3.4 Hz, CH(*C*H$_3$)$_2$, 2C), 20.00 (vt, $^{v}J_{PC}$ = 2.7 Hz, CH(*C*H$_3$)$_2$, 2C), 23.74 (vt, $^{v}J_{PC}$ = 9.5 Hz, *C*H(CH$_3$)$_2$, 2C), 25.90 (vt, $^{v}J_{PC}$ = 11.4 Hz, *C*H$_2$P, 2C), 25.94 (vt, $^{v}J_{PC}$ = 8.3 Hz, *C*H(CH$_3$)$_2$, 2C), 31.02 (s, CH$_2$(*C*H$_2$)$_2$CH$_3$, 1C), 36.41 (t, $^3J_{PC}$ = 2.3 Hz, CH$_2$(*C*H$_2$)$_2$CH$_3$, 1C), 37.45 (vt, $^{v}J_{PC}$ = 10.2 Hz, *C*H$_2$CH$_2$P, 2C), 57.50 (t, $^2J_{PC}$ = 9.5 Hz, *C*HNi, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 68.1.

$\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiC{\equiv}CPh$ (8). Method A. Reaction of complex **4** (0.021 g, 0.06 mmol) with HC≡CPh (6 μL, 0.06 mmol) in DMSO-d_6 (0.8 mL) for 15 h led to full conversion of the starting material into complex **8**, as observed by NMR spectroscopy. Method B. Refluxing a mixture of complex **5** (0.020 g, 0.05 mmol) and excess HC≡CPh (100 μL, 0.91 mmol) in toluene (0.8 mL) for 2 h led to the full conversion of the starting material into the phenylacetylide complex **8**, as observed by $^{31}P\{^1H\}$ NMR spectroscopy. Method C. Reacting LiC≡CPh (0.110 g, 1.02 mmol) with complex **2** (0.300 g, 0.679 mmol) in toluene (3 mL) at room temperature for 1 h gave complex **8,** as observed by $^{31}P\{^1H\}$ NMR spectroscopy. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 17.87 (s, CH(CH$_3$)$_2$, 2C), 18.72 (s, CH(CH$_3$)$_2$, 2C), 19.36 (s, CH(CH$_3$)$_2$, 2C), 19.67 (s, CH(CH$_3$)$_2$, 2C), 23.84 (vt, $^{v}J_{PC}$ = 11.4 Hz, CH(CH$_3$)$_2$, 2C), 24.31 (vt, $^{v}J_{PC}$ = 9.9 Hz, CH$_2$P, 2C), 25.79 (vt, $^{v}J_{PC}$ = 10.4 Hz, CH(CH$_3$)$_2$, 2C), 37.89 (vt, $^{v}J_{PC}$ = 10.3 Hz, CH$_2$CH$_2$P, 2C), 57.35 (t, $^{2}J_{PC}$ = 9.4 Hz, CHNi, 1C), 120.12 (t, $^{2}J_{PC}$ = 29.0 Hz, C≡CPh, 1C), 122.29 (s, 1C), 123.71 (s, *Ph*, 1C), 127.79 (s, *Ph*, 2C), 130.06 (s, 1C), 130.34 (s, *Ph*, 2C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 77.9.

$\{(i\text{-}Pr_2PCH_2CH_2)_2CH\}NiX_2$ (9). To a solution of **2** (0.100 g, 0.23 mmol) in CH_2Cl_2 (10 mL) was added $FeCl_3$ (0.037 g, 0.23 mmol) or $FeBr_3$ (0.067 g, 0.23 mmol). The mixture was stirred five minutes and filtered through a glass frit. Complex **9a** was quantitatively obtained as a red powder after evaporation of the filtrate to dryness. ^1H NMR (C_6D_6): 0.5-3.0 (broad resonances). The combustion data are consistent with either $Ni(PC_{sp3}P^{i\text{-}Pr})ClBr$ or an equimolar mixture of $Ni(PC_{sp3}P^{i\text{-}Pr})Br_2$ and $Ni(PC_{sp3}P^{i\text{-}Pr})Cl_2$. Anal. Calcd for $C_{17}H_{37}BrNiClP_2$: C, 42.76; H, 7.81. Found: C, 42.96; H, 7.21. Complex **9b** could not be purified due to similar solubility properties with $FeBr_2$; single crystals used in the X-ray diffraction studies were obtained by recrystallizing a small batch from the slow evaporation of a CH_2Cl_2 solution of the complex.

General procedure for Kumada coupling. MeMgCl (0.98 mL of a 3.0 M solution in THF, 2.94 mmol) was added to a solution of PhCl (200 μL, 1.97 mmol), *p*-xylene (60 μL, 0.49 mmol, used as an internal standard) and the catalyst in THF (1.0 mL). The mixture was heated to reflux for the desired time. A sample of the reaction was then withdrawn, diluted with diethyl ether and washed with water. The organic phase was dried over $MgSO_4$, filtered and the resultant solution was analyzed by GC/MS.

Crystal Structure Determinations. Single crystals of these complexes were grown from : slow diffusion of hexanes into a saturated solution of the complex in benzene-d_6 (**1**), slow evaporation of a dichloromethane solution (**9b**), hexanes solutions at -15°C (**2**, **4**, **6**), and at room temperature (**3** and **5**). The crystallographic data (Table 3.I) for complexes **1**, **3** and **5** were collected on a Bruker CCD 2K diffractometer (sealed tube) using graphite monochromatic Cu K_α radiation, equipped with a 3 circle platform goniometer and a Bruker Smart 2000 area detector. The crystallographic data for complexes **2**, **4**, **6** and **9b** were collected on a Nonius FR591 generator (rotating anode) equipped with a Montel 200, a D8 goniometer and a Bruker Smart 6000 area detector.

Cell refinement and data reduction were done using SAINT[34]. An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[35] The space group was confirmed by XPREP routine[36] in the program SHELXTL.[37] The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97.[38] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. For complex **3**, the possible presence of ethanol molecules in the structure (237 electrons corresponding to 9 molecules per unit cell) has been determined using the program PLATON[39] but no correction of the data has been applied.

Cyclic Voltammetry Experiments. Cyclic voltammetry measurements were performed using a BAS Epsilon potentiostat. A typical three-electrode system was used, consisting of a Pt working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode ($E_{½}$ ($FeCp_2^+/FeCp_2$) = +0.63 V under these conditions). The experiments were carried out in CH_2Cl_2 at room temperature with TBAH as electrolyte (0.1 M) and the solutions were bubbled with nitrogen before each experiment.

Supporting Information. Complete details of the X-ray analyses for complexes **1-6** and **9b** have been deposited at The Cambridge Crystallographic Data Centre (CCDC 631839 (**1**), 631840 (**2**), 671730 (**3**), 631841 (**4**), 631843 (**5**), 631842 (**6**), 689350 (**9b**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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[16] Since complex **5** is, to our knowledge, the first reported molecular structure of a Ni-C≡CMe complex where the propynyl ligand is not bridged with another metal, we compared the Ni-C_{sp} bond distance in **5** to the mean of all the Ni-alkynyl bond lengths reported in the literature.

[17] In the case of the reaction involving Ni-Ph (**6**) or Ni-Bu (**7**), some uncharacterized minor products were noted by $^{31}P\{^1H\}$ NMR spectroscopy.

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$CH(CH_3)_2$, 2C), 18.68 (s, $CH(CH_3)_2$, 2C), 19.54 (vt, ${}^{v}J_{PC}$ = 2.4 Hz, $CH(CH_3)_2$, 2C), 20.41 (s, $CH(CH_3)_2$, 2C), 22.69 (vt, ${}^{v}J_{PC}$ = 10.3 Hz, CH_2P, 2C), 24.44 (vt, ${}^{v}J_{PC}$ = 11.4 Hz, $CH(CH_3)_2$, 2C), 26.35 (vt, ${}^{v}J_{PC}$ = 10.3 Hz, $CH(CH_3)_2$, 2C), 38.81 (vt, ${}^{v}J_{PC}$= 10.0 Hz, CH_2CH_2P, 2C), 57.97 (t, ${}^{2}J_{PC}$ = 8.3 Hz, CHNi, 1C); ${}^{31}P\{{}^{1}H\}$ NMR (C_6D_6): 70.5.

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[26] One of the reviewers of our manuscript has invoked the possibility the second oxidation step is due to a Ni^{III} species featuring an unpaired electron stabilized on the pincer ligand. This scenario seems less realistic to us because we believe that the aliphatic skeleton of the $PC_{sp3}P$ ligand should not be suited to stabilizing an unpaired electron, but this alternative explanation can not be ruled out.

[27] We believe that the disorder found in single crystals obtained from this compound arises from the presence of a mixture of Cl and Br atoms in the coordination sphere of Ni^{III}.

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[28] The corresponding value for the second independent molecule of the asymmetric unit was found to be 0.331 Å.

[29] The τ parameter is calculated according to the relationship $\tau = (\beta - \alpha)/60$ wherein α and β refer to the largest basal angles in the complex (β>α); values approaching zero imply small degrees of deviation from an ideal square pyramidal geometry, whereas values approaching 1 signal significant distortions toward a trigonal bipyramidal geometry: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.

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Chapitre 4: New Derivatives of PCP-Type Pincer Complexes of Nickel

Article 3

manuscrit soumis à *Inorganic Chemistry*

Annie Castonguay, André L. Beauchamp and Davit Zargarian*
Département de chimie, Université de Montréal, Montréal (Québec), Canada H3C 3J7

Abstract

The pincer-type complexes ($(PC_{sp3}P^{i\text{-}Pr})NiR$) ($PC_{sp3}P^{i\text{-}Pr}$ = ($(i\text{-}Pr_2PCH_2CH_2)_2CH$)) react with HBF_4 (R= $C{\equiv}CMe$, Ph, Me) or $AgBF_4$ (R= Br) to give $(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$, **1**, which was found to involve fluxional $Ni\text{-}F\text{-}BF_3$ interactions. Competition experiments revealed that the relative ease of protonation of the Ni-hydrocarbyl moiety follows the order Ni-Me > $Ni\text{-}C{\equiv}CMe$ > Ni-Ph. Complex **1** reacts with water to give $[(PC_{sp3}P^{\text{-}Pr})Ni(H_2O)][BF_4]$, **2**, that in turn undergoes H_2O exchange with CH_3CN, $i\text{-}PrNH_2$, and CO to give the corresponding cationic adducts **3**, **4**, and **5**; alternatively, **3-5** can also be obtained directly from the reaction of **1** with CH_3CN, $i\text{-}PrNH_2$, and CO, respectively. Deprotonation of complex **2** gives the neutral hydroxo complex $(PC_{sp3}P^{i\text{-}Pr})Ni(OH)$, **6**. All complexes have been characterized by NMR spectroscopy and, in the case of **2-6**, by X-ray crystallography.

Introduction

Most PCP-type pincer complexes[1] of late transition metals are well-known for their air-, water-, and thermal-stabilities and the numerous catalytic reactions they promote.[2] The most extensively investigated complexes feature ligands based on a *meta*-disubstituted arene skeleton ($PC_{sp2}P$), but ligands based on an aliphatic skeleton and an sp^3-hybridized metallated carbon atom ($PC_{sp3}P$) are becoming popular since it has been demonstrated that their complexes possess enhanced or unique reactivities. For example, the ($PC_{sp3}P$)-Pd complex $\kappa^P,\kappa^C,\kappa^P\text{-}\{1\text{-}CH_2\text{-}2,6\text{-}(CH_2P(i\text{-}Pr)_2)_2\text{-}3,5\text{-}(CH_3)_2\text{-}C_6H\}Pd(O_2CCF_3)$ is a more active precatalyst for the Heck coupling in comparison to its corresponding ($PC_{sp2}P$)-Pd analogue,[3] some ($PC_{sp3}P$)-Ir complexes facilitate alkane metathesis[4] and activate the N-H bond of ammonia[5] and the C-H bond of benzene,[6] while an ($PC_{sp3}P$)-Os complex has allowed the stabilization of a rare silylene species.[7]

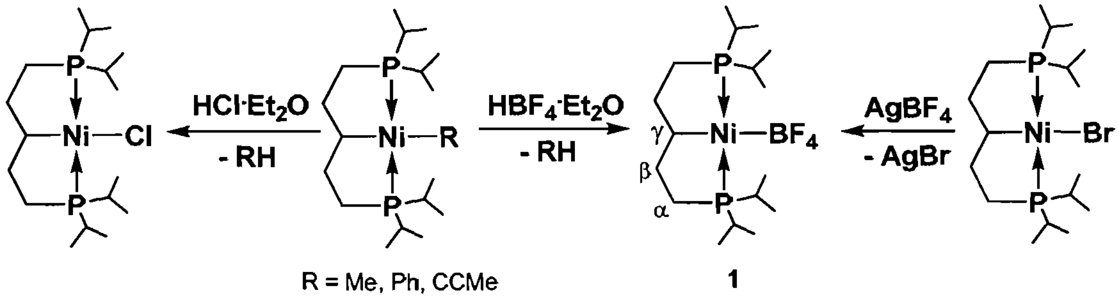
We are interested in exploring the reactivities of PCP-Ni complexes in catalytic transformations. The first such complexes to be reported in the literature were based on a $PC_{sp2}P$ framework,[8] but an increasing number of $PC_{sp3}P$-based complexes of nickel have appeared in the literature over the past few years, including $\kappa^P,\kappa^C,\kappa^P$-{1-$CH_2$-2,6-($CH_2P$(*i*-Pr)$_2$)$_2$-3,5-($CH_3$)$_2$-$C_6H$}NiI[8h] and $[(PC_{sp3}P^{t\text{-}Bu})NiL]^{n+}$ ($PC_{sp3}P^{t\text{-}Bu}$ = (*t*-$Bu_2PCH_2CH_2$)$_2$CH; n= 0: L= Cl, Br, I, H, Me; n= 1: L= MeCN, CH_2=CHCN).[9] Very recently, we have introduced a new series of Ni^{II} and Ni^{III} complexes based on the ligand $PC_{sp3}P^{i\text{-}Pr}$, ($PC_{sp3}P^{i\text{-}Pr}$= (*i*-$Pr_2PCH_2CH_2$)$_2$CH), and studied their structural characteristics and reactivities.[10]

Our investigations have revealed significant structural and reactivity differences among Ni complexes based on $PC_{sp2}P$ vs. $PC_{sp3}P$ and $PC_{sp3}P^{t\text{-}Bu}$ vs. $PC_{sp3}P^{i\text{-}Pr}$ ligands.[11] For example, we have found[10b] that $(PC_{sp3}P^{i\text{-}Pr})Ni(Bu)$ is quite stable to β-H elimination, in contrast to its $PC_{sp3}P^{t\text{-}Bu}$ analogue. Moreover, whereas $(PC_{sp3}P^{i\text{-}Pr})NiBr$ is an efficient catalyst for the Corriu-Kumada coupling of MeMgCl and PhCl, the $PC_{sp2}P^{i\text{-}Pr}$ analogue of this complex was found to be almost completely inactive under the same conditions. Finally, it has been possible to isolate a thermally stable $(PC_{sp3}P^{i\text{-}Pr})Ni^{III}Br_2$ species,[10b] whereas no trivalent complexes of the analogous $PC_{sp2}P$ ligands have been isolated to date.[12,13]

During the course of our studies on the reactivities of PCP-Ni complexes, we have found that protonolysis of $(PC_{sp3}P^{i\text{-}Pr})$Ni(hydrocarbyl) with HBF_4 gives the Ni-BF_4 derivative $(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$, **1**, a species which appears to involve weak Ni-F-BF_3 interactions. The present report describes the characterization of this new compound and its use as a precursor for the preparation of $[(PC_{sp3}P^{i\text{-}Pr})Ni(L)][BF_4]$ (L= H_2O (**2**), CH_3CN (**3**), *i*-$PrNH_2$ (**4**), CO (**5**)) and $(PC_{sp3}P^{i\text{-}Pr})Ni(OH)$, **6**.

Results and Discussion

Preparation of ($PC_{sp3}P^{i\text{-}Pr}$)Ni(BF_4), 1. Reacting the complexes ($PC_{sp3}P^{i\text{-}Pr}$)NiR (R = Me, Ph, C≡CMe) with HCl·Et_2O produces the previously reported[10b] Ni-Cl derivative (Scheme 4.1).We reasoned that the analogous protonolysis reaction with Brønsted acids HX wherein X is a weakly coordinating conjugate base should generate either the coordinatively and electronically unsaturated cation [($PC_{sp3}P^{i\text{-}Pr}$)Ni][X] or [($PC_{sp3}P^{i\text{-}Pr}$)Ni-X, both of which should be highly reactive species. Monitoring the reaction of ($PC_{sp3}P^{i\text{-}Pr}$)Ni(C≡CMe) with one equivalent of HBF_4·Et_2O by $^{31}P\{^1H\}$ NMR spectroscopy showed that all the starting material was instantaneously converted into a new species that displayed a broad resonance at 63.5 ppm. An identical spectrum was obtained from the reaction of ($PC_{sp3}P^{i\text{-}Pr}$)NiBr with one equivalent of $AgBF_4$ (Scheme 4.1).



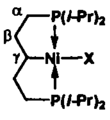
Scheme 4.1

The facile protonation of ($PC_{sp3}P^{i\text{-}Pr}$)Ni(C≡CMe) and access to the corresponding Ni-Me and Ni-Ph analogues prompted us to probe the reactivities of the Ni-R moieties in these complexes as a function of the different hybridizations of the nickellated carbon atom (C_{sp}, C_{sp2}, C_{sp3}). Monitoring the reactions of ($PC_{sp3}P^{i\text{-}Pr}$)NiR with HBF_4·Et_2O by $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of the product obtained from the reaction of the Ni-C≡CMe derivative (Scheme 4.1). Competition experiments were performed in order to assess the relative rates of protonation of the

Ni-R derivatives. Thus, to two C_6D_6 solutions containing one equivalent of each of the three complexes ($PC_{sp3}P^{i\text{-}Pr}$)NiR (R= Me, Ph, C≡CMe) were added three equivalents of $HBF_4{\cdot}Et_2O$ or $HCl{\cdot}Et_2O$, one equivalent at a time, and $^{31}P\{^1H\}$ NMR spectra were recorded between successive additions. The results revealed that the relative ease of protonation of the three complexes by either acid follows the decreasing order Ni-Me > Ni-C≡CMe > Ni-Ph. It is noteworthy that the kinetic reactivities of these Ni-C bonds, as defined by the relative ease of protonation of the Ni-R moiety, follows the order Ni-C_{sp3} > Ni-C_{sp} > Ni-C_{sp2}, whereas the thermodynamic strength of the Ni-C bond, as reflected in the respective Ni-C bond lengths for these compounds,[10b] follows the order Ni-C_{sp} > Ni-C_{sp2} > Ni-C_{sp3}.

Characterization of ($PC_{sp3}P^{i\text{-}Pr}$)Ni(BF_4), 1. All attempts to characterize the new complex **1** by elemental analysis or X-ray diffraction studies gave results consistent with the water-coordinated adduct [($PC_{sp3}P^{i\text{-}Pr}$)Ni(H_2O)][BF_4], **2** (*vide infra*); nevertheless, a number of NMR spectral features and comparisons to literature precedents (Table 4.I) indicate that **1** possesses the structure illustrated in Scheme 4.1 wherein the Ni-BF_4 moiety involves fluxional Ni-F-BF_3 interactions. To begin with, the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of **1** are very similar to the corresponding spectra for ($PC_{sp3}P^{i\text{-}Pr}$)NiX (X= Cl, Br; Table 4.I), which implies that the overall structure of **1** must be quite similar to those of the completely characterized halide derivatives. On the other hand, the $^{19}F\{^1H\}$ NMR spectrum of **1** supports the proposal that BF_4^- has bonding interactions with the Ni center: a very broad ^{19}F resonance was observed at -179 ppm (in C_6D_6), significantly upfield of the corresponding signals displayed by $HBF_4{\cdot}Et_2O$ (-153 ppm in C_6D_6) and the closely related complexes [($PC_{sp3}P^{i\text{-}Pr}$)NiL][BF_4] in which BF_4 is a non-coordinating anion (e.g., -145 to -152 ppm, *vide infra*). In a similar fashion, the PCN-type pincer complexes {2-($CH_2P(t\text{-}Bu)_2$),6-(CH_2NEt_2)C_6H_3}Rh(BF_4)(CH_3)[14a] and {2-($CH_2P(t\text{-}Bu)_2$),6-($(CH_2)_nNR_2$)C_6H_3}Pt(BF_4) (n = 1: R = Et; n = 2: R = Me)[14b] show $^{19}F\{^1H\}$ signals at ca. -164 and -162 ppm for the Rh and Pt complexes, respectively, significantly upfield of the signal for Bu_4NBF_4 (ca. -151 ppm).

