Université de Montréal

Preparation and Characterization of Nickel Imidato Complexes and Study of Their Reductive Elimination Reactions

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Presenté par

Ying Cao

A été évalué par un jury composé des personnes suivantes:

André L. Beauchamp :Président rapporteur

Davit Zargarian :Directeur de recherches

François Brisse :Membre du jury

Mémoire accepté le:……………………………

Sommaire

Afin d'étudier les facteurs qui influencent et différencient les réactions de couplage entre les halogénures d'aryle et les imidates, nous avons préparé une série de complexes de nickel de type $L_2Ni(R)(phthal)$ (L= PMe_3, PPh_3, PCy_3, PBu_3, ½ DPPE; R=Ph, Ph-(C=O), Me, H). Ces nouveaux composés ont tous été caractérisés par spectroscopie RMN ainsi que par diffraction des rayons X pour les complexes suivants: $(PMe_3)_2Ni(Ph)(phthal)$ **7a**, (DPPE)Ni(Ph)(phthal) **9a**, (DPPE)Ni(3-Me-Ph)(phthal) **9b** et $(PCy_3)_2Ni(H)(phthal)$ **13**.

La potentielle élimination réductrice du composé $L_2Ni(R)(phthal)$ a été étudiée dans l'espoir de développer une nouvelle façon de former le lien carbone-azote (R-phthal). Pour les complexes (DPPE)Ni(Ar)(phthal), **9**, (Ar= Ph, **9a**; 3-Me-Ph, **9b**; 2,5,-Me_2-Ph, **9c**), $(PPh_3)_2Ni(Me)(phthal)$, **11**, et $(PPh_3)_2Ni(Ar)(phthal)$, **22**, (Ar= Ph, **22a**; 3-Ph-Me, **22b**), l'élimination réductrice n'a pas été observée et ce, même en présence d'un excès de PR_3 à haute température. Les complexes $(PMe_3)_2Ni(Ar)(phthal)$, **7**, (Ar= Ph, **7a**; 3-Me-Ph, **7b**; 2,5,-Me_2-Ph, **7c**), $(PMe_3)_2Ni(Me)(phthal)$, **10**, et $(PMe_3)_2Ni(CH_2SiMe_3)(phthal)$, **14**, ont quant à eux permis, en présence de PR_3 à la température ambiante, la formation de l'espèce Ni(0). Cependant, la formation du lien C-N n'a pas été observée. Une discussion est présentée sur la conséquence de ces résultats, qui sont, entre autres, comparés au système analogue $L_2Pd(R)(NR_2)$.

Abstract

In order to study the factors that influence the coupling reaction between aryl halides and imidates, we have prepared a series of nickel imidato complexes of the type $L_2Ni(R)(phthal)$ (L= PMe_3, PPh_3, PCy_3, PBu_3, ½ DPPE; R=Ph, Ph-(C=O), Me, H). The new compounds have been characterized by NMR spectroscopy and, in the case of $(PMe_3)_2Ni(Ph)(phthal)$ **7a**, (DPPE)Ni(Ph)(phthal) **9a**, (DPPE)Ni(3-Me-Ph)(phthal) **9b** and $(PCy_3)_2Ni(H)(phthal)$ **13,** by X-ray diffraction studies.

The reductive elimination from the Ni(II) complexes $L_2Ni(R)(phthal)$ has been studied in the hope of developing a method for forming C-N bonds. The complexes (DPPE)Ni(Ar)(phthal), **9**, (Ar= Ph, **9a**; 3-Me-Ph, **9b**; 2,5,-Me_2-Ph, **9c**), $(PPh_3)_2Ni(Me)(phthal)$, **11**, and $(PPh_3)_2Ni(Ar)(phthal)$, **22**, (Ar= Ph, **22a**; 3-Ph-Me