Table 4.I. Comparison of NMR Data for Complexes ($(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$) (**1**), $[(PC_{sp3}P^{i\text{-}Pr})Ni(OH_2)][BF_4]$ (**2**), and $(PC_{sp3}P^{i\text{-}Pr})NiX$ (X= Cl, Br, I)[a]

	Assignment	1		2	$(PC_{sp3}P^{i\text{-}Pr})NiX$ (C_6D_6)		
		(C_6D_6)	($CDCl_3$)	($CDCl_3$)	X= Cl	X= Br	X= I
$^{31}P\{^1H\}$		63.5	64.0	66.5	66.5	67.4	70.5
$^{19}F\{^1H\}$		-179		-145[b]	---	---	---
$^{13}C\{^1H\}$	$CH(\mathit{C}H_3)_2$	17.5, 18.4, 19.3, 19.4	17.7, 18.6, 19.3, 19.4	17.7, 18.6, 19.4, 19.5	17.6, 18.6, 19.3, 19.7	17.6, 18.6, 19.4, 19.9	17.7, 18.7, 19.5, 20.4
	α	18.6	18.7	19.3	21.8	22.1	22.7
	$\mathit{C}H(CH_3)_2$	22.7, 24.5	22.6, 24.4	22.5, 24.4	22.9, 25.0	23.4, 25.5	24.4, 26.4
	β	38.7	38.5	38.2	39.0	38.9	38.8
	γ	---[c]	---[c]	43.3	48.7	52.3	58.0

[a]Data for the Ni-halide derivatives are taken from ref. 10b.

[b]This spectrum was recorded in C_6D_6.

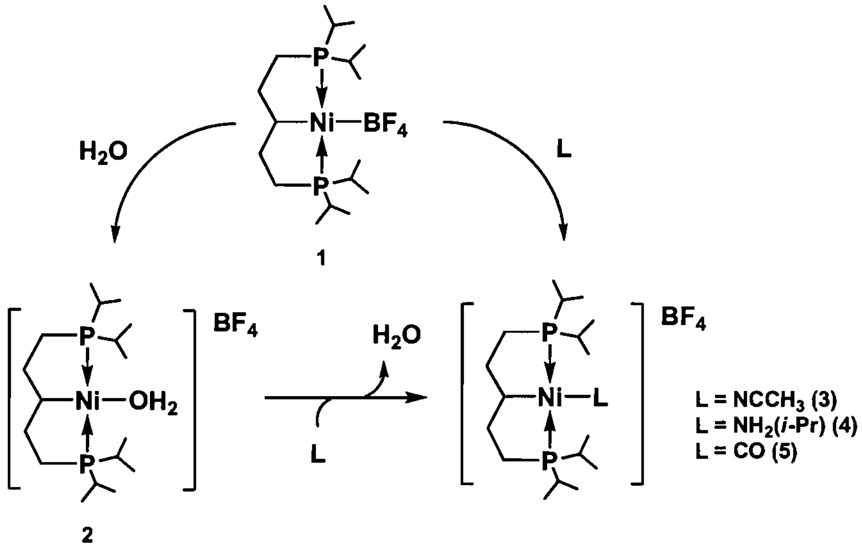
[c]A DEPT 90 NMR experiment has hinted that these signals appear at ca. 38.7 (C_6D_6) and 38.5 ppm ($CDCl_3$) but are obscured in the $^{13}C\{^1H\}$ NMR spectrum by the signal due to the β-carbons.

Comparisons of variable temperature NMR data obtained for **1** and reported for related complexes provided additional support for the existence of fluxional Ni-F-BF_3 interactions. For instance, observation of two ^{31}P signals coalescing at ca. -30 °C for the closely related PCP complex $(PC_{sp3}P^{t\text{-}Bu})Pd(BF_4)$ has been attributed to a rapid exchange between BF_4^- and CD_2Cl_2.[15] Our own variable temperature NMR experiments showed that the broad ^{31}P signal observed at room temperature for **1** splits into two sharp singlets at -25 °C (ca. 65 and 63 ppm, ratio 1:1.9, toluene-d_8), which coalesce at ~10 °C into a broad resonance at ~ 64 ppm; the latter then sharpens as the temperature is increased. These observations imply a fairly slow exchange between coordinated and free BF_4^-, but the data can not be used to establish whether solvent coordination takes place.

The issue of BF_4^-/solvent exchange has been discussed in a report on the Rh-BF_4 complex $\{2\text{-}(CH_2P(t\text{-}Bu)_2),6\text{-}(CH_2NEt_2)C_6H_3\}Rh(BF_4)(CH_3)$.[14b] Thus, the low-temperature $^{19}F\{^1H\}$ NMR experiments of this compound supported BF_4^-/solvent exchange in a coordinating solvent such as THF, whereas the ^{19}F signal remained unchanged when the experiments were performed in a non coordinating solvent such as 2,6-dimethyltetrahydrofuran. On the other hand, spin-saturation experiments carried out on this compound in the same non-coordinating solvent supported the exchange between the coordinated and free BF_4^-, implying that solvent coordination might not be required for this exchange process. In the case of our complexes, we have considered the possibility that the observed exchange process involves BF_4^-/N_2 exchange as opposed to solvent binding, but this was ruled out because identical $^{31}P\{^1H\}$ NMR spectra were obtained for samples of **1** prepared from the reaction of $(PC_{sp3}P^{i\text{-}Pr})NiBr$ with $AgBF_4$ under a nitrogen or argon atmosphere.

We conclude on the basis of the above observations and literature comparisons that complex **1** is more appropriately described as the charge-neutral species $(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$ (Scheme 4.1) involving rapidly fluxional Ni-F-BF_3 interactions, as opposed to the charge-separated species $[(PC_{sp3}P^{i\text{-}Pr})Ni][BF_4]$. The proposed structure for **1** is also consistent with the empirical correlation we have noted in $(PC_{sp3}P^{i\text{-}Pr})NiX$ complexes between the ^{31}P chemical shift values and nature of X (size, electronegativity, polarizability, and π-donor strength of the atom bonded to Ni): F-BF_3 (~64 ppm) < OH_2 ~ Cl (66.5 ppm) < Br (67.4 ppm) < I (70.5 ppm).

Preparation of cationic adducts from 1. Reaction of **1** with one equivalent of water in C_6D_6 or $CDCl_3$ led to a color change from orange to yellow, and NMR spectra indicated the clean conversion of **1** to the new aquo species $[(PC_{sp3}P^{i\text{-}Pr})Ni(OH_2)][BF_4]$, **2** (Table 4.I, Scheme 4.2). Thus, the $^{31}P\{^1H\}$ NMR showed a singlet at 66.5 ppm, ~2 ppm downfield of the corresponding signal for **1**; similar downfield displacements were also observed for the ^{13}C signals corresponding to α- and γ-carbons. It is noteworthy that the signal for γ-C was a triplet ($^2J_{PC}$= 7.2 Hz) and the $^{19}F\{^1H\}$ NMR spectrum of **2** showed a broad signal at -145 ppm (Table 4.I), which is characteristic of a non coordinated BF_4^- counterion (*vide supra*). The ^1H NMR spectrum of **2** did not show a signal for the coordinated water molecule, but addition of a few equivalents of water to an NMR sample[16] gave rise to a signal at 5.29 ppm (C_6D_6) whose intensity grew with successive additions of water. The presence of a water molecule in solid samples of **2** has been confirmed by the combustion data, as well as by the IR spectrum (KBr pellets) that showed a strong band at 3444 cm^{-1} assigned to ν(OH).



Scheme 4.2

Single crystals of **2** were easily grown and its solid-state structure was established from an X-ray diffraction study. The ORTEP view is shown in Figure 4.1, crystal data and collection details are listed in Table 4.II, and selected bond distances and angles are given in Table 4.III. Solid-state structure of **2** consists of a square planar complex featuring a Ni-OH_2 moiety. Relative to the neutral complex ($PC_{sp3}P^{i\text{-}Pr}$)NiBr,[10b] the Ni-C_γ distance is nearly unchanged (~1.97 Å vs ~1.98 Å), but the Ni-P bond distances are longer in **2** (~2.21 Å vs ~2.18 Å). The Ni-O bond distance observed in **2** (~2.00 Å) is shorter than the mean of all the Ni-O bond lengths reported in the literature for monocationic water-coordinated complexes (~2.09 Å).[17]

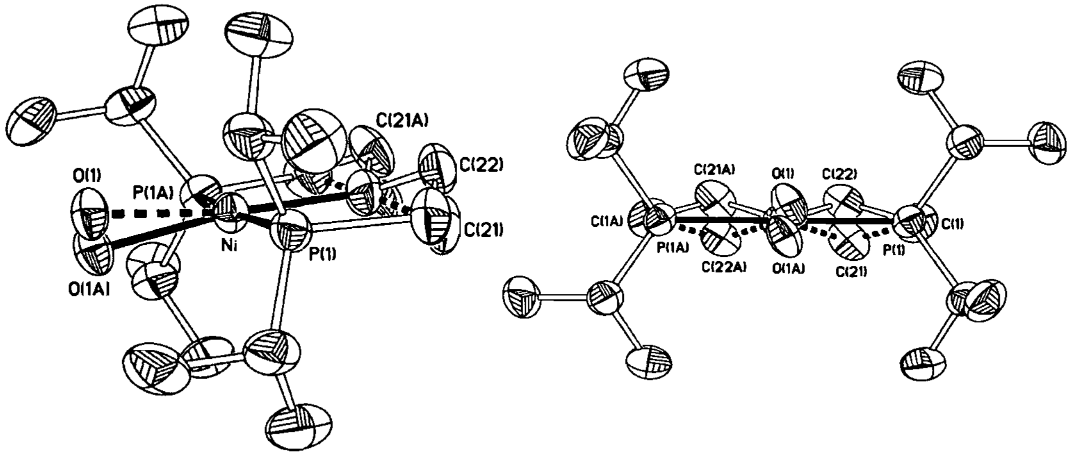


Figure 4.1. Side and front views of the ORTEP diagram for complex **2**. Thermal ellipsoids are shown at the 30% probability level. The hydrogens as well as the BF_4^- counterion are omitted for clarity. The β carbons as well as the Ni-coordinated oxygen atom were found to occupy two positions (50:50).

Three other cationic adducts $[(PC_{sp3}P^{i\text{-}Pr})Ni(L)][BF_4]$ were prepared from the reaction of **1** with CH_3CN (**3**), *i*-$PrNH_2$ (**4**) or CO (**5**); these new complexes were also obtained by the reaction of the aquo adduct **2** with one equivalent of CH_3CN or NH_2(*i*-Pr), or with 1 atm of CO (Scheme 4.2). The conversion of **2** to **3** was indicated by the emergence of a new ^{31}P signal at 76.7 ppm. The presence of a coordinated acetonitrile in **3** was confirmed by the observation of a new ^1H signal at 0.63 ppm and two ^{13}C signals at δ 3.24 (CH_3CN) and 132.59 (CH_3CN). The change in the $^{31}P\{^1H\}$ spectrum was nearly imperceptible during the reaction of **2** with *i*-$PrNH_2$ (singlet shifting from 65.8 to 65.5 ppm), but the formation of **4** was inferred from the emergence of two new ^{13}C signals for the coordinated *i*-$PrNH_2$, a singlet at ~25 ppm for CH_3 (vs. a singlet at ~26 ppm in free *i*-$PrNH_2$) and a triplet at ~50 ppm for *C*H ($^3J_{PC}$ = 3.8 Hz, vs. a singlet at ~43 ppm in free *i*-$PrNH_2$). In contrast, formation of the CO adduct **5** caused significant downfield shifts of the ^{31}P signal (>20 ppm) and the ^{13}C resonance attributed to γ-C (>30 ppm). Curiously, the signal for γ-C is a singlet, not the anticipated triplet, but we were able to confirm this assignment based on a DEPT135 experiment.[18] Finally, the corresponding ^{13}C resonance for *C*O was not detected, but the observation of a ν(CO) band in the solid-state IR spectrum indicated a significant Ni→CO π-donation (2040 cm^{-1} for **5** vs. 2143 cm^{-1} for free CO).[19]

X-Ray analyses allowed us to study the solid-state structures of complexes **3**-**5**. Crystal data and collection details are listed in Table 4.II, and selected bond distances and angles are given in Table 4.III. As seen in the ORTEP diagrams (Figure 4.2), the Ni center maintains a square-planar geometry and the Ni-P bond distances (~2.20-2.23 Å) are quite similar to the corresponding distances in the aquo precursor **2**. The Ni-C bond lengths are also similar in **2**-**4** (~1.98-1.99 Å) but slightly longer in the case of **5** (~2.00 Å), which can be explained by the greater *trans* influence of CO compared to water. The Ni-N (1.897(2) Å) and the N≡C (1.141(3) Å) bond distances in **3** are similar to the corresponding bond lengths in the analogous complex $[(PC_{sp3}P^{t\text{-}Bu})Ni(N{\equiv}CCH_3)][BPh_4]$,[9a] which probably implies that the Ni-$NCCH_3$ bond is dominated by N→Ni σ-donation. The Ni-N bond distance in **4** (2.0261(18) Å) is significantly shorter than the mean of all the Ni-N bond lengths of coordinated primary amines reported in the literature for Ni^{II} monocationic species (2.074(3) Å).[17] The hydrogen atoms of the NH_2 moiety were positioned from residual peaks in the difference Fourier map and the N-H bond distances (0.86(3) Å) were found to be comparable to other N-H bond length values found in the literature.[17] The C-O bond distance in **5** was found to be 1.139(3) Å, which is similar to the one found in free CO (~1.128 Å).[20]

Table 4.II. Data Collection and Refinement Parameters for Complexes **2-6**.

	2	**3**	**4**	**5**	**6**
chemical formula	$C_{17}H_{39}NiP_2F_4OB$	$C_{19}H_{40}NiP_2F_4NB$	$C_{20}H_{46}NiP_2F_4NB$	$C_{18}H_{37}NiP_2F_4OB$	$C_{17}H_{38}NiP_2O$
Fw	466.94	489.98	508.04	476.94	379.12
T (K)	220(2)	150(2)	150(2)	150(2)	100(2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
space group	$P4_22_12$	$P2_12_12_1$	P-1	P2/c	$P2_1/n$
a (Å)	14.6664(9)	11.3041(5)	8.7544(4)	13.8041(6)	10.3090(4)
b (Å)	14.6664(9)	14.7679(7)	11.5109(5)	8.3146(4)	17.0475(6)
c (Å)	11.0426(14)	15.4458(8)	13.6825(5)	20.7105(8)	11.9074(4)
α (deg)	90	90	72.912(2)	90	90
β (deg)	90	90	87.199(2)	100.103(2)	105.6150(10)
γ (deg)	90	90	83.003(2)	90	90
Z	4	4	2	4	4
V ($Å^3$)	2375.3(4)	2578.5(2)	1307.99(10)	2340.20(18)	2015.40(13)
ρ_{calcd} (g cm^{-3})	1.306	1.262	1.290	1.354	1.249
μ (cm^{-1})	27.64	25.54	25.31	28.20	28.53
θ range (deg)	4.26-72.01	4.14-60.44	3.38-71.80	3.25-73.15	4.65-67.06
$R1^a$ [$I > 2\sigma(I)$]	0.0477	0.0343	0.0441	0.0392	0.0309
$wR2^b$ [$I > 2\sigma(I)$]	0.1300	0.0910	0.1192	0.1099	0.0850
R1 [all data]	0.0493	0.0354	0.0484	0.0467	0.0322
wR2 [all data]	0.1316	0.0919	0.1222	0.1142	0.0859
GOF	1.040	1.052	0.957	1.096	1.049

$^aR1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ $^bwR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

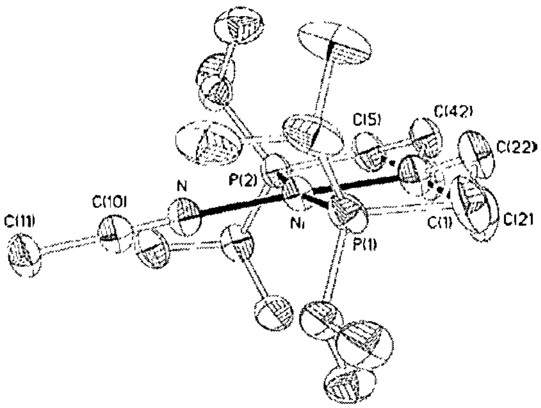
Table 4.III. Selected Bond Distances (Å) and Angles (deg) for Complexes **2**-**6**.

	2 (X = O)	**3**(X = N)	**4** (X = N)	**5** (X = C)	**6** (X = O)
Ni-C(3)	1.965(8)	1.981(3)	1.989(2)	2.000(2)	1.9856(16)
Ni-P(1)	2.2086(18)	2.1971(7)	2.2305(6)	2.2010(6)	2.1687(5)
Ni-P(2)	2.2086(18)*	2.2016(7)	2.2014(6)	2.2013(6)	2.1635(5)
Ni-X	1.997(8)	1.897(2)	2.0261(18)	1.780(2)	1.8793(14)
C(3)-Ni-X	171.4(7)	176.96(12)	173.04(11)	177.36(10)	173.51(7)
P(1)-Ni-P(2)	171.20(11)*	169.99(3)	168.54(3)	169.25(3)	170.26(2)
P(1)-Ni-X	95.0(8)	93.89(7)	97.64(6)	94.77(7)	98.38(5)
P(2)-Ni-X	95.0(8)*	96.08(7)	93.80(6)	95.74(7)	90.93(5)
P(1)-Ni-C(3)	85.6(5)	84.97(8)	84.82(6)	84.54(7)	85.58(5)
P(2)-Ni-C(3)	85.6(5)*	85.11(8)	83.88(6)	85.07(7)	84.90(5)

* symmetry transformation used to generate equivalent atoms : y, x, -z+2

Deprotonation of 2. NMR monitoring of the reaction of **2** with one equivalent of $KN(SiMe_3)_2$ showed the disappearance of the $^{31}P\{^1H\}$ singlet at 65.8 ppm (C_6D_6)[16] and the emergence of a signal at 62.8 ppm along with variable amounts of side-products (< 5%) at 66.2 ppm and 60.3 ppm. These minor species have not been characterized, but the major product was identified as the hydroxo complex **6** (Scheme 4.3). The ^1H NMR spectrum of **6** showed a triplet signal at -3.05 ppm ($^3J_{HP}$ = 6.1 Hz), assigned to the O*H* moiety, whereas the $^{19}F\{^1H\}$ NMR spectrum showed no signals at all. A $PC_{sp2}P$ analogue of **6**, $[\{(i\text{-}Pr_2PCH_2)_2C_6H_3\}NiOH]$, has been reported recently[8f] and the NMR data for this complex are similar to those of **6**, in particular the ^1H NMR triplet attributed to its O*H* moiety (-2.52 ppm, $^3J_{HP}$ = 6.4 Hz).

3



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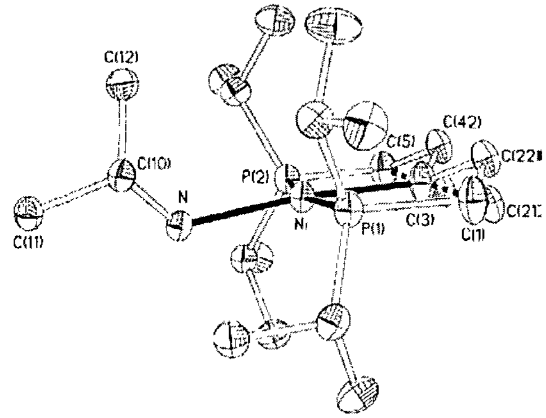

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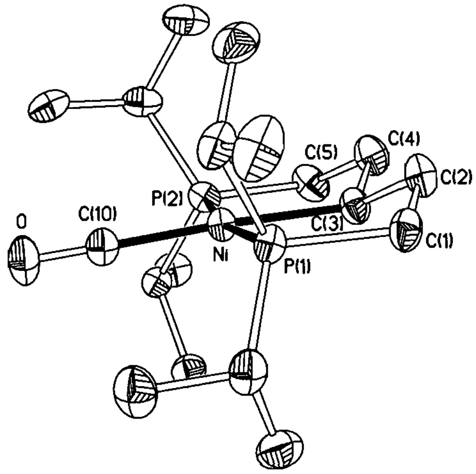
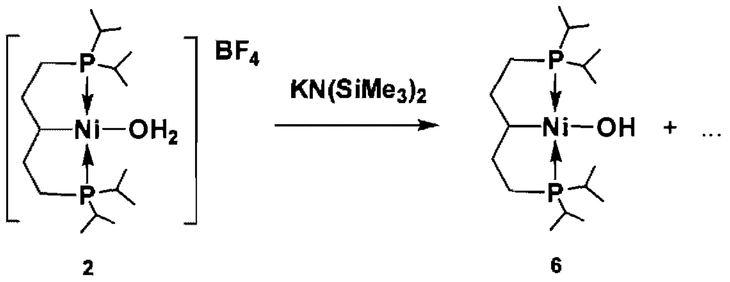


Figure 4.2. ORTEP diagrams for complex **3**, **4** and **5**. Thermal ellipsoids are shown at the 30% probability level. The hydrogens as well as the BF_4^- counterions are omitted for clarity. Some disorder was taken into account for the β carbons of **3** (40:60) and **4** (30:70), and for half of the BF_4 moieties of the molecular structure of **5** (50:50).



Scheme 4.3

Single crystals of **6** were grown and its solid-state structure was confirmed by an X-ray analysis. The ORTEP view is shown in Figure 4.3, the crystal data and collection details are listed in Table 4.II, and selected bond distances and angles are given in Table 4.III. In the molecular structure of **6**, the geometry around the nickel center is square planar and the PCP-Ni bond distances are in the same range as those observed for the previously reported neutral complexes $(PC_{sp3}P^{i\text{-}Pr})NiR$ bearing the same ligand (R = Br, Me, Ph, C≡CMe).[10b] Curiously, there seems to be a weak hydrogen-bonding type interaction between the oxygen of one molecule of **6** and an *i*-Pr proton of the other molecule; a similar situation was observed in the structure of $[\{(i\text{-}Pr_2PCH_2)_2C_6H_3\}Ni(OH)]$.[8f] The Ni-O bond distance observed in the latter $PC_{sp2}P$ analogue is slightly shorter than the corresponding distances found in **6** and *cis*-$\{i\text{-}Pr_2P(CH_2)_2P(i\text{-}Pr)_2\}Ni(OH)(Me)$[21] (~1.86 vs ~1.88 Å).

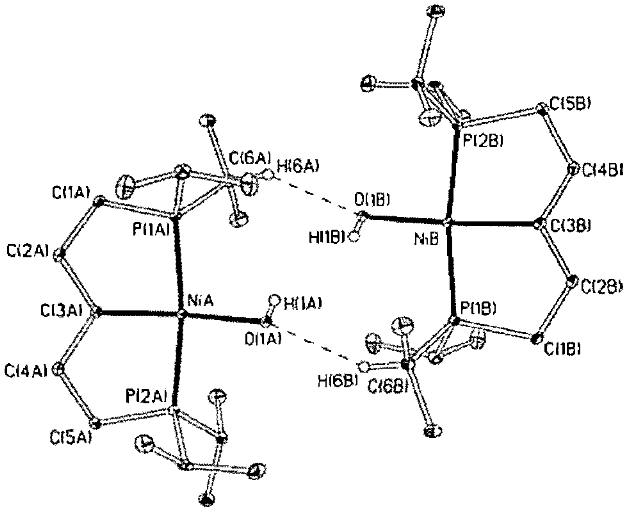


Figure 4.3. ORTEP diagram for complex **6**. Thermal ellipsoids are shown at the 30% probability level. The hydrogens of the PCP ligand which are not involved in the weak intermolecular interaction are omitted for clarity.

Conclusion

It has been shown that $(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$ involves fluxional Ni-F-BF_3 interactions. This species can be used to prepare cationic adducts with relatively weak nucleophiles such as water, and it is hoped that the lability of the BF_4^- moiety will prove useful in catalytic applications requiring the coordination of weakly coordinating substrates. The new hydroxo complex $(PC_{sp3}P^{i\text{-}Pr})Ni(OH)$ was also prepared from its aquo precursor and efforts are underway to study its reactivity in insertion reactions.

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and/or in nitrogen-filled glovebox, except where noted. Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received from commercial vendors while precursors have been prepared according to a previously reported article.[10b] All the NMR spectra were recorded at ambient temperature on Bruker instruments : AV400 (^{1}H, ^{1}H{^{31}P}), AV300 (^{31}P{^{1}H}, ^{19}F{^{1}H}) and ARX400 (^{13}C{^{1}H}). The ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to solvent resonances while the ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra were respectively referenced to an external 85% H_3PO_4 and $C_6H_5CF_3$ samples (0 ppm). The IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000-450 cm^{-1}) with samples prepared as KBr pellets. The ^vJ term used refers to the apparent coupling constant of the virtual triplets. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal).

{(i-$Pr_2PCH_2CH_2)_2CH$}Ni(BF_4) (1). Method A. HBF_4 (5 µL of a 54% wt solution in Et_2O, 0.04 mmol) was added to an NMR tube containing a solution of ($PC_{sp3}P^{i\text{-}Pr}$)NiC≡CMe (0.015 g, 0.04 mmol) in C_6D_6 (0.6 mL). The color of the solution changed from yellow to dark orange instantaneously. Method B. To a solution of ($PC_{sp3}P^{i\text{-}Pr}$)NiBr (0.100 g, 0.23 mmol) in C_6D_6 (0.6 mL) was added $AgBF_4$ (0.053 g, 0.27 mmol) and the suspension was heated to 80 °C for 1h. The reaction mixture was then filtered into an NMR tube. In both cases, the orange solution obtained was analyzed by NMR spectroscopy and the resultant product was identified as complex **1**. ^{1}H NMR (C_6D_6): 0.30-1.50 (m, CH_2CH_2P, NiCH, 9H), 0.87 (dvt, $^vJ_{PH} \sim J_{HH}$ = 6.1-7.0 Hz, CH(CH_3)$_2$, 6H), 1.05 (dvt, $^vJ_{PH} \sim J_{HH}$ = 6.8-7.0 Hz, CH(CH_3)$_2$, 6H), 1.38 (dvt, $^vJ_{PH} \sim J_{HH}$ = 7.4-7.8 Hz, CH(CH_3)$_2$, 6H), 1.45 (dvt, $^vJ_{PH} \sim J_{HH}$ = 8.1-8.3 Hz, CH(CH_3)$_2$, 6H), 1.97 (m, CH(CH_3)$_2$, 2H), 2.11 (m, CH(CH_3)$_2$, 2H). ^{13}C{^{1}H} NMR (C_6D_6): 17.46 (s, CH(CH_3)$_2$, 2C), 18.43 (s, CH(CH_3)$_2$, 2C), 18.56 (partially hidden vt, $^vJ_{PC}$ = 11.4 Hz, CH_2P, 2C), 19.27 (s, CH(CH_3)$_2$, 2C), 19.44 (s, CH(CH_3)$_2$, 2C), 22.70 (vt, $^vJ_{PC}$ = 9.5 Hz, *C*H(CH_3)$_2$, 2C), 24.46 (vt, $^{v}J_{PC}$ = 9.5 Hz, *C*H(CH_3)$_2$, 2C), 38.68 (hidden t, $^{2}J_{PC}$ = 9.3 Hz, Ni*C*, 1C), 38.72 (vt, $^{v}J_{PC}$ = 8.5 Hz, *C*H$_2$CH$_2$P, 2C). ^{31}P{^{1}H} NMR (C_6D_6): 63.5 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): 64.0 (s). ^{19}F{^{1}H} NMR (C_6D_6): -179 (br s).

[{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}NiOH$_2$][BF$_4$] (2). Method A. To a solution of (PC$_{sp3}$P$^{i\text{-}Pr}$)NiC≡CMe (0.100 g, 0.25 mmol) in toluene (5 mL) was added HBF_4 (35 µL of a 54% wt solution in Et_2O, 0.25 mmol). Water (0.2 mL) was added to the reaction mixture and complex **2** was obtained as a yellow powder after evaporation of the solvent to dryness (0.045 g, 39%). Method B. A solution of (PC$_{sp3}$P$^{i\text{-}Pr}$)NiBr (0.120 g, 0.27 mmol) in toluene (3 mL) was added to a schlenk containing $AgBF_4$ (0.063 g, 0.32 mmol) and the reaction mixture was heated to 80 °C for 1h. The resultant suspension was filtered and water (5 µL) was added to the filtrate. Complex **2** was obtained as a yellow powder after evaporation of the solvent to dryness (0.031 g, 24%). ^{1}H NMR (C_6D_6): 0.55-1.50 (m, C*H*$_2$C*H*$_2$P, NiC*H*, 9H), 0.92 (m, CH(C*H*$_3$)$_2$, 6H), 1.05 (m, CH(C*H*$_3$)$_2$, 6H), 1.39 (m, CH(C*H*$_3$)$_2$, 12H), 2.01 (m, C*H*(CH$_3$)$_2$, 2H), 2.13 (m, C*H*(CH$_3$)$_2$, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): 17.65 (s, CH(*C*H$_3$)$_2$, 2C), 18.64 (s, CH(*C*H$_3$)$_2$, 2C), 19.26 (partially hidden vt, $^{v}J_{PC}$ = 13.1 Hz, *C*H$_2$P, 2C), 19.39 (s, CH(*C*H$_3$)$_2$, 2C), 19.52 (s, CH(*C*H$_3$)$_2$, 2C), 22.48 (vt, $^{v}J_{PC}$ = 10.3 Hz, *C*H(CH$_3$)$_2$, 2C), 24.42 (vt, $^{v}J_{PC}$ = 9.3 Hz, *C*H(CH$_3$)$_2$, 2C), 38.24 (vt, $^{v}J_{PC}$ = 9.0 Hz, *C*H$_2$CH$_2$P, 2C), 43.26 (t, $^{2}J_{PC}$ = 7.2 Hz, Ni*C*, 1C). ^{31}P{^{1}H} NMR ($CDCl_3$): 66.5 (s). ^{31}P{^{1}H} NMR (C_6D_6): 65.8 (s). ^{19}F{^{1}H} NMR (C_6D_6): -145 (br s). IR (KBr) : 3444 cm^{-1}, ν(O-H). Anal. Calcd for $C_{17}H_{39}NiP_2OF_4B$: C, 43.73; H, 8.42. Found: C, 43.43; H, 8.47.

[{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}Ni(NCCH$_3$)][BF$_4$] (3). Method A. To a solution of complex (PC$_{sp3}$P$^{i\text{-}Pr}$)NiC≡CMe (0.145 g, 0.36 mmol) in toluene (2 mL) was added HBF_4 (55 µL of a 54% wt solution in Et_2O, 0.40 mmol). CH_3CN was added to the reaction mixture and complex **3** was obtained as a yellow-brown oily compound after evaporation of the solvent to dryness (0.071 g, 40%). Method B. CH_3CN (2 µL, 0.03 mmol) was added to a NMR tube filled with a suspension[16] of **2** (0.014 g, 0.03 mmol) in C_6D_6 (0.6 mL). A bleaching of the solution was instantaneously observed and NMR spectroscopy confirmed that the substitution reaction took place. ^{1}H NMR (C_6D_6): 0.63 (s, CH_3CN, 3H), 0.80-1.70 (m, CH_2CH_2P, NiC*H*, 9H), 0.99 (m, $CH(CH_3)_2$, 12H), 1.23 (m, $CH(CH_3)_2$, 12H), 1.98 (m, $CH(CH_3)_2$, 2H), 2.19 (m, $CH(CH_3)_2$, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): 3.24 (s, CH_3CN, 1C), 17.69 (s, $CH(CH_3)_2$, 2C), 18.75 (s, $CH(CH_3)_2$, 2C), 19.43 (s, $CH(CH_3)_2$, 2C), 19.52 (s, $CH(CH_3)_2$, 2C), 20.21 (vt, $^vJ_{PC}$ = 12.0 Hz, CH_2P, 2C), 22.98 (vt, $^vJ_{PC}$ = 10.2 Hz, $CH(CH_3)_2$, 2C), 25.16 (vt, $^vJ_{PC}$ = 9.9 Hz, $CH(CH_3)_2$, 2C), 38.55 (vt, $^vJ_{PC}$ = 8.6 Hz, CH_2CH_2P, 2C), 53.92 (t, $^2J_{PC}$ = 5.8 Hz, NiC, 1C), 132.59 (s, CH_3CN, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 76.7 (s). $^{19}F\{^1H\}$ NMR (C_6D_6): -152 (br s).

[{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}Ni{NH$_2$(*i*-Pr)}][BF$_4$] (4). Method A. To a solution of complex ($PC_{sp3}P^{i\text{-}Pr}$)NiC≡CMe (0.145 g, 0.36 mmol) in toluene (2 mL) was added HBF_4 (55 μL of a 54% wt solution in Et_2O, 0.40 mmol). NH_2(*i*-Pr) was added to the reaction mixture and complex **4** was obtained as a yellow-brown oily compound after evaporation of the solvent to dryness. Method B. NH_2(*i*-Pr) (2 μL, 0.02 mmol) was added to an NMR tube filled with a suspension[16] of **2** (0.010 g, 0.02 mmol) in C_6D_6 (0.6 mL). A bleaching of the solution was instantaneously observed and NMR spectroscopy confirmed that the substitution reaction took place. ^{1}H NMR (C_6D_6): 0.75-3.40 (m, CH_2CH_2P, NiC*H*, $CH(CH_3)_2$, $NH_2CH(CH_3)_2$, 46H). $^{13}C\{^1H\}$ NMR (C_6D_6): 17.96 (s, $CH(CH_3)_2$, 2C), 18.15 (s, $CH(CH_3)_2$, 2C) 19.51 (s, $CH(CH_3)_2$, 2C), 19.96 (s, $CH(CH_3)_2$, 2C), 20.28 (vt, $^vJ_{PC}$ = 12.5 Hz, CH_2P, 2C), 23.89 (vt, $^vJ_{PC}$ = 9.1 Hz, $CH(CH_3)_2$, 2C), 25.33 (vt, $^vJ_{PC}$ = 8.7 Hz, $CH(CH_3)_2$, 2C), 25.42 (s, $NH_2CH(CH_3)_2$, 2C), 38.17 (vt, $^vJ_{PC}$ = 8.7 Hz, CH_2CH_2P, 2C), 48.47 (t, $^2J_{PC}$ = 8.7 Hz, NiC, 1C), 49.77 (t, $^3J_{PC}$ = 3.8 Hz, $NH_2CH(CH_3)_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 65.5 (s). $^{19}F\{^1H\}$ NMR (C_6D_6): -149 (br s). Anal. Calcd for $C_{20}H_{46}NiP_2F_4NB{\cdot}H_2O$: C, 45.66; H, 9.20; N, 2.66. Found: C, 45.75; H, 9.04; N, 2.76.

[{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}Ni(CO)][BF$_4$] (5). Method A. To a schlenk tube containing a solution of complex ($PC_{sp3}P^{i\text{-}Pr}$)NiC≡CMe (0.100 g, 0.25 mmol) in toluene (2 mL) was slowly added HBF_4 (38 μL of a 54% wt solution in Et_2O, 0.28 mmol). Replacing the N_2 atmosphere with CO led to precipitation of **5** within a few minutes (0.025 g, 21 %).

Method B. An NMR tube filled with a suspension[16] of **2** (0.010 g, 0.02 mmol) in C_6D_6 (0.6 mL) was purged with CO (1 atm) for a few minutes, leading to precipitation of **5**. Method C. A solution of $(PC_{sp3}P^{i\text{-}Pr})NiBr$ (0.100 g, 0.23 mmol) in THF (5 mL) was added to a Schlenk tube containing $AgBF_4$ (0.057 g, 0.29 mmol) and the reaction mixture was stirred at room temperature for 1 h. The resultant suspension was filtered and the reaction vessel was purged with CO (1 atm). The color of the solution changed instantaneously and complex **5** was obtained as a pale yellow powder after evaporation of the solvent to dryness (0.095 g, 88%). ^{1}H NMR ($CDCl_3$): 0.60-3.90 (m, $C\mathit{H}_2C\mathit{H}_2P$, $C\mathit{H}(CH_3)_2$, NiC*H*, 13H), 1.33 (m, $CH(C\mathit{H}_3)_2$, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 18.17 (s, $CH(\mathit{C}H_3)_2$, 2C), 18.91 (s, $CH(\mathit{C}H_3)_2$, 2C), 19.36 (s, $CH(\mathit{C}H_3)_2$, 2C), 19.64 (s, $CH(\mathit{C}H_3)_2$, 2C), 22.39 (vt, $^{v}J_{PC}$ = 12.6 Hz, $\mathit{C}H_2P$, 2C), 25.48 (vt, $^{v}J_{PC}$ = 10.3 Hz, $\mathit{C}H(CH_3)_2$, 2C), 26.52 (vt, $^{v}J_{PC}$ = 9.3 Hz, $\mathit{C}H(CH_3)_2$, 2C), 38.31 (vt, $^{v}J_{PC}$ = 6.2 Hz, $\mathit{C}H_2CH_2P$, 2C). (*N.B.* The Ni*C* signal is presumed to be obscured by the one due to $\mathit{C}DCl_3$, and the *C*O resonance was not observed.) $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 18.32 (s, $CH(\mathit{C}H_3)_2$, 2C), 19.06 (s, $CH(\mathit{C}H_3)_2$, 2C), 19.60 (s, $CH(\mathit{C}H_3)_2$, 2C), 19.84 (s, $CH(\mathit{C}H_3)_2$, 2C), 22.79 (vt, $^{v}J_{PC}$ = 12.6 Hz, $\mathit{C}H_2P$, 2C), 25.91 (vt, $^{v}J_{PC}$ = 12.1 Hz, $\mathit{C}H(CH_3)_2$, 2C), 27.06 (vt, $^{v}J_{PC}$ = 11.8 Hz, $\mathit{C}H(CH_3)_2$, 2C), 38.70 (s, $\mathit{C}H_2CH_2P$, 2C), 77.26 (s, Ni*C*, 1C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 99.1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 99.0. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): -151 (br s). IR (KBr) : 2041 cm^{-1}, ν(CO). Anal. Calcd for $C_{18}H_{37}NiP_2F_4OB\cdot H_2O$: C, 43.68; H, 7.94. Found: C, 43.53; H, 8.24.

[{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}Ni(OH)] (6). To a solution of complex **2** (0.105 g, 0.22 mmol) in C_6H_6 (2 mL) was added $KN(SiMe_3)_2$ (0.45 mL of a 0.5 M solution in toluene, 0.23 mmol). The solvent was evaporated after 5-10 min and hexanes was added (5 mL). The resultant suspension was filtered and crystals of **6** were obtained by concentrating the filtrate to a minimum and keeping the solution at –14 °C for a few hours (0.035 g, 41%). ^{1}H NMR (C_6D_6): -3.05 (t, $^3J_{PH}$ = 6.1 Hz, NiO*H*, 1H), 0.80-1.60 (m, $C\mathit{H}_2C\mathit{H}_2P$, NiC*H*, 9H), 1.08 (m, $CH(C\mathit{H}_3)_2$, 6H), 1.23 (m, $CH(C\mathit{H}_3)_2$, 6H), 1.45 (m, $CH(C\mathit{H}_3)_2$, 12H), 1.92 (m, $C\mathit{H}(CH_3)_2$, 4H). $^1H\{^{31}P\}$ NMR (C_6D_6): -3.05 (s, NiO*H*, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): 17.67 (s, $CH(\mathit{C}H_3)_2$, 2C), 18.65 (s, $CH(\mathit{C}H_3)_2$, 2C), 19.33 (vt, $^{v}J_{PC}$ = 3.5 Hz, $CH(\mathit{C}H_3)_2$, 2C), 19.36 (vt, $^{v}J_{PC}$ = 2.8 Hz, $CH(\mathit{C}H_3)_2$, 2C), 22.13 (vt, $^{v}J_{PC}$ = 10.7 Hz, *C*H$_2$P, 2C), 22.59 (vt, $^vJ_{PC}$ = 8.6 Hz, *C*H(CH$_3$)$_2$, 2C), 24.42 (vt, $^vJ_{PC}$ = 7.9 Hz, *C*H(CH$_3$)$_2$, 2C), 38.78 (vt, $^vJ_{PC}$ = 11.0 Hz, *C*H$_2$CH$_2$P, 2C), 42.15 (t, $^2J_{PC}$ = 11.0 Hz, Ni*C*, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 62.8 (s). Anal. Calcd for $C_{17}H_{38}NiOP_2$: C, 53.86; H, 10.10. Found: C, 53.39; H, 9.95.

Crystal Structure Determinations. Single crystals of **2-6** were grown from a benzene-d$_6$ (**2** and **5**) or hexanes solutions at room temperature (**3**) or at -15 °C (**6**), or by slow diffusion of hexanes into a saturated solution of the complex in benzene-d$_6$ (**4**). The crystallographic data for complexes **2-5** were collected on a Nonius FR591 generator (rotating anode) equipped with a Montel 200 optics, a D8 goniometer and a Bruker Smart 6000 CCD area detector. The crystallographic data for complex **6** were collected on a Bruker Microstar generator (micro source) equipped with a Helios optics, a Kappa Nonius goniometer and a Platinum135 detector.

Cell refinement and data reduction were done using SAINT[22]. An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[23] The space group was confirmed by XPREP routine[24] in the program SHELXTL.[25] The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter, except for those of the NH$_2$ and OH moieties of complexes **4** and **6**, respectively, which were positioned from residual peaks in the difference Fourier map. Some disorder was taken into account for two positions of the water-coordinated molecule and the BF$_4$ counterion of **2** (50:50), the β carbons of **2** (50:50), **3** (40:60), and **4** (30:70), in addition for half of the BF$_4$ moieties of the molecular structure of **5** (50:50). The absolute configuration of the non centrosymmetric crystals was determined using the Flack parameter.

Supporting Information Available. Tables of X-ray data for complexes **2-6** and a graph correlating NMR chemical shift values (^{31}P signals for phosphine moieties vs. ^{13}C signals for the γ-C). This material is available free of charge via the Internet at http:/pubs.acs.org. Complete details of the X-ray analyses for complexes **2-6** have also been deposited at The Cambridge Crystallographic Data Centre (CCDC 631844 (**2**), 692059 (**3**), 692060 (**4**), 692061 (**5**), 631845 (**6**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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[11] Significant reactivity differences also exist between $PC_{sp2}P$- and $NC_{sp2}N$-Ni complexes. For a lead reference on the reactivities of $NC_{sp2}N$-Ni complexes see van Koten's review in ref. 2a.

[12] Similarly, we have shown that oxidation of the phosphinite analogues of our $PC_{sp3}P^{i\text{-}Pr}$-Ni complexes, $(POC_{sp2}OP^{i\text{-}Pr})NiX$ (X= Cl, Br), give isolable Ni^{III} complexes, whereas Ni^{III} complexes based on the ligand $POC_{sp2}OP^{i\text{-}Pr}$ can be generated electrochemically but do not appear to be isolable. For the chemistry of $(POC_{sp3}OP^{i\text{-}Pr})$-Ni complexes see: (a) Pandarus, V.; Zargarian, D. *Chem. Commun.* **2007**, 978. (b) Pandarus, V.; Zargarian, D. *Organometallics* **2007**, *26*, 4321.

[13] It's worth noting that van Koten's group has reported the first examples of Ni^{III} pincer complexes based on the $NC_{sp2}N$-type ligands: Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379.

[14] (a) Gandelman, M.; Konstantinovski, L.; Rozenberg, H.; Milstein, D. *Chem. Eur. J.* **2003**, *9*, 2595. (b) Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Organometallics* **2005**, *24*, 1082.

[15] Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738.

[16] The sample is a suspension because complex **2** is only partially soluble in C_6D_6.

[17] Cambridge Structural Database search (Version 5.28 with updates up to November 2006 : Allen, F. H. *Acta Cryst.* **2002**, *B58*, 380). It should be added, however, that most

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aquo and amino complexes of Ni are penta- or hexa-coordinated species that would be expected to have somewhat longer Ni-ligand bond lengths.

[18] It is interesting to note that there seems to be a correlation between the chemical shifts of the γ-C and the ^{31}P signals for $PC_{sp3}P^{i\text{-}Pr}$-Ni complexes. See graph included in the Supporting Information section.

[19] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: Hoboken, N.J., **2005**.

[20] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, N.Y., **1980**.

[21] Cámpora, J.; Matas, I.; Palma, P; Graiff, C.; Tiripicchio, A. *Organometallics* **2005**, *24*, 2827.

[22] SAINT (**1999**) Release 6.06; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, Wisconsin, USA.

[23] Sheldrick, G.M. (**1999**). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, Wisconsin, USA.

[24] XPREP (**1997**) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program. Bruker AXS Inc., Madison, Wisconsin, USA.

[25] SHELXTL (**1997**) Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, Wisconsin, USA.

[26] (a) Sheldrick, G.M. (**1997**). SHELXS97, Program for the Solution of Crystal Structures. Univ. of Gottingen, Germany. (b) Sheldrick, G.M. (**1997**). SHELXL97, Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

Chapitre 5: Regioselective Hydroamination of Acrylonitrile Catalyzed by Cationic Pincer Complexes of Nickel

Article 4

manuscrit soumis à *Organometallics*

Annie Castonguay, Denis Spasyuk, Nathalie Madern, André L. Beauchamp et Davit
Zargarian*
Département de chimie, Université de Montréal, Montréal (Québec), Canada H3C 3J7

Abstract

The cationic pincer-type complexes [{(i-$Pr_2PCH_2CH_2)_2CH$}Ni($NCCH_3$)][BPh_4] (**1**), [{2,6-(i-$Pr_2PCH_2)_2$-C_6H_3}Ni($NCCH_3$)][BPh_4] (**2**), [{2,6-(i-$Pr_2PO)_2$-C_6H_3}Ni($NCCH_3$)][BPh_4] (**3**), and [{2,6-(i-$Pr_2PO)_2$-3,5-Cl_2-C_6H}Ni($NCCH_3$)][BPh_4] (**6**) have been prepared and fully characterized by NMR spectroscopy and X-ray crystallography. Cyclic voltammetry measurements of the Ni-Br precursors of **2**, **3**, and **6** indicated that substituting the CH_2 moiety in the ligand skeleton by O, or some of the aromatic protons by Cl, renders the metal center less susceptible to oxidation. Evaluating the catalytic activities of **1-3**, **6**, and the *t*-Bu analogue of **1** for addition of aniline to acrylonitrile showed **3** to be the most competent catalyst precursor. Isolation of [{(t-$Bu_2PCH_2CH_2)_2CH$}Ni($NCCH_2CH_2NHPh$)][BPh_4] (**7**) from the reaction of [{(t-$Bu_2PCH_2CH_2)_2CH$}Ni($NCCH{=}CH_2$)][BPh_4] with aniline suggests that these cationic precursors act as Lewis acids that bind the nitrile moiety of acrylonitrile, thereby activating the olefinic moiety toward nucleophilic attack by aniline.

Introduction

A number of PCP-type pincer complexes, introduced by Shaw and co-workers in the 1970's,[1] have demonstrated good catalytic activities for a variety of organic reactions of interest.[2] In the past two decades, many groups have worked on modifying the pincer ligands to improve particular reactions or applications. Thus, Milstein, Andersson, Shibasaki, Sabounchei and Jensen have shown that the efficiency of PCP-type Pd complexes for the Heck coupling can be increased by changing the nature of the cyclometallated carbon from sp^2 to sp^3 hybridization, incorporating oxygens in the ligand backbone, varying the phosphorus substituents from *t*-Bu to *i*-Pr, or increasing the size of the metallocycles from five to six-membered.[3] Different donor moieties also play an important role on reactivities of pincer complexes. For instance, Milstein has found that systems based on PCN-type unsymmetrical ligands show reactivities different from those of their better-known PCP analogues in C-C vs. C-H bond activation reactions,[4] and van Koten has demonstrated that the SO_2-sensing activities of Pt complexes based on NCN-type ligands can be completely altered by varying the amino substituents from Me to Et.[2a]

In the course of our recent studies on the PCP-type pincer complexes of nickel,[5] we have found that systems based on the ligand $PC_{sp3}P^{i\text{-}Pr}$ (Chart 5.1) are better catalysts for the Kumada-Corriu coupling in comparison to the closely analogous ligands $PC_{sp3}P^{t\text{-}Bu}$ and $PC_{sp2}P^{i\text{-}Pr}$.[5h] Electrochemical experiments have also shown that complexes based on $PC_{sp3}P^{i\text{-}Pr}$ and $POC_{sp3}OP^{i\text{-}Pr}$ ligands are easier to oxidize ($Ni^{II} \rightarrow Ni^{III}$) than their counterparts based on $PC_{sp2}P^{i\text{-}Pr}$ and $POC_{sp2}OP^{i\text{-}Pr}$ (Chart 5.1).[5e,h] Finally, we have shown that the cationic complexes $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH{=}CH_2)]^+$ and $[(POC_{sp2}OP^{i\text{-}Pr})Ni(NCCH{=}CH_2)]^+$ catalyze the regioselective addition of aniline to acrylonitrile,[5b,f] but the influence of the various ligands on this reaction has not been studied.

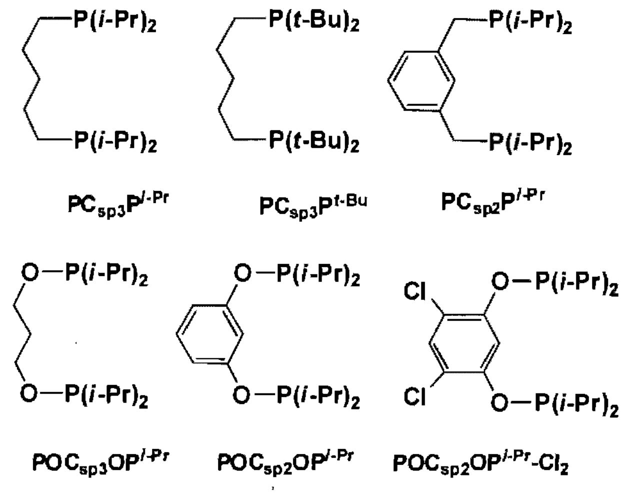


Chart 5.1

As a continuation of the above studies, we have prepared a series of cationic adducts of acetonitrile and evaluated their catalytic activities for the addition of aniline to acrylonitrile. Previous studies[5c] have demonstrated that acrylonitrile- and acetonitrile-adducts are in equilibrium (K_{eq}~1), which implies that the latter should be precatalysts for the target reaction. In addition to the ligands $PC_{sp3}P^{i\text{-}Pr}$, $PC_{sp3}P^{t\text{-}Bu}$, $PC_{sp2}P^{i\text{-}Pr}$, and $POC_{sp2}OP^{i\text{-}Pr}$, we selected a new ligand, $POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$ (Chart 5.1), in order to study the difference in reactivity brought about by the incorporation of electronegative Cl elements in the aromatic ring.

Results and Discussion

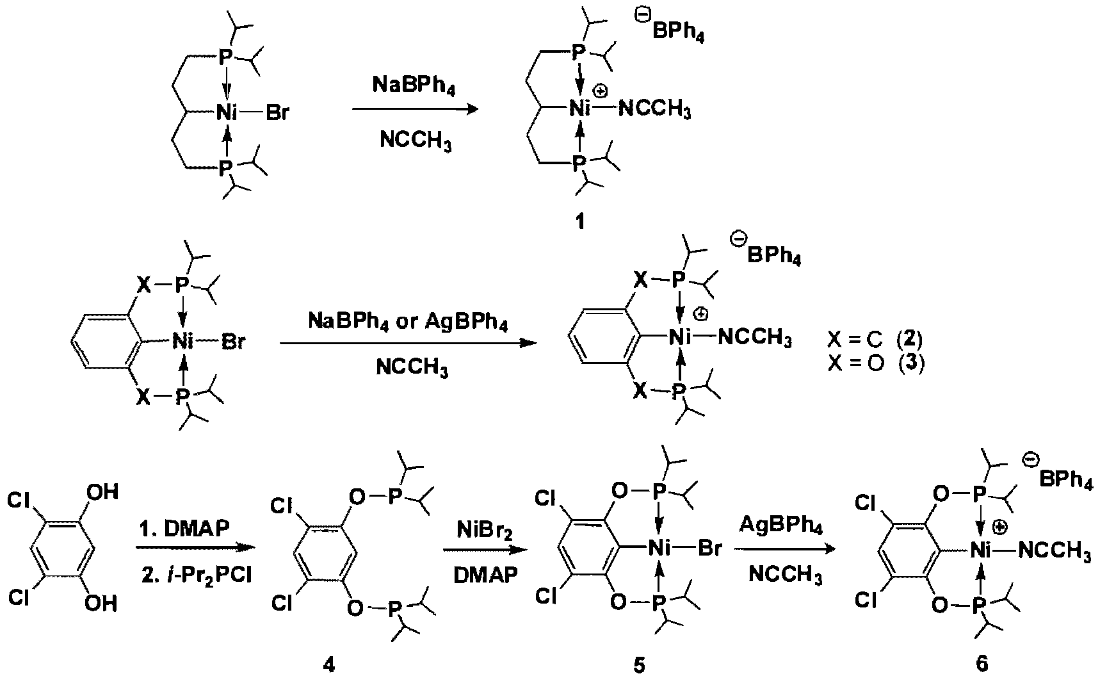
Synthesis and characterization. The cationic species bearing the $PC_{sp3}P^{i\text{-}Pr}$ and $PC_{sp2}P^{i\text{-}Pr}$ ligands were prepared by reacting the previously reported[5h,6] precursors ($PC_{sp3}P^{i\text{-}Pr}$)NiBr and ($PC_{sp2}P^{i\text{-}Pr}$)NiBr with $NaBPh_4$ in CH_3CN; the target complexes **1** and **2** were obtained as pale yellow powders in 85% and 79% yields, respectively (Scheme 5.1). Curiously, the analogous reaction of ($POC_{sp2}OP^{i\text{-}Pr}$)NiBr[5e] with $NaBPh_4$ gave very low yields of [($POC_{sp2}OP^{i\text{-}Pr}$)Ni($NCCH_3$)][$BPh_4$], **3**, even with extended reaction times, but the use of $AgBPh_4$ allowed the preparation of the desired complex in 65% yield. The new ligand $POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$, **4**, bearing electronegative oxygen and chlorine atoms, was synthesized as shown in Scheme 5.1 with the intention of preparing a more electrophilic cationic complex. Reacting **4** with $NiBr_2$ and DMAP in refluxing toluene afforded complex **5** as an orange-brown solid (73% yield) that reacted with $AgBPh_4$ in acetonitrile to give the target cationic species **6** (73% yield, Scheme 5.1).[7]

All new complexes have been characterized by NMR spectroscopy using samples prepared in $CDCl_3$ (**1-3**), C_6D_6 (**5**), or CD_3CN (**6**).[8] Observation of one singlet in the $^{31}P\{^1H\}$ NMR spectra and virtual triplets in the ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes confirmed the equivalence of the two phosphorus nuclei and suggested their mutually *trans* disposition. The greater electrophilicity of the Ni centers in the cationic complexes is reflected in the more downfield ^{31}P chemical shifts of **1-3** and **6** compared to those of the corresponding neutral Ni-Br precursors: δ 76.5

for **1** vs. 67.4 for ($PC_{sp3}P^{i\text{-}Pr}$)NiBr (C_6D_6); 70.6 for **2** vs. 61.8 for ($PC_{sp2}P^{i\text{-}Pr}$)NiBr ($CDCl_3$); 191.6 for **3** vs. 188.2 for $POC_{sp2}OP^{i\text{-}Pr}$)NiBr ($CDCl_3$); 197.2 for **6** vs. 192.2 for **5** (C_6D_6). The presence of a coordinated acetonitrile in **1-3** was indicated by a singlet resonance in their ^1H and $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$): 0.7-0.8 ppm (CH_3CN) and ~1 ppm (CH_3CN).[9] On the other hand, the quaternary carbon of the coordinated acetonitrile molecule (CH_3CN) was only observed in the $^{13}C\{^1H\}$ NMR spectra recorded on a high-field spectrometer (176 MHz, CD_2Cl_2, δ): 130.7 (**1**), 133.0 (**2**), 128.8 (**3**), and 127.7 (**6**). These high-field spectra also allowed us to detect the triplet resonance for the cyclometallated carbon in **2** (~153 ppm, $^2J_{PC}$ = 14 Hz), **3** (~123 ppm, $^2J_{PC}$ = 20 Hz), and **6** (~124 ppm, $^2J_{PC}$ = 20 Hz), while the corresponding signal for **1** (~55 ppm, $^2J_{PC}$ = 6 Hz) was also detectable at lower fields. The assignment of the cyclometallated carbon resonance in **3** has been confirmed by a ^{31}P INEPT experiment performed in CD_3CN. Finally, bands in the 2274-2282 cm^{-1} range of the IR spectra for these complexes were assigned to ν(C≡N), consistent with a similar assignment for the previously reported [($PC_{sp3}P^{t\text{-}Bu}$)Ni($NCCH_3$)][BPh_4] (2270 cm^{-1});[5c] comparison of these values to ν(C≡N) for free acetonitrile (2254 cm^{-1}) implies little or no π-backdonation in these cationic complexes.

Solid state structural studies carried out on single crystals of all complexes allowed us to confirm the structural assignments based on the above-discussed spectral data. ORTEP views of complexes **1-3** and **5** are shown in Figures 5.1-5.4, the crystal data and collection details are listed in Table 5.I, and selected bond distances and angles are given in Table 5.II; in the case of complex **6**, X-ray analysis allowed us to establish the connectivities, but low quality of the results obtained precludes reporting the molecular structure of this compound here.[10] All complexes adopt a distorted square planar geometry around the nickel center. The Ni-P bond distances vary between 2.15-2.19 Å, which is a typical range for this type of pincer complexes bearing *i*-Pr substituents on the phosphorus atoms. The Ni-C(3) bond lengths observed for complexes **2**, **3** and **5** are also in the range of 1.88-1.92 Å usually observed for Ni-C_{sp2} bonds.[11] The Ni-$N_{acetonitrile}$ bond distances in complexes **2** and **3** are very similar to the corresponding bond lengths seen in previously studied monocationic Ni-$NCCH_3$

complexes.[11,12] Finally, comparing the molecular structure of the neutral complex **5** to that of the previously reported (POC$_{sp2}$OP$^{i\text{-}Pr}$)NiBr analogue[5e] shows that introducing chloride atoms on the aromatic core of the ligand causes little or no change in ligand-metal bond distances and angles.



Scheme 5.1

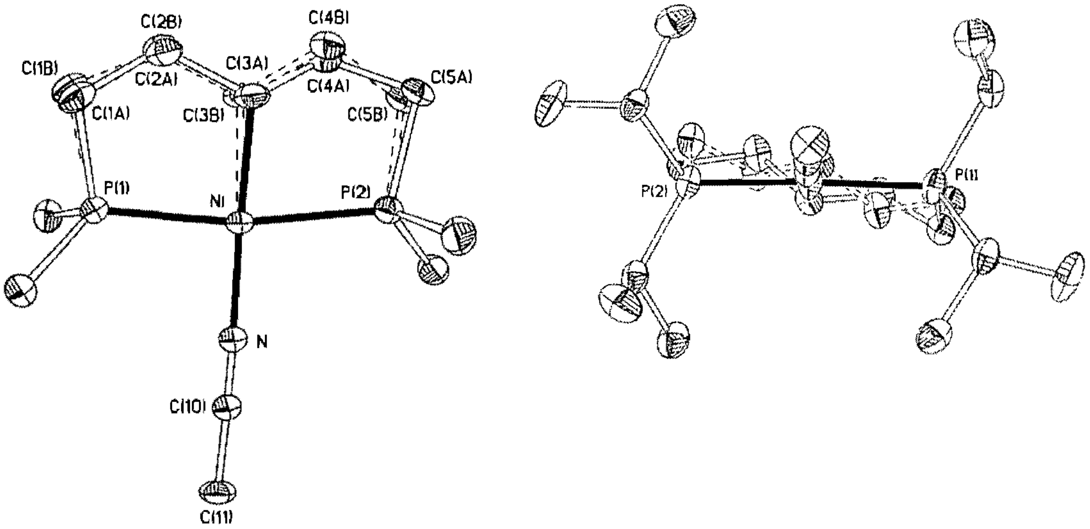


Figure 5.1. ORTEP diagrams for complex **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity. The alkyl chain of the ligand was found to occupy two positions, in a 7:3 ratio (A:B).

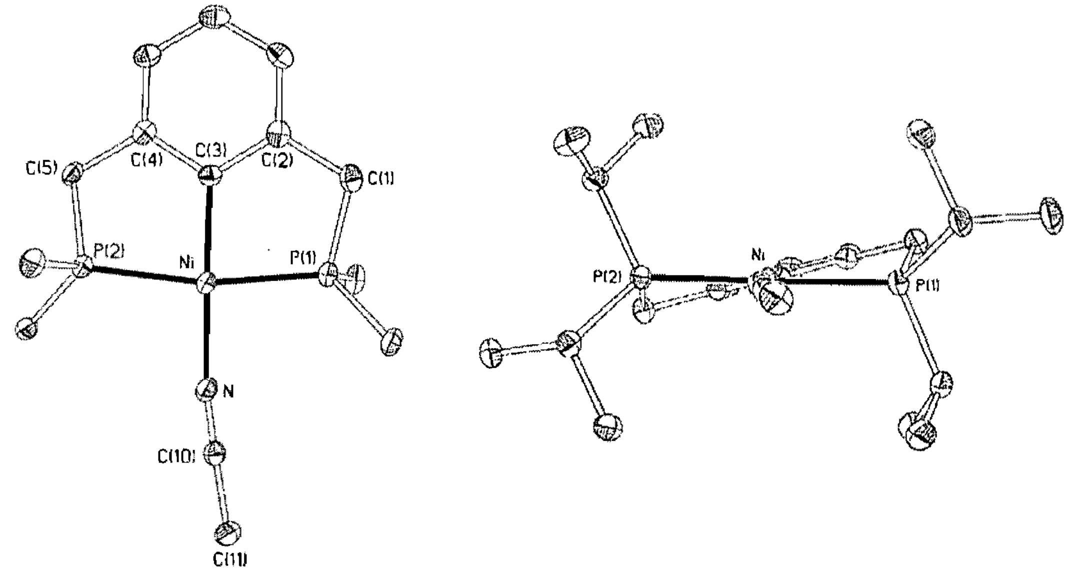


Figure 5.2. ORTEP views for complex **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity.

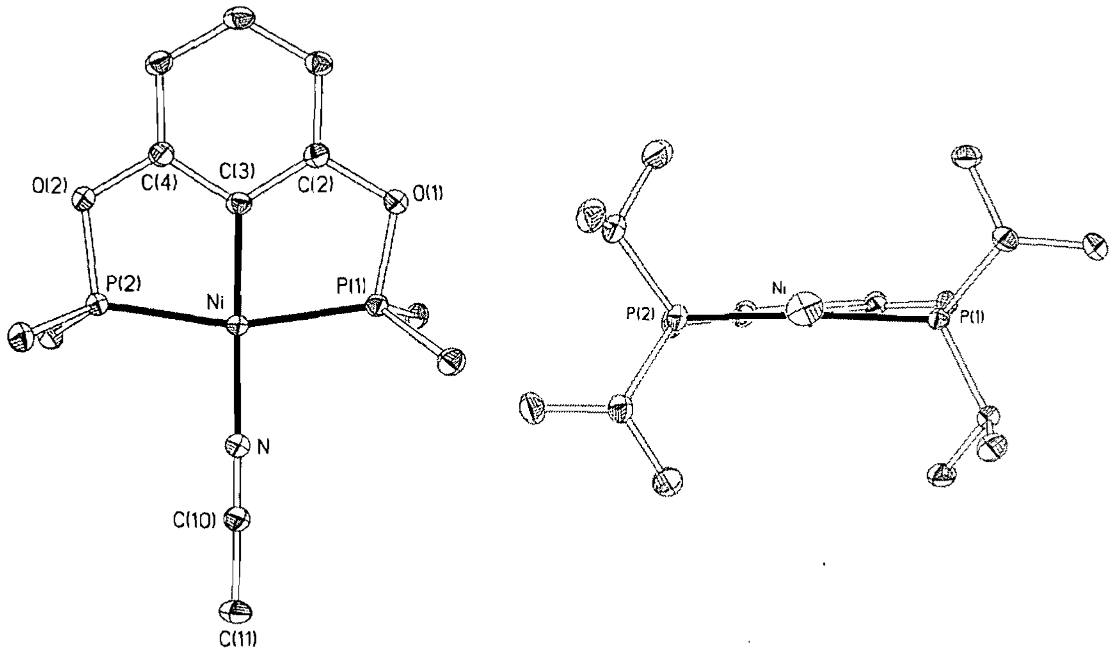


Figure 5.3. ORTEP views for complex **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity.

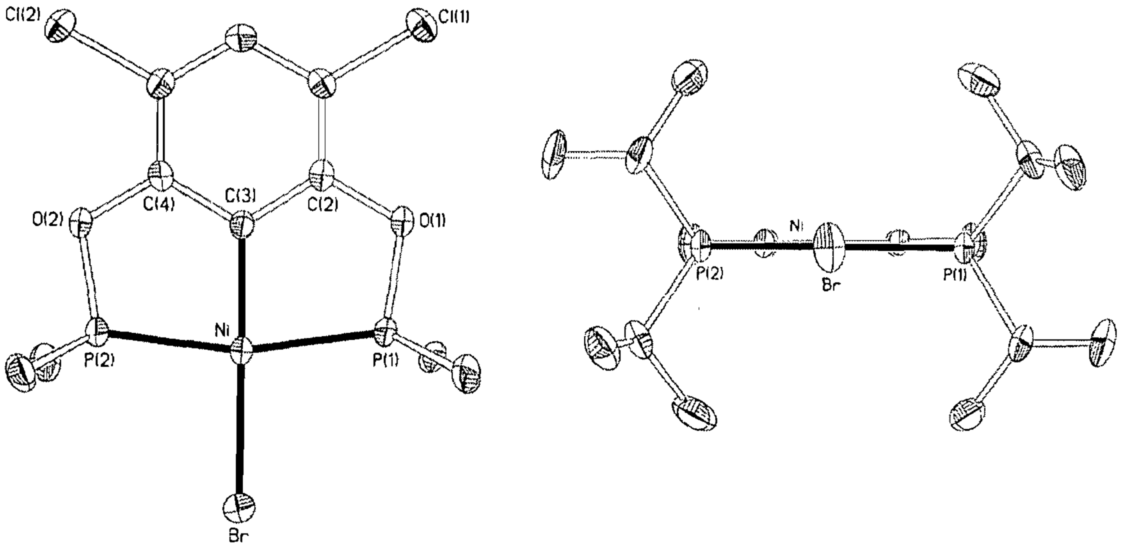


Figure 5.4. ORTEP diagrams for complex **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity.

Table 5.I. Crystal Data Collection and Refinement Parameters for Complexes **1-3**, **5** and **7**.

	1	**2**	**3**	**5**	**7**
chemical formula	$C_{43}H_{60}NiP_2NB$	$C_{46}H_{58}NiP_2NB$	$C_{44}H_{54}NiP_2O_2NB \cdot CH_3CN$	$C_{18}H_{29}BrNiCl_2P_2O_2$	$C_{54}H_{75}NiP_2N_2B$
Fw	722.38	756.39	801.40	548.87	883.62
T (K)	150(2)	100(2)	153(2)	200(2)	150(2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
space group	Pbca	Pbca	$P2_1/c$	$P2_1/n$	Pbca
a (Å)	17.8194 (6)	18.9665(9)	11.8122(4)	11.0281(5)	18.7220(3)
b (Å)	19.0036 (6)	17.7718(8)	17.2040(6)	17.9155(7)	18.4056(3)
c (Å)	23.9586 (7)	24.7209(11)	21.9175(8)	13.0131(5)	28.4880(5)
α (deg)	90	90	90	90	90
β (deg)	90	90	103.087(2)	111.017(2)	90
γ (deg)	90	90	90	90	90
Z	8	8	4	4	8
V ($Å^3$)	8113.2 (4)	8332.6(7)	4338.3(3)	2400.01(17)	9816.7(3)
ρ_{calcd} (g cm^{-3})	1.183	1.206	1.227	1.519	1.196
μ (cm^{-1})	16.41	16.23	16.31	65.08	14.52
θ range (deg)	3.69-78.99	3.58-69.05	3.30-72.06	4.40-72.41	3.10-69.04
R1[a] [I > 2σ(I)]	0.0524	0.0461	0.0376	0.0478	0.0499
wR2[b] [I > 2σ(I)]	0.1429	0.1128	0.0921	0.1224	0.1306
R1 [all data]	0.0704	0.0805	0.0442	0.0509	0.0761
wR2 [all data]	0.1566	0.1290	0.0949	0.1250	0.1473
GOF	1.137	0.935	0.971	1.129	1.036

[a] $R1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ [b] $wR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table 5.II. Selected Bond Distances (Å) and Angles (deg) for Complexes **1-3**, **5** and **7**.

	Ni(PC$_{sp3}$P$^{i\text{-Pr}}$)$^+$ (**1**)	Ni(PC$_{sp3}$P$^{t\text{-Bu}}$)$^+$	Ni(PC$_{sp2}$P$^{i\text{-Pr}}$)$^+$ (**2**)	Ni(POC$_{sp2}$OP$^{i\text{-Pr}}$)$^+$ (**3**)	Ni(POC$_{sp2}$OP$^{i\text{-Pr}}$-Cl$_2$)Br (**5**)	Ni(PC$_{sp3}$P$^{t\text{-Bu}}$)$^+$ (**7**)
Ni-C(3)	1.9751(10)	1.969(3)	1.916(3)	1.8839(14)	1.879(2)	1.978(3)
	1.9787(10)	---	---	---	---	---
Ni-P(1)	2.1495(9)	2.2154(10)	2.1724(8)	2.1692(5)	2.1571(6)	2.2208(8)
Ni-P(2)	2.1882(9)	2.2142(10)	2.1889(8)	2.1753(5)	2.1482(6)	2.2162(8)
Ni-N or -Br	1.807(2)	1.908(3)	1.887(3)	1.8862(13)	2.3114(5)	1.900(2)
N-C(10)	1.090(3)			1.140(2)	---	1.139(4)
C(10)-C(11)	1.383(4)	1.122(4)	1.132(4)	1.455(2)	---	1.461(4)
C(3)-Ni-N or -Br	174.93(15)	1.471(5)	1.452(4)	177.78(7)	178.48(6)	
	164.4(3)	173.98(16)	177.51(11)	---	---	175.40(12)
		---	---			

P(1)-Ni-P(2)	169.72(4)	169.31(4)	168.55(4)	162.719(1)	165.64(3)	170.54(3)
P(1)-Ni-N or -Br	91.49(8)	95.08(9)	93.75(8)	98.35(4)	98.30(2)	94.59(7)
P(2)-Ni-N or -Br	98.69(8)	95.56(8)	97.69(7)	98.66(4)	96.03(2)	94.86(7)
P(1)-Ni-C(3)	91.13(10)	84.75(12)	83.78(9)	81.16(5)	82.80(6)	85.10(9)
	84.3(2)	---	---	---		---
P(2)-Ni-C(3)	78.61(10)	84.79(12)	84.77(9)	81.95(5)	82.89(6)	85.44(9)
	86.3(2)	---	---	---		---

Electrochemical measurements. The cyclic voltammogram of **5** was measured and compared to those of the analogous Ni-Br complexes based on the $PC_{sp2}P^{i-Pr}$ and $POC_{sp2}OP^{i-Pr}$ ligands (Figure 5.5). This comparison has confirmed the anticipated order of electron-richness for these complexes : $(PC_{sp2}P^{i-Pr})NiBr$[5h,6] > $(POC_{sp2}OP^{i-Pr})NiBr$[5e] > $(POC_{sp2}OP^{i-Pr}\text{-}Cl_2)NiBr$. Inspection of these voltammograms also shows that substituting hydrogens in the aromatic core of the ligand by chlorine atoms has a smaller impact on the electronic density around the metal than the substitution of carbons by oxygens in the ligand backbone; the higher electronegativity of oxygen atoms and their proximity to the metal center are the likely explanations for these observations.

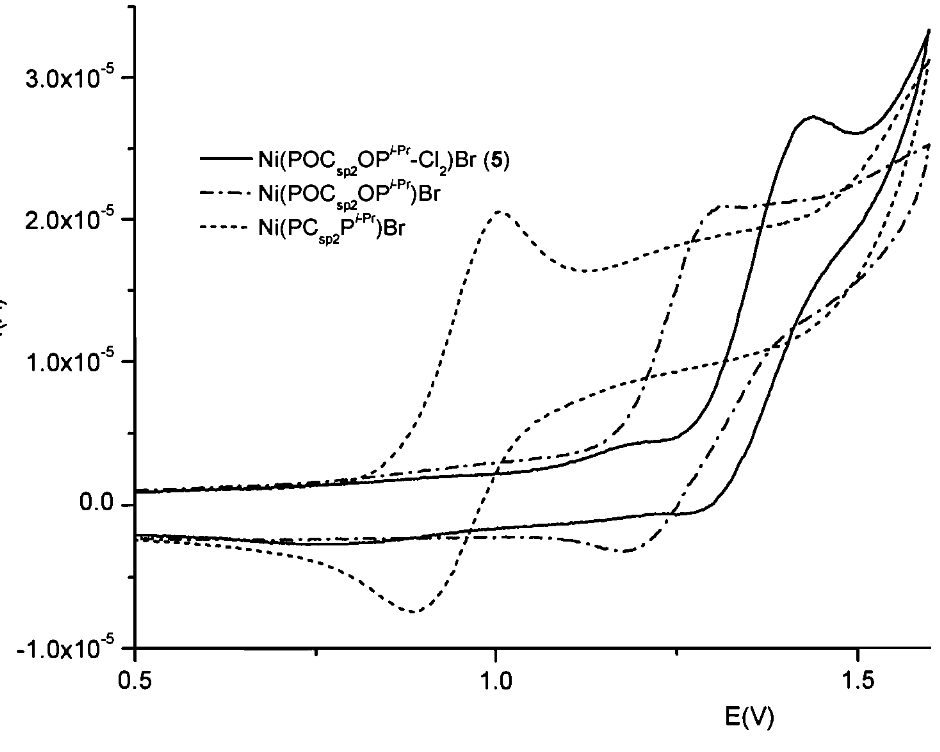


Figure 5.5. Cyclic voltammograms of **5**, $(POC_{sp2}OP^{i-Pr})NiBr$, and $(PC_{sp2}P^{i-Pr})NiBr$ in CH_2Cl_2 (1 mM solutions) measured at 298K with 0.1 M of TBAH as electrolyte (scan rate 100 mV s^{-1}).

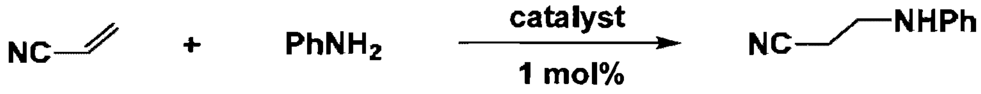
Hydroamination of acrylonitrile. Direct addition of N-H bonds to olefins is an atom-efficient approach toward the preparation of substituted amines since no by-products are formed.[13] Such additions are characterized by negative entropies and high enthalpic barriers, which are believed to be due to the repulsion between the HOMO's of the substrates (the amine lone pair and the olefinic π-bond);[13s,t] therefore, a catalyst is essential in most cases. Although many transition metal complexes are known to catalyze amination of olefins, very few are commercially viable in terms of being based on inexpensive metals, operating at sufficiently low catalyst loadings and temperatures, and promoting the addition of weakly nucleophilic amines.[13t]

We have reported that $[(PC_{sp3}P^{t\text{-}Bu})NiL]^+$ and $[(POC_{sp2}OP^{i\text{-}Pr})NiL]^+$ (L= acrylonitrile) promote the addition of aniline to acrylonitrile.[5b,f] The present report extends these studies to the cationic acetonitrile complexes discussed above in order to allow a direct comparison of the catalytic activities as a function of ligand structure.

The catalytic reactions were performed at 60 °C in THF or toluene for 6 or 18 h, using a 1 mol% loading of catalyst precursors and an aniline:olefin ratio of 1:1, 1:2, or 2:1. The main product of the catalysis is 3-anilinopropionitrile, which does not form in catalyst-free, control reactions. Small amounts of a second product were also detected in some of the runs performed in THF; the molecular ion of this product suggests that it arises from the addition of the N-H bond of the main product, 3-anilinopropionitrile, to acrylonitrile ($PhN(CH_2CH_2CN)_2$: m/z 199).

As can be noticed from the results listed in Table 5.III (runs 1, 6, 11, 16 and 21), complex **3** is by far the most efficient to catalyze the addition of aniline to acrylonitrile. For reactions run in THF, varying the amine to olefin ratio from 1:1 to 2:1 gave better yields in all reactions except those catalyzed by complex **6** (runs 2, 7, 12, and 17 vs. run 22), whereas a 1:2 ratio was significantly more beneficial only for reactions catalyzed by complex **3** (run 18); therefore, the 2:1 ratio was used for all reactions run in toluene. Overall, the catalysis proceeds better in toluene relative to THF in all cases except reactions of complex **3** (runs 5, 10, 15 and 25 vs. run 20). Longer reaction times (18 vs. 6 h) gave better yields only for reactions catalyzed by complexes **1** and **6** (runs 5 vs 4, and 25 vs 24). Interestingly, reactions run for 18 h and catalyzed by **1**, **2**, **3**, and **6** gave very similar yields (70-74%), while the reaction catalyzed by the *t*-Bu analogue of **1** gave quite low yields (runs 9 and 10, 25%); this can be explained by the greater steric hindrance of the bulky *t*-Bu groups.

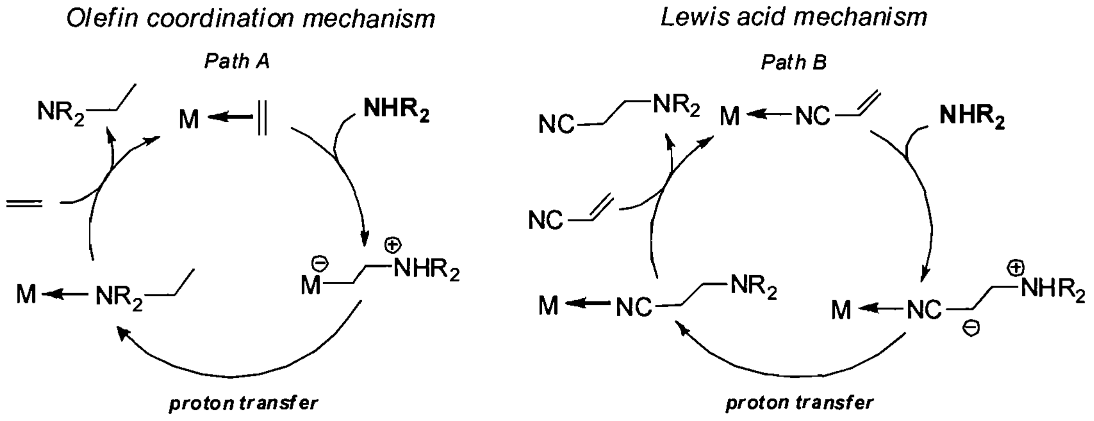
Table 5.III. Results obtained for the hydroaminatioan of acrylonitrile.[a]



Run	Catalyst	Solvent	Time	amine:olefin	Yield (%)[b]
1	$PC_{sp3}P^{i\text{-}Pr}$ (1)	THF	18 h	1:1	18
2		THF	18 h	2:1	51
3		THF	18 h	1:2	12
4		Toluene	6 h	2:1	44
5		Toluene	18 h	2:1	74
6	$PC_{sp3}P^{t\text{-}Bu}$	THF	18 h	1:1	6
7		THF	18 h	2:1	14
8		THF	18 h	1:2	10
9		Toluene	6 h	2:1	25
10		Toluene	18 h	2:1	25
11	$PC_{sp2}P^{i\text{-}Pr}$ (2)	THF	18 h	1:1	37
12		THF	18 h	2:1	63
13		THF	18 h	1:2	45
14		Toluene	6 h	2:1	70
15		Toluene	18 h	2:1	70
16	$POC_{sp2}OP^{i\text{-}Pr}$ (3)	THF	18 h	1:1	63
17		THF	18 h	2:1	>95
18		THF	18 h	1:2	86
19		Toluene	6 h	2:1	68
20		Toluene	18 h	2:1	73
21	$POC_{sp2}OP^{i\text{-}Pr}\text{-}Cl_2$ (6)	THF	18 h	1:1	12
22		THF	18 h	2:1	6
23		THF	18 h	1:2	10
24		Toluene	6 h	2:1	57
25		Toluene	18 h	2:1	74

[a] Reaction conditions : 0.007 mmol of Ni complex, 100-200 equivalents of the substrate, 1 mL of solvent, 60 °C. [b] Yields were determined by GC/MS and are the average of 3 experiments.

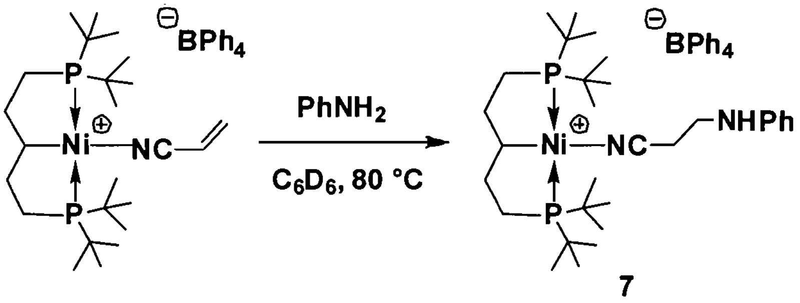
Mechanistic insights. The most frequently cited mechanistic proposal for olefin hydroaminations catalyzed by late transition metal complexes involves nucleophilic attack of the amine to the coordinated olefin, followed by proton transfer to generate the hydroaminated product (*path A*, Scheme 5.2). In the hydroamination of acrylonitrile, the nitrile moiety might compete with the olefin moiety for coordination to the electrophilic metal center, thus making possible the so-called Lewis-acid mechanism (*Path B*, Scheme 5.2) involving the indirect activation of the C=C bond for a nucleophilic attack.



Scheme 5.2

In order to obtain mechanistic information for the hydroamination reactions promoted by our cationic complexes, we monitored a typical catalytic experiment by $^{31}P\{^{1}H\}$ NMR spectroscopy using 2 mol% of $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH{=}CH_2)][BPh_4]$ and a 2:1 ratio of aniline to acrylonitrile in C_6D_6. Throughout the course of this catalytic reaction, we observed the resonance due to the starting complex (89.4 ppm) in addition to a new singlet very close-by (88.2 ppm) and a third singlet more downfield (95.6 ppm). In an attempt to isolate and identify these two unknown species, we reacted $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH{=}CH_2)][BPh_4]$ with an excess of aniline in C_6D_6 at 80 °C for 16 h. Monitoring this reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy showed the disappearance of the starting compound and the emergence of a new species displaying a singlet at

~88 ppm. This reaction mixture gave some crystals, which were isolated and analyzed by NMR spectroscopy and X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectrum confirmed that the crystals represented one of the species observed during the catalytic run (~88 ppm), whereas crystallography allowed us to identify this complex as 7 (Scheme 5.3), the 3-anilinopropionitrile adduct of the precursor. Unfortunately, we did not obtain any other evidence that might help identify the second unknown species observed during the catalysis.



Scheme 5.3

The ORTEP diagram of complex 7 is shown in Figure 5.6, the crystal data and collection details are listed in Table 5.I, and selected bond distances and angles are given in Table 5.II. In this molecular structure, the metal-ligand bonds are quite similar to the previously reported acrylonitrile adduct bearing the same ligand.[5c] The N-C(10) bond is also about the same length in both complexes (1.139(4) Å in 7 vs. 1.144(3) Å for the acrylonitrile adduct), indicating a similar degree of σ-donation/π-backdonation. The C(11)-C(12) bond distance is indeed longer in 7 and is characteristic of a single C-C bond (1.536(4) Å in 7 vs. 1.300(3) Å).

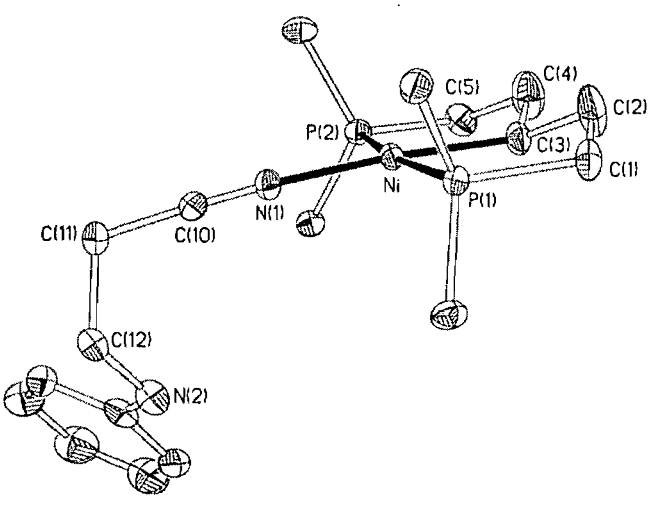


Figure 5.6. ORTEP diagrams for complex **7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and *t*-Bu methyl groups are omitted for clarity.

Conclusion

Structural and reactivity studies have been performed on different cationic pincer complexes of nickel. The comparison of the oxidation potentials and solid state structures for (POC$_{sp2}$OP$^{i\text{-Pr}}$)NiBr and its dichloro analogue **5**, (POC$_{sp2}$OP$^{i\text{-Pr}}$-Cl$_2$)NiBr, the neutral precursors of **3** and **6**, respectively, has shown that the introduction of chlorides on the aromatic moiety reduces the Ni center's electron-richness, whereas solid state parameters such as Ni-C and Ni-P bonds are fairly insensitive to this substitution. Similarly, reactivity studies have shown that structural differences have little impact on the catalytic competence of the cationic complexes in promoting the hydroamination of acrylonitrile with aniline, the only major exception being the inhibiting effect introduced by the *t*-Bu substituents. Indeed, it appears that the catalysis is most sensitive to the choice of solvent, toluene giving the best results for all complexes except **3**. The amine:olefin ratio is also an important factor, 2:1 being the best ratio in most cases. The available data suggests that the hydroamination reaction proceeds via a mechanism in which the Ni center is acting simply as a Lewis acid for activating the olefin toward nucelophilic attack. Future studies will be directed to screening the catalytic activities of complex **3** for the addition of other nucleophiles.

Experimental Section

General Comments. Except where noted, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and/or in nitrogen-filled glovebox. Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received from commercial vendors. Literature procedures were used to prepare the nickel precursors $(PC_{sp3}P^{i\text{-}Pr})NiBr$,[5h] $(PC_{sp2}P^{i\text{-}Pr})NiBr$,[5h] and $(POC_{sp2}OP^{i\text{-}Pr})NiBr$;[5e] $AgBPh_4$ was prepared via the reaction of $AgNO_3$ and $NaBPh_4$ in H_2O. The NMR spectra were recorded at ambient temperature on BrukerAV400 (^1H,$^{31}P\{^1H\}$) and BrukerARX400 ($^{13}C\{^1H\}$) instruments. The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent resonances, and spectral assignments were confirmed by DEPT135, COSY, and HMQC experiments; ^vJ refers to the apparent coupling constant of the virtual triplets. The $^{31}P\{^1H\}$ NMR spectra were referenced to an external 85% H_3PO_4 (0 ppm). All chemical shifts and coupling constants are expressed in ppm and Hz, respectively. The IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000-450 cm^{-1}) with samples prepared as KBr pellets. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal).

[{(*i*-Pr₂PCH₂CH₂)₂CH}Ni(NCCH₃)][BPh₄] (1). CH_3CN (10 mL) was added to a Schlenk tube containing $(PC_{sp3}P^{i\text{-}Pr})NiBr$ (400 mg, 0.90 mmol) and $NaBPh_4$ (341 mg, 1.00 mmol) and the mixture was stirred at room temperature for 1 h. Evaporation of the solvent and extraction of the solid residue with CH_2Cl_2 (10 mL) gave a yellow suspension, which was filtered on a glass frit and evaporated to dryness to give compound **1** as a pale yellow solid (554 mg, 85%). ^1H NMR ($CDCl_3$): 0.71 (s, $NCCH_3$, 3H), 0.85-1.90 (m, $CH(CH_3)_2$, CH_2CH_2, NiC*H*, 33H), 2.03 (m, $CH(CH_3)_2$, 2H), 2.13

(m, C*H*(CH$_3$)$_2$, 2H), 6.91 (t, $^3J_{HH}$ = 7, B*Ph*$_4$, 4H), 7.08 (t, $^3J_{HH}$ = 7, B*Ph*$_4$, 8H), 7.50 (br s, B*Ph*$_4$, 8H). ^{13}C{^{1}H} NMR (CDCl$_3$): 1.2 (s, NC*C*H$_3$, 1C), 17.7 (s, CH(*C*H$_3$)$_2$, 2C), 18.7 (s, CH(*C*H$_3$)$_2$, 2C), 19.3 (vt, $^vJ_{PC}$ = 3, CH(*C*H$_3$)$_2$, 2C), 19.4 (vt, $^vJ_{PC}$ = 2, CH(*C*H$_3$)$_2$, 2C), 20.4 (vt, $^vJ_{PC}$ = 12, *C*H$_2$P, 2C), 23.3 (vt, $^vJ_{PC}$ = 10, *C*H(CH$_3$)$_2$, 2C), 25.1 (vt, $^vJ_{PC}$ = 10 Hz, *C*H(CH$_3$)$_2$, 2C), 38.2 (vt, $^vJ_{PC}$ = 8, *C*H$_2$CH$_2$P, 2C), 54.9 (t, $^2J_{PC}$ = 6, Ni*C*, 1C), 121.8 (s, B*Ph*$_4$, 4C), 125.8 (s, B*Ph*$_4$, 8C), 136.1 (s, B*Ph*$_4$, 8C), 164.1 (J_{BC} = 49, B*Ph*$_4$, 4C). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 176 MHz): 130.7 (s, N*C*CH$_3$, 1C). ^{31}P{^{1}H} NMR (CDCl$_3$): 76.5. IR (KBr) : 2274 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{43}H_{60}Ni_1P_2N_1B_1$: C,71.49; H, 8.37; N,1.94. Found: C, 71.49; H, 8.41; N, 1.96.

[{(*i*-Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}Ni(NCCH$_3$)][BPh$_4$] (2). CH$_3$CN (5 mL) was added to a Schlenk tube containing (PC$_{sp2}$P$^{i\text{-}Pr}$)NiBr (0.500 g, 1.05 mmol) and NaBPh$_4$ (0.431 g, 1.26 mmol) and the mixture was stirred at room temperature for 2 h. Evaporation of the solvent and extraction of the solid residues with CH$_2$Cl$_2$ (10 mL) gave a yellow suspension, which was filtered on a glass frit and evaporated to give compound **2** as a pale yellow solid (0.665 g, 79%). ^{1}H NMR (CDCl$_3$): 0.78 (s, NCC*H*$_3$, 3H), 1.14 (dvt, $^vJ_{PH} \sim J_{HH}$ = 7.0-7.2, CH(C*H*$_3$)$_2$, 12H), 1.30 (dvt, $^vJ_{PH} \sim J_{HH}$ = 7.5-8.5, CH(C*H*$_3$)$_2$, 12H), 2.14 (m, C*H*(CH$_3$)$_2$, 4H), 3.14 (s, C*H*$_2$P, 4H), 6.88 (t, $^3J_{HH}$ = 6.8, B*Ph*$_4$, 4H), 6.80-7.10 (m, Ar*H*, 3H), 7.05 (t, $^3J_{HH}$ = 7.4, B*Ph*$_4$, 8H), 7.49 (br s, B*Ph*$_4$, 8H). ^{13}C{^{1}H} NMR (CDCl$_3$): 1.0 (s, NC*C*H$_3$, 1C), 18.3 (s, CH(*C*H$_3$)$_2$, 4C), 19.0 (s, CH(*C*H$_3$)$_2$, 4C), 23.9 (vt, $^vJ_{PC}$ = 11, *C*H(CH$_3$)$_2$, 4C), 30.8 (vt, $^vJ_{PC}$ = 15, *C*H$_2$P, 2C), 121.8 (s, B*Ph*$_4$, 4C), 123.5 (vt, $^vJ_{PC}$ = 9, *Ar*H, 2C), 125.8 (s, B*Ph*$_4$, 8C), 127.8 (s, *Ar*H, 1C), 136.2 (s, B*Ph*$_4$, 8C), 152 (vt, $^vJ_{PC}$ = 12, *Ar*CH$_2$P, 2C), 164.4 (J_{BC} = 49, B*Ph*$_4$, 4C). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 176 MHz): 133.0 (s, N*C*CH$_3$, 1C), 153.0 (t, $^2J_{PC}$= 14, Ni*C*, 1C). ^{31}P{^{1}H} NMR (CDCl$_3$): 70.6. IR (KBr) : 2282 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{46}H_{58}Ni_1P_2N_1B_1$: C,73.04; H,7.73; N,1.85. Found: C, 72.67; H, 7.68; N, 1.91.

[{(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}Ni(NCCH$_3$)][BPh$_4$] (3). CH$_3$CN (5 mL) was added to a Schlenk tube containing Ni(POC$_{sp2}$OP$^{i\text{-}Pr}$)Br (0.500 g, 1.04 mmol) and AgBPh$_4$ (0.489 g, 1.15 mmol) and the mixture was allowed to react for 4 h. The resultant suspension was filtered in air through a layer of Celite® and a glass frit; evaporation of the solvent gave complex **3** as a yellow solid (0.515 g, 65%). ^{1}H NMR (CDCl$_3$): 0.65 (s, NCCH_3, 3H), 1.30 (m, CH(CH_3)$_2$, 24H), 2.34 (m, CH(CH$_3$)$_2$, 4H), 6.51 (m, ArH, 2H), 6.91 (br s, BPh_4, 4H), 7.07 (br s, BPh_4, 8H), 7.52 (br s, BPh_4 + ArH, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): 1.0 (s, NCCH$_3$, 1C), 17.0 (s, CH(CH$_3$)$_2$, 4C), 17.6 (s, CH(CH$_3$)$_2$, 4C), 28.6 (vt, $^{\mathrm{v}}J_{\mathrm{PC}}$ = 12, CH(CH$_3$)$_2$, 4C), 106.6 (vt, $^{\mathrm{v}}J_{\mathrm{PC}}$ = 7, ArH, 2C), 121.8 (s, BPh_4, 4C), 125.8 (m, BPh_4, 8C), 131.8 (s, ArH, 1C), 136.2 (s, BPh_4, 8C), 164.4 ($^1J_{\mathrm{BC}}$ = 49, BPh_4, 4C), 168.8 (vt, $^{\mathrm{v}}J_{\mathrm{PC}}$ = 9, ArO, 2C). ^{13}C{^{1}H} NMR (CD$_3$CN): 17.0 (s, CH(CH$_3$)$_2$, 4C), 17.8 (s, CH(CH$_3$)$_2$, 4C), 29.3 (vt, $^{\mathrm{v}}J_{\mathrm{PC}}$ = 10, CH(CH$_3$)$_2$, 4C), 107.1 (vt, $^{\mathrm{v}}J_{\mathrm{PC}}$ = 5, ArH, 2C), 122.8 (s, BPh_4, 4C), 123.4 (very weak m, NiC, 1C), 126.6 (m, BPh_4, 8C), 132.6 (s, ArH, 1C), 136.7 (s, BPh_4, 8C), 164.8 ($^1J_{\mathrm{BC}}$ = 39, BPh_4, 4C), 170.1 (vt, $^{\mathrm{v}}J_{\mathrm{PC}}$ = 7, ArO, 2C). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 176 MHz): 122.5 (t, J_{PC} = 20, NiC, 1C), 128.8 (s, NCCH$_3$, 1C). ^{31}P{^{1}H} NMR (CDCl$_3$ or CD$_3$CN): 191.6. IR (KBr) : 2277 cm^{-1} ($\nu_{\mathrm{C\equiv N}}$). Anal. Calcd for $C_{44}H_{54}Ni_1P_2O_2N_1B_1$: C, 69.50; H, 7.16; N, 1.84. Found: C, 69.27; H, 7.46; N, 1.82.

(*i*-Pr$_2$PO)$_2$C$_6$H$_2$Cl$_2$ (4). To a solution of 2,4-dichloro-1,3-resorcinol (0.562 g, 3.14 mmol) and DMAP (0.768 g, 6.28 mmol) in THF (40 mL) that had been stirred for 0.5 h and cooled to 0 °C was added dropwise *i*-Pr$_2$PCl (1.00 mL, 6.28 mmol) and the final reaction mixture allowed to react for 1 h at room temperature. Evaporation of THF to dryness, followed by addition of hexanes, stirring, filtration of the resultant suspension, and evaporation of hexanes gave ligand **4** as a highly water-sensitive oil (0.650 g, 50%); this material was used immediately after its preparation and without further purification. ^{1}H NMR (C$_6$D$_6$): 0.93 (dd, J_{PH} = 16, J_{HH} = 7, CH(CH_3)$_2$, 12H), 1.13 (dd, J_{PH} = 11, J_{HH} = 7, CH(CH_3)$_2$, 12H), 1.74 (m, CH(CH$_3$)$_2$, 4H), 7.24 (s, ArH, 1H), 7.80 (t, J_{PH} = 4, ArH, 1H). ^{1}H{^{31}P} NMR (C$_6$D$_6$): 0.93 (ps t, J = 7-8, CH(CH_3)$_2$, 12H), 1.13 (ps t, J = 6, CH(CH_3)$_2$, 12H), 1.75 (m, CH(CH$_3$)$_2$, 4H), 7.23 (s, ArH, 1H), 7.79 (s, ArH, 1H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 17.1 (d, J_{PC} = 8, CH(CH$_3$)$_2$, 4C), 17.7 (d, J_{PC} = 20, CH(CH$_3$)$_2$, 4C), 28.6 (d, J_{PC} = 19, CH(CH$_3$)$_2$ 4C), 109.7 (t, J_{PC} = 22, ArH, 1C), 117.0 (s, ArCl, 2C), 130.5 (s, ArH, 1C), 154.6 (d, J_{PC} = 10, ArO, 1C). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 156.0.

$\{(i\text{-}Pr_2PO)_2C_6HCl_2\}NiBr$ (5). Ligand **4** (0.460 g, 1.12 mmol) was added to a suspension of anhydrous $NiBr_2$ (0.278 g, 1.27 mmol) and DMAP (0.137 g, 1.12 mmol) in toluene (15 mL) and the reaction mixture was refluxed for 5 h. The solvent was then evaporated to dryness, hexanes (20 mL) added and the resultant mixture was filtered in the air on a glass frit. The filtrate was washed with water and concentrated until a minimum of hexanes was left. Orange-brown crystals of **5** formed by keeping the solution at -14 °C (0.450 g, 73%). ${}^{1}H$ NMR (C_6D_6): 1.08 (dvt, ${}^{v}J_{PH} \sim J_{HH} = 7\text{-}8$, $CH(CH_3)_2$, 12H), 1.27 (dvt, ${}^{v}J_{PH} \sim J_{HH} = 7\text{-}9$, $CH(CH_3)_2$, 12H), 2.14 (m, $CH(CH_3)_2$, 4H), 7.07 (s, Ar*H*, 1H). ${}^{1}H\{{}^{31}P\}$ NMR (C_6D_6): 1.1 (d, $J_{HH} = 7$, $CH(CH_3)_2$, 12H), 1.3 (d, $J = 7$, $CH(CH_3)_2$, 12H), 2.14 (m, $CH(CH_3)_2$, 4H), 7.07 (s, Ar*H*, 1H). ${}^{13}C\{{}^{1}H\}$ NMR (C_6D_6): 16.6 (s, $CH(CH_3)_2$, 4C), 17.7 (vt, ${}^{v}J_{PC} = 2$, $CH(CH_3)_2$, 4C), 28.4 (vt, ${}^{v}J_{PC} = 11$, $CH(CH_3)_2$, 4C), 110.8 (vt, ${}^{v}J_{PC} = 7$, ArCl, 2C), 128.9 (s, *Ar*H, 1C), 131.4 (t, $J_{PC} = 20$, Ni*C*, 1C), 162.3 (vt, ${}^{v}J_{PC} = 11$, *Ar*O, 2C). ${}^{31}P\{{}^{1}H\}$ NMR (C_6D_6): 192.2. Anal. Calcd for $C_{18}H_{29}BrNiCl_2P_2O_2$: C, 39.39; H, 5.33. Found:C, 39.41; H, 5.20.

$[\{(i\text{-}Pr_2PO)_2C_6HCl_2\}Ni(NCCH_3)][BPh_4]$ (6). CH_3CN (10 mL) was added to a Schlenk tube containing $(POC_{sp2}Cl_2OP^{i\text{-}Pr})NiBr$ (0.450 g, 0.82 mmol) and $AgBPh_4$ (0.419 g, 0.98 mmol) and the mixture was allowed to react for 15 min at room temperature. The resultant solution was filtered in air through a layer of Celite® and a glass frit, and the solvent evaporated to dryness to give complex **6** as a pale yellow solid (0.496 g, 73%). ${}^{1}H$ NMR (CD_3CN): 1.00-1.20 (m, $CH(CH_3)_2$, 24H), 2.39 (m, $CH(CH_3)_2$, 4H), 6.62 (t, ${}^{3}J_{HH} = 7$, B*Ph*$_4$, 4H), 6.78 (t, ${}^{3}J_{HH} = 7$, B*Ph*$_4$, 8H), 6.90-7.10 (s, B*Ph*$_4$ + Ar*H*, 9H). ${}^{13}C\{{}^{1}H\}$ NMR (CD_3CN): 17.0 (s, $CH(CH_3)_2$, 4C), 17.7 (s, $CH(CH_3)_2$, 4C), 29.5 (vt, ${}^{v}J_{PC} = 11$, $CH(CH_3)_2$, 4C), 111.7 (vt, ${}^{v}J_{PC} = 7$, ArCl, 2C), 122.7 (s, B*Ph*$_4$, 4C), 126.6 (m, B*Ph*$_4$, 8C), 131.4 (s, *Ar*H, 1C), 136.7 (s, B*Ph*$_4$, 8C), 163.1 (vt, ${}^{v}J_{PC} = 10$, *Ar*O, 2C), 164.8 (${}^{1}J_{BC} = 49$, B*Ph*$_4$, 4C). ${}^{13}C\{{}^{1}H\}$ NMR (CD_2Cl_2, 176 MHz): 123.7 (t, ${}^{2}J_{PC} = 20$, Ni*C*, 1C), 127.7 (s, N*C*CH$_3$, 1C). ${}^{31}P\{{}^{1}H\}$ NMR (CD_3CN): 197.2. IR (KBr) : 2282 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{44}H_{52}NiCl_2P_2O_2N_1B_1{\cdot}H_2O$: C, 62.37; H, 6.42; N, 1.65. Found: C, 62.59; H, 6.36; N, 1.72.

Typical procedure for hydroamination reactions. Aniline (63 μL, 0.69 mmol), acrylonitrile (46 μL, 0.70 mmol), and the catalyst stock solution (1.0 mL of a 6.9 M THF solution) were added into a sealable vessel, which was put in an oil bath at 60 °C for 6 or 18 h. The reaction vessel was then allowed to cool to room temperature and *p*-xylene was added (to serve as an internal standard). Hexanes (5 mL) was then added to the tube. A small fraction of the resulting suspension/solution was filtered through a Celite® pad and the filtrate was analyzed by GC/MS. The yields were determined from a calibration curve based on the product (anilinopropionitrile / *p*-xylene).

Cyclic Voltammetry Experiments. Cyclic voltammetry measurements were performed using a BAS Epsilon potentiostat. A typical three-electrode system was used, consisting of a glassy carbon working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode ($E_{½}$ ($FeCp_2^+/FeCp_2$) = +0.60 V under these conditions). The experiments were carried out in CH_2Cl_2 at room temperature with TBAH as electrolyte (0.1 M) and the solutions were bubbled with nitrogen before each experiment.

Crystal Structure Determinations. Single crystals of the complexes were grown by: slow diffusion of diethyl ether into a saturated solution of the complex in $CDCl_3$ (**1**) or into a saturated solution of THF (**2** and **3**); slow evaporation (at room temperature) of a hexanes solution (**5**) or a C_6D_6 solution (**7**). The crystallographic data (Table 5.I) for all complexes were collected on a Nonius FR591 generator (rotating anode) equipped with a Montel 200, a D8 goniometer and a Bruker Smart 6000 area detector.

Cell refinement and data reduction were done using SAINT.[14] An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[15] The space group was confirmed by XPREP routine[16] in the program SHELXTL.[17] The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97.[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter.

Supporting Information. Complete details of the X-ray analyses for complexes **1-3**, **5** and **7** have been deposited at The Cambridge Crystallographic Data Centre (CCDC 691621 (**1**), 691622 (**2**), 691623 (**3**), 691624 (**5**), 691625 (**7**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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[7] The high sensitivity of **4** to hydrolysis requires it to be used right after its preparation, whereas complex **6** is fairly stable to hydrolysis.

[8] Curiously, dissolving some batches of **6** in chloroform or methylene chloride converted this complex into either **3** or (POC$_{sp2}$OP$^{i\text{-}Pr}$-Cl$_2$)NiCl, as confirmed by ^{31}P{^{1}H} NMR spectroscopy. Residual hydrochloric acid, known to be present in chloroform, is known to transform our cationic pincer complexes into their Ni-Cl analogues, and we have confirmed that reaction of **6** with $HCl\cdot Et_2O$ gives the corresponding Ni-Cl derivative. However, the conversion of **6** into **3**, and the fact that this transformation is not reproducible, can not be explained at this point.

[9] The ^{13}C{^{1}H} NMR spectrum of **6** in CD_2Cl_2 also displayed a singlet corresponding to CH_3CN (2.77 ppm).

[10] The X-Ray data for **6** were recorded on a multiply-twinned crystal; numerous attempts at growing better quality crystals of this compound failed.

[11] Cambridge Structural Database search (Version 5.28 with updates up to November 2006 : Allen, F. H. *Acta Cryst.* **2002**, *B58*, 380).

[12] We can not include the comparison of the Ni-C bond distance observed in complex **1** with that of the analogous complex [(PC$_{sp3}$P$^{t\text{-}Bu}$)Ni(NCCH$_3$)][BPh$_4$] since the highly disordered alkyl chain in **1** required us to fix some of the distances during the refinement.

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Chapitre 6: Conclusion générale et perspectives

Malgré le fait que les complexes « pincer » ont vu le jour dans les années 1970, ce n'est que depuis les deux dernières décennies qu'ils ont connu un essor important dans la littérature. Les premiers complexes « pincer » rapportés furent de type PCP et, malgré la panoplie de nouveaux ligands publiée jusqu'à aujourd'hui, les complexes de ce type sont demeurés très populaires. Plusieurs de ces composés PCP sont reconnus pour être d'excellents catalyseurs pour plusieurs réactions organiques d'intérêt, telles le couplage de Heck et la déshydrogénation des alcanes ainsi que pour entraîner des réactivités surprenantes.

Les différents objectifs visés par ce projet doctoral ont été atteints. Plusieurs complexes de type $PC_{sp3}P$ et $PC_{sp2}P$ ont été préparés. Aussi, des modifications apportées aux ligands utilisés ont permis l'évaluation de différences structurales, électroniques ainsi que de réactivité de certains de ces complexes.

Ce chapitre de conclusion consistera en une récapitulation de ce qui a été accompli au cours de cette thèse, mettant l'accent sur les éléments importants des voies synthétiques employées, des méthodes de caractérisation utilisées ainsi que des réactivités étudiées. Quelques perspectives de travaux futurs seront aussi présentées.

Voies synthétiques pour les différents précurseurs halogénés

Quelques voies générales pour la préparation de complexes « pincer » ont été établies dans la littérature, soit par *addition oxydante du ligand*, par usage d'un agent organométallique (*transmétallation*) ou bien par *transcyclométallation*. La plupart des composés PCP du nickel rapportés jusqu'à présent ont emprunté celle de *l'addition oxydante du ligand* et c'est cette voie qui a aussi été exploitée pour les complexes qui sont rapportés dans cette thèse. Comme au début du projet aucun complexe $PC_{sp3}P$ du nickel n'avait été rapporté, nous nous sommes, en premier lieu, intéressés à la préparation de tels ligands.

Comme décrit au chapitre 2, nous avons premièrement tenté de complexer au nickel un ligand qui était déjà existant dans la littérature et qui avait mené, avec succès, à la synthèse de différents complexes « pincer » à base d'une variété de métaux de transition (Pd, Ir, Rh, etc.).[1] Ce ligand $PC_{sp3}P^{t\text{-}Bu}$, possédant des groupements *t*-Bu sur les atomes de phosphore, a mené à l'obtention des complexes « pincer » désirés par chauffage avec NiX_2, mais avec des rendements plutôt faibles de même qu'accompagnés de sous-produits (Figure 6.1).

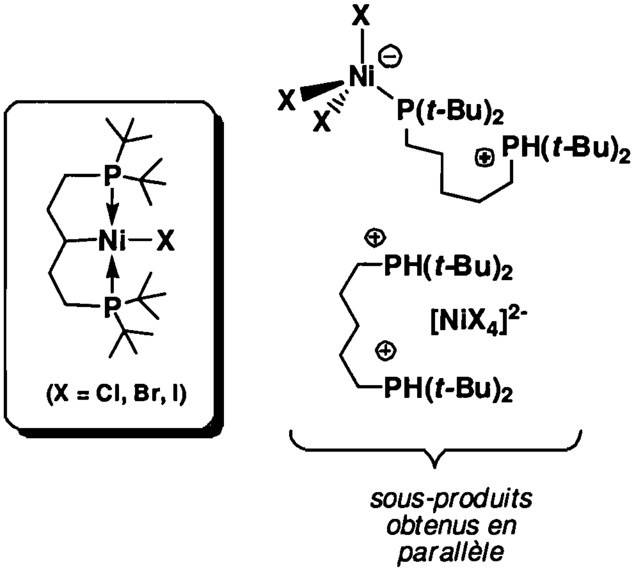

Figure 6.1. Complexes obtenus à partir de la réaction du ligand $PC_{sp3}P^{t\text{-}Bu}$ et de NiX_2.

Après avoir déterminé la nature des complexes obtenus en parallèle de ces réactions comme étant des produits de protonation (du ligand ou bien du complexe « pincer » formé), il fut possible de comprendre la cause des faibles rendements obtenus. Toutes les tentatives d'ajout de bases dans le milieu réactionnel pour neutraliser l'acide généré par le processus de cyclométallation n'ont malheureusement pas été fructueuses, menant à des mélanges de produits paramagnétiques dont la caractérisation n'a pas été poursuivie. Pour tenter d'éviter la formation de ces sous-produits de protonation, l'usage d'un ligand quelque peu différent fut envisagé.

Au chapitre 3, nous avons rapporté la synthèse d'un ligand qui diffère au niveau des groupements sur les atomes de phosphore, $PC_{sp3}P^{i\text{-}Pr}$, qui existait lui aussi dans la littérature mais qui avait été utilisé à une fin autre que celle de la préparation de complexes « pincer »; bien qu'il nécessite l'usage d'un large excès de lithium métallique, le mode préparatoire que nous avons décrit pour ce ligand est plus détaillé et mène à de meilleurs rendements. Pour obtenir le complexe « pincer » désiré par réaction du ligand $PC_{sp3}P^{i\text{-}Pr}$ avec $NiBr_2$, il fut déterminé qu'un chauffage est nécessaire et que la présence de DMAP augmente le rendement (de < 10% à 37%). Malheureusement, la formation d'un sous-produit bimétallique empêche l'obtention d'un haut rendement pour l'obtention du complexe « pincer » qui était tant convoitée. De façon surprenante, contrairement au cas des produits de protonation obtenus en utilisant le ligand $PC_{sp3}P^{t\text{-}Bu}$, il est possible de procéder à la cyclométallation de cet espèce bimétallique, obtenant ainsi un rendement similaire à celui noté pour la synthèse initiale (Figure 6.2), tout simplement en le chauffant en présence de DMAP.

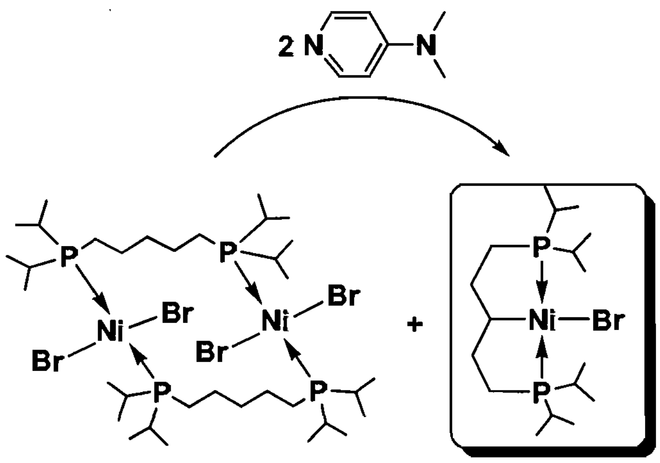

Figure 6.2. Complexes obtenus à partir de la réaction du ligand $PC_{sp3}P^{i\text{-}Pr}$ et de $NiBr_2$

Cette observation nous indique qu'il est possible que ce complexe « anneau » soit un intermédiaire dans le processus de formation des complexes « pincer ». Plusieurs composés cycliques de ce type ont été rapportés dans la littérature à base de différents métaux.[2]

La plupart des précurseurs halogénés dont il a été question dans les chapitres 2 à 5 ont été caractérisés par RMN, par diffraction des rayons X ainsi que par analyse élémentaire. Des études électrochimiques ont démontré l'impact des différents ligands utilisés sur le métal en terme de richesse électronique (Figure 6.3). Il s'avère que le ligand $PC_{sp3}P^{i\text{-}Pr}$ est plus riche en électrons que son analogue $PC_{sp3}P^{t\text{-}Bu}$, ce qui démontre que malgré le fait que les groupements *t*-Bu soient plus électrodonneurs, ils sont beaucoup plus stériquement encombrés que les groupements *i*-Pr, ce qui empêche les atomes de phosphore de s'approcher du métal. Cette hypothèse fut appuyée par les études cristallographiques de $(PC_{sp3}P^{i\text{-}Pr})$NiBr et de $(PC_{sp3}P^{t\text{-}Bu})$NiBr qui ont confirmé que les liaisons Ni-P sont significativement plus longues dans le cas du complexe $(PC_{sp3}P^{t\text{-}Bu})$NiBr. Comme on s'y serait attendu, les études électrochimiques ont confirmé que le métal est appauvri électroniquement lorsque l'on change la nature du carbone cyclométallé d'hybridation sp^3 à sp^2 de même que lorsque l'on incorpore des atomes électronégatifs au ligand (O, Cl).

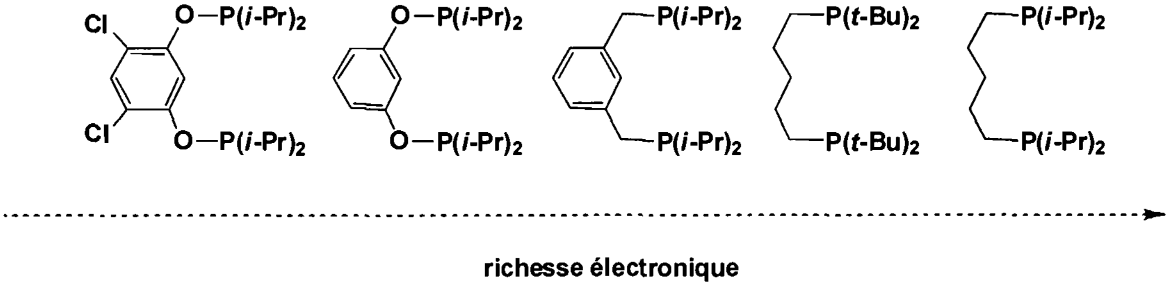

Figure 6.3. Influence des différents ligands sur la richesse électronique du nickel.

Réactivité des précurseurs halogénés

Formation d'espèces de Ni^{III}

Comme rapporté au chapitre 3, il fut possible de procéder à l'oxydation du composé halogéné le plus riche en électrons, soit $(PC_{sp3}P^{i\text{-}Pr})NiBr$, en espèces de Ni^{III}, $(PC_{sp3}P^{i\text{-}Pr})NiX_2$ ($X = Cl, Br$) en faisant usage de composés de Fe^{III} ($FeCl_3$ et $FeBr_3$). Ce degré d'oxydation est très rare pour le nickel et les seuls exemples connus dans la littérature qui sont basés sur des ligands « pincer » sont les complexes de type $NC_{sp2}N$ rapportés par van Koten[3] ainsi que ceux de type $POC_{sp3}OP^{i\text{-}Pr}$, rapportés par ma collègue Valérica Pandarus.[4] Il serait intéressant d'explorer la réactivité de telles espèces qui ne font que leur apparition dans la littérature. Comme le métal est dans un état d'oxydation peu commun, il pourrait susciter des réactions inusuelles.

Formation de liens Ni-C

Un des nombreux avantages des complexes « pincer » comportant un carbone cyclométallé est qu'ils peuvent former des composés comportant deux liaisons Ni-C, ces dernières pouvant rester en position *trans* l'une par rapport à l'autre et ainsi éviter l'élimination réductrice. Plusieurs composés de ce type ont été formés à partir des ligands $PC_{sp3}P^{i\text{-}Pr}$ et $PC_{sp3}P^{t\text{-}Bu}$ et certaines différences de réactivité ont été notées en ce qui a trait aux tentatives de préparation de dérivés $(PC_{sp3}P^{i\text{-}Pr})NiR$ ($R = Me, Ph, Bu$) par la réaction de métathèse des présurseurs $(PC_{sp3}P)NiBr$ et des réactifs MeMgCl, PhMgBr et *n*-BuLi, respectivement.

Par exemple, il fut noté que la préparation de $(PC_{sp3}P^{i\text{-}Pr})NiMe$ s'effectue instantanément à la température ambiante tandis que celle de $(PC_{sp3}P^{t\text{-}Bu})NiMe$ nécessite un chauffage de 80 °C durant 1 h. Le complexe $(PC_{sp3}P^{i\text{-}Pr})NiPh$ se prépare par chauffage durant 1 h tandis que l'espèce $(PC_{sp3}P^{t\text{-}Bu})NiPh$ ne se forme pas, même en chauffant les réactifs sur une longue période. Finalement, le complexe $(PC_{sp3}P^{i\text{-}Pr})NiBu$ se prépare sans complication à la température de la pièce tandis que le composé $(PC_{sp3}P^{t\text{-}Bu})NiBu$ n'est jamais observé et subit une élimination β-H pour donner lieu à la formation de l'espèce $(PC_{sp3}P^{t\text{-}Bu})NiH$.

Aussi, d'autres dérivés neutres ont été préparés, dont les composés alcynyles $(PC_{sp3}P^{i\text{-}Pr})NiR$ (R = C≡CMe, C≡CPh).

Formation d'espèces cationiques

Plusieurs composés cationiques ont été préparés par la réaction des précurseurs halogénés avec $AgBPh_4$ ou $NaBPh_4$ dans l'acétonitrile. Comme il fut discuté aux chapitres 2 et 5, le $NaBPh_4$ s'est avéré un réactif de choix pour remplacer l'halogène des composés $(PC_{sp3}P^{t\text{-}Bu})NiBr$, $(PC_{sp3}P^{i\text{-}Pr})NiBr$, et $(PC_{sp2}P^{i\text{-}Pr})NiBr$. Pour les complexes $(POC_{sp2}OP^{i\text{-}Pr})NiBr$ et $(POC_{sp2}OP^{i\text{-}Pr}\text{-}Cl_2)NiBr$, il fut nécessaire de faire appel au réacif $AgBPh_4$ étant donné leur faible réactivité avec le sel de sodium.

Un fait intéressant à noter est que l'acétonitrile qui se coordonne aux différents complexes n'est pas très labile. Il est rapporté au chapitre 2 que de faire réagir le complexe cationique $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH_3)][BPh_4]$ avec un excès de différents amines et oléfines ne mène à aucune substitution, même partielle, du nitrile coordonné. Il fut démontré que la molécule d'acétonitrile de ce complexe peut subir un échange avec un autre nitrile, l'acrylonitrile, et cette constante d'équilibre a été évaluée à ~1.

Une autre méthode menant à la coordination de ligands plus faibles tels que H_2O ou $i\text{-}PrNH_2$ a été présentée au chapitre 4. $(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$, un composé possédant de faibles interactions Ni-F, s'est avéré un précurseur de choix. Ce complexe fut préparé par deux méthodes, soit par la réaction du précurseur halogéné $(PC_{sp3}P^{i\text{-}Pr})NiBr$ avec $AgBF_4$ ou bien par la réaction de protonation du complexe alcynyle $(PC_{sp3}P^{i\text{-}Pr})Ni(CCMe)$, avec HBF_4.

La préparation des cations possédant un contre-ion BF_4^- mène généralement à de faibles rendement lorsque comparée à ceux dotés d'un ion BPh_4^-, la seule exception étant le rendement obtenu pour la préparation d'un complexe cationique stabilisé par une molécule de CO, $[(PC_{sp3}P^{i\text{-}Pr})Ni(CO)][BF_4]$.

Comme la coordination de différentes molécules au complexe $(PC_{sp3}P^{i\text{-}Pr})Ni(BF_4)$ peut être détectée aisément par spectroscopie RMN de $^{19}F\{^1H\}$, il serait plus qu'intéressant de tester la coordination de différents ligands très faibles; ceci pourrait mener à des réactivités catalytiques qui n'auraient pas lieu avec les complexes cationiques où une molécule non labile stabilise le métal.

Activité catalytique des différentes espèces préparées

Certains des complexes préparés se sont avérés actifs pour certaines des réactions catalytiques pour lesquelles ils ont été testés, notamment pour l'oligomérisation de phénylsilane, pour le couplage de Kumada-Corriu ainsi que pour l'hydroamination de l'acrylonitrile.

Oligomérisation du phénylsilane

Comme discuté dans le chapitre 2, les complexes hydrure et méthyle, $(PC_{sp3}P^{t\text{-}Bu})NiH$ et $(PC_{sp3}P^{t\text{-}Bu})NiMe$, ont démontré une certaine activité catalytique pour l'oligomérisation de phénylsilane. De façon surprenante, le complexe méthyle a mené à un mélange d'oligomères linéaires et cycliques tandis que le complexe hydrure n'a généré que des oligomères linéraires; un produit de réaction similaire aurait été attendu et ces résultats n'ont pu être justifiés jusqu'à présent.

Couplage de Kumada-Corriu

Au chapitre 3 est rapporté que certains des complexes préparés sont d'actifs catalyseurs pour la réaction de couplage de Kumada-Corriu. L'activité catalytique des complexes $(PC_{sp3}P^{i\text{-}Pr})NiBr$, $(PC_{sp2}P^{i\text{-}Pr})NiBr$ et $(PC_{sp3}P^{t\text{-}Bu})NiBr$ a été comparée à partir de la réaction de couplage de PhCl et de MeMgCl (Figure 6.4) et les résultats obtenus après 20 h dans le THF à reflux en faisant usage de 1 mol % des différents complexes ont démontré qu'il semble exister une correlation entre l'activité catalytique et l'ordre de richesse électronique du métal qui a préalablement été établi par électrochimie (Figure 6.5) : $(PC_{sp3}P^{i\text{-}Pr})NiBr$ (57%) > $(PC_{sp3}P^{t\text{-}Bu})NiBr$ (34%) > $(PC_{sp2}P^{i\text{-}Pr})NiBr$ (1%).

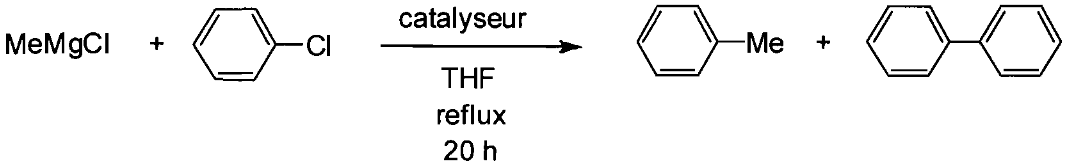

Figure 6.4. Réaction de couplage de Kumada-Corriu.

Il est intéressant de noter que de changer les substituants sur les phosphores de *i*-Pr à *t*-Bu a un impact moins important sur les résultats catalytiques que de changer la nature du carbone cyclométallé de sp^3 à sp^2, qui mène à un complexe quasi-inactif.

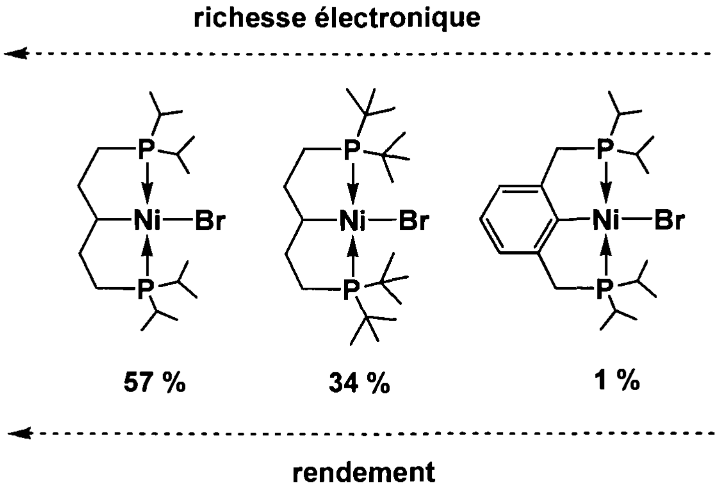

Figure 6.5. Comparaison de différents catalyseurs pour la réaction de Kumada-Corriu.

Pour les réactions impliquant le catalyseur le plus performant, $(PC_{sp3}P^{i\text{-}Pr})NiBr$, il est possible d'obtenir jusqu'à 84 « TON » lorsque 0,5 mol % du complexe est utilisé et des études préliminaires ont démontré qu'il est aussi possible d'effectuer le couplage de PhCl et de *n*-BuMgCl, un réactif de Grignard possédant une chaîne alkyle portant des atomes d'hydrogène en position β. Comme l'élimination β-H est une réaction compétitive lorsque ce type de Grignard est utilisé, des catalyseurs pouvant effectuer efficacement ces réactions de couplage de Kumada sont très convoités. L'étude de réactions de couplage de Kumada utilisant le complexe $(PC_{sp3}P^{i\text{-}Pr})NiBr$, qui semble retarder cette élimination en comparaison à son analogue $(PC_{sp3}P^{t\text{-}Bu})NiBr$ (en ce qui a trait à la formation de complexes butyles, chapitre 3), devrait être poursuivie.

Il est à noter que le mécanisme généralement proposé pour la réaction de couplage de Kumada est décrit par un cycle catalytique passant par des espèces de Ni^0/Ni^{II}. Comme durant une catalyse typique impliquant le complexe $(PC_{sp3}P^{i\text{-}Pr})NiBr$, seulement l'espèce $(PC_{sp3}P^{i\text{-}Pr})NiMe$ fut observé par spectroscopie RMN $^{31}P\{^1H\}$, il est possible que le cycle catalytique en opération pour notre système ne passe pas par un intermédiaire de Ni^0. Aussi, comme il fut démontré que le complexe $(PC_{sp3}P^{i\text{-}Pr})NiBr$ réagit avec MeMgX pour générer le complexe $(PC_{sp3}P^{i\text{-}Pr})NiMe$ et que ce dernier réagit avec PhCl pour générer le complexe $(PC_{sp3}P^{i\text{-}Pr})NiCl$, il est tentant de proposer que le cycle catalytique pourrait être celui présenté à la Figure 6.6.

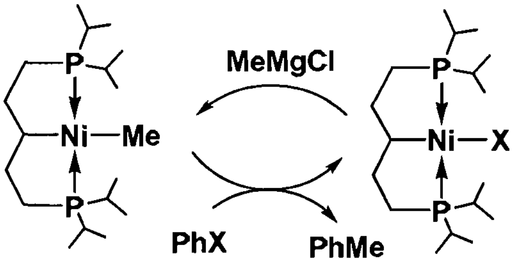

Figure 6.6. Mécanisme plausible pour la réaction de couplage effectuée.

Il est aussi important de noter que de petites quantités de produit d'homo-couplage (biphényle) ont été observées pour certaines des réactions effectuées, ce qui est généralement dû à un processus de transfert d'électron.[5] Il serait donc très intéressant de poursuivre ces études pour tenter de démontrer le ou les mécanismes en action pour cette réaction de Kumada-Corriu impliquant les complexes de type « pincer ».

Hydroamination de l'acrylonitrile

Plusieurs des espèces cationiques préparées se sont avérées de bons catalyseurs pour la réaction d'hydroamination de l'acrylonitrile avec aniline. Les complexes qui ont été comparés sont ceux comportant les ligands $PC_{sp3}P^{i\text{-}Pr}$, $PC_{sp3}P^{t\text{-}Bu}$, $PC_{sp2}P^{i\text{-}Pr}$, $POC_{sp2}OP^{i\text{-}Pr}$ et $POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$, stabilisés par une molécule de $NCCH_3$ et ayant comme contre-ion BPh_4^- (Figure 6.7).

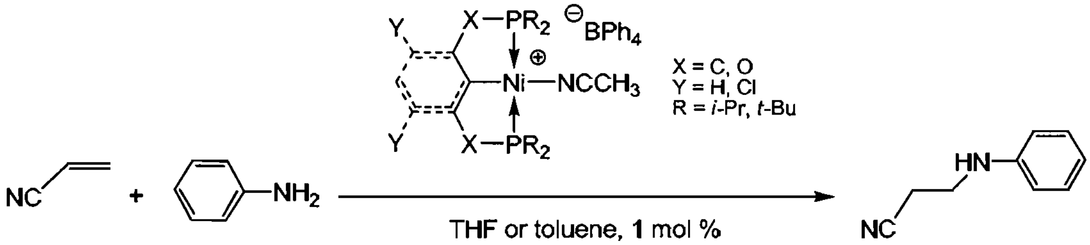

Figure 6.7. Comparaison de différents catalyseurs pour la réaction d'hydroamination.

Les résultats obtenus ont démontré qu'un ratio amine:oléfine 2:1 donne généralement de meilleurs résultats qu'un ratio 1:1 ou encore 1:2. Ils ont aussi démontré que les differences structurales entre les complexes ont un certain impact sur la catalyse lorsque les réactions sont effectuées dans le THF mais qu'elles n'ont presque pas d'influence lorsque le solvent utilisé est le toluène; de loin, le meilleur catalyseur pour cette réaction s'est avéré être celui comportant le ligand $POC_{sp2}OP^{i\text{-}Pr}$ lorsque les réactions furent effectuées dans THF (> 95%) mais lorsque menées dans le toluène, presque tous les catalyseurs ont donné lieu à un rendement de 70-74% sauf dans le cas de celui comportant le ligand ayant des groupements *t*-Bu sur les atomes de phosphore (25%), probablement à cause de l'important encombrement stérique de ces substituants compararivement aux groupements *i*-Pr.

Des observations captant notre attention ont été effectuées lors du suivi d'une réaction catalytique effectuée à partir de 2 mol % du complexe $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH{=}CH_2)][BPh_4]$ et d'un ratio amine:oléfine 2:1 par spectroscopie RMN $^{31}P\{^1H\}$. Il fut établi que, durant la catalyse, deux espèces autres que le catalyseur sont présentes. Un de ces deux complexes fut identifié comme étant le produit d'addition de l'aniline sur l'unité oléfinique du catalyseur. Ce résultat nous a conduits à l'hypothèse que les complexes « pincer » préparés pourraient agir en tant que simples acides de Lewis (Figure 6.8). Des études plus complètes telle l'identification de la seconde espèce présente durant la catalyse pourraient permettre de confirmer ou bien d'infirmer cette hypothèse.

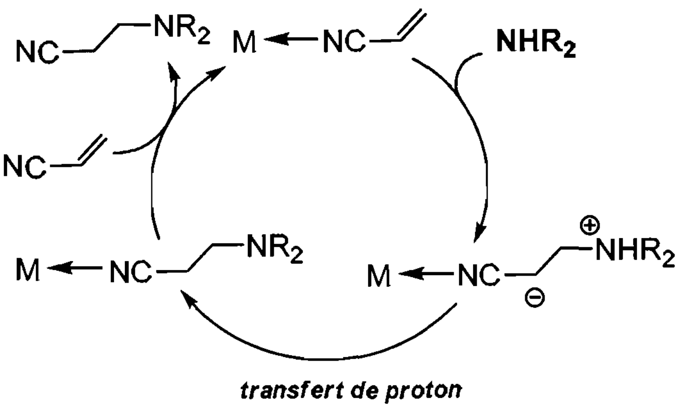

Figure 6.8. Cycle catalytique où le complexe agirait en tant que simple acide de Lewis.

Non seulement il serait très intéressant de poursuivre les études mécanistiques de cette réaction d'hydroamination mais aussi d'utiliser d'autres amines et d'autres oléfines pour vraiment évaluer son potentiel. L'usage d'autres nucléophiles serait aussi à envisager.

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Annexe

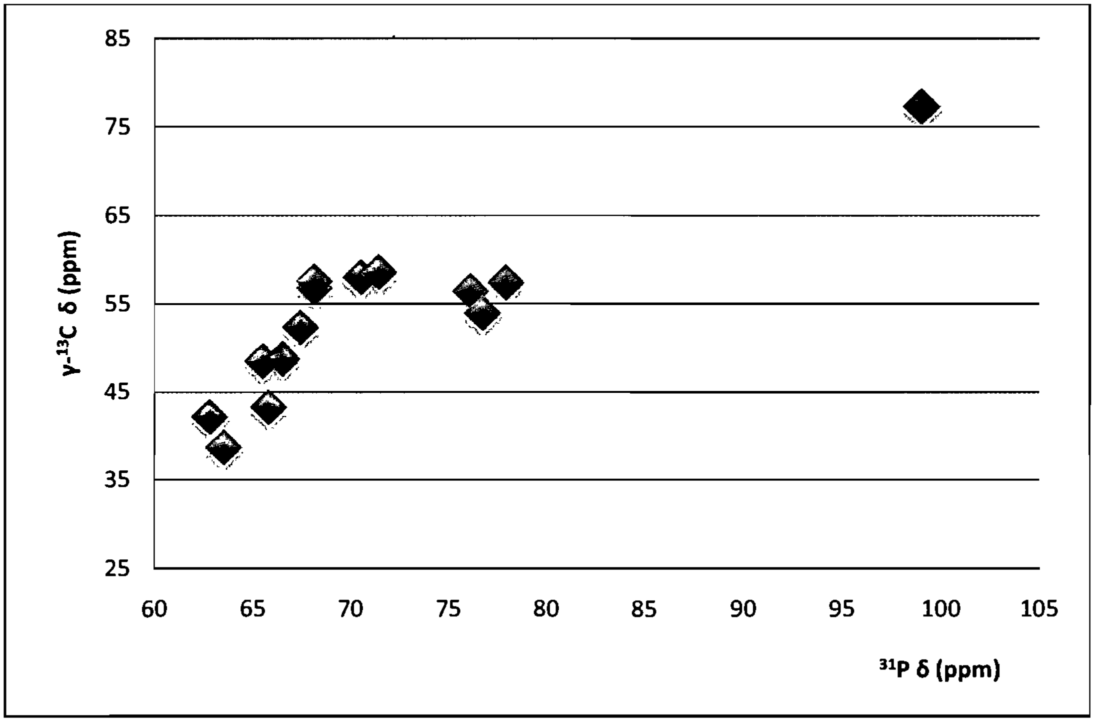
Annexe 1 : Informations supplémentaires des chapitres II, III, IV et V

	Composés		N° CCDC
Chapitre II	$\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiCl}$	**1a**	283327
	$\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiBr}$	**1b**	283328
	$\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiI}$	**1c**	283329
	$[\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(NCCH}_3)][\text{BPh}_4]$	**4**	283330
	$[\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(NCCHCH}_2)][\text{BPh}_4]$	**5**	284336
Chapitre III	$\{i\text{-Pr}_2\text{P(CH}_2)_5\text{P}(i\text{-Pr})_2\}_2\text{Ni}_2\text{Cl}_4$	**1**	631839
	$\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiBr}$	**2**	631840
	$\{(i\text{-Pr}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\}\text{NiBr}$	**3**	671730
	$\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiMe}$	**4**	631841
	$\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiC}\equiv\text{CMe}$	**5**	631843
	$\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiPh}$	**6**	631842
	$\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiBr}_2$	**9a**	689350
Chapitre IV	$[\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(OH}_2)][\text{BF}_4]$	**2**	631844
	$[\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(NCCH}_3)][\text{BF}_4]$	**3**	692059
	$[\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni}(i\text{-PrNH}_2)][\text{BF}_4]$	**4**	692060
	$[\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(CO)}][\text{BF}_4]$	**5**	692061
	$\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{NiOH}$	**6**	631845
Chapitre V	$[\{(i\text{-Pr}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(NCCH}_3)][\text{BPh}_4]$	**1**	691621
	$[\{(i\text{-Pr}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\}\text{Ni(NCCH}_3)][\text{BPh}_4]$	**2**	691622
	$[\{(i\text{-Pr}_2\text{PO})_2\text{C}_6\text{H}_3\}\text{Ni(NCCH}_3)][\text{BPh}_4]$	**3**	691623
	$\{(i\text{-Pr}_2\text{PO})_2\text{C}_6\text{HCl}_2\}\text{NiBr}$	**5**	691624
	$[\{(t\text{-Bu}_2\text{PCH}_2\text{CH}_2)_2\text{CH}\}\text{Ni(NC(CH}_2)_2\text{NHPh)}][\text{BPh}_4]$	**7**	691625

Les rapports cristallographiques et les fichiers cif des structures des composés parus dans les chapitres II, III, IV et V sont téléchargeables à partir du site Internet http://pubs.acs.org. Ces données ont été déposées au Cambridge Crystallographic Data Centre (CCDC) et sont également téléchargeables via le site internet de CCDC : www.ccdc.cam.ac.uk/data_request/cif, ou en envoyant un message électronique à data_request@ccdc.cam.ac.uk, ou par courrier, en contactant the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 IEZ, UK; fax : +44-1223 336033.

Annexe 2: Informations supplémentaires du chapitre IV

Correlation between the chemical shifts of the $^{31}P\{^1H\}$ and the γ-$^{13}C\{^1H\}$ NMR resonances for some $(PC_{sp3}P^{i\text{-}Pr})NiX$ and $[(PC_{sp3}P^{i\text{-}Pr})NiL][BF_4]$ complexes



ligand X or L	$^{31}P\{^1H\}$ NMR chemical shift (ppm)	γ-$^{13}C\{^1H\}$ NMR chemical shift (ppm)	solvent
OH (complex **6**)	62.8	42.15	benzene-d_6
BF_4 (complex **1**)	63.5	38.68	benzene-d6
NH_2(*i*-Pr) (complex **4**)	65.5	48.47	benzene-d6
H_2O (complex **2**)	65.8	43.26	benzene-d6
Cl	66.5	48.74	benzene-d6
Br	67.4	52.30	benzene-d6
Ph	68.1	56.81	benzene-d6
Bu	68.1	57.50	benzene-d6
I	70.5	57.97	benzene-d6
Me	71.4	58.56	benzene-d6
CCMe	76.1	56.38	benzene-d6
$NCCH_3$ (complex **3**)	76.7	53.92	benzene-d6
CCPh	77.9	57.35	chlorform-d
CO (complex **5**)	99.0	77.26	dichloromethane-d_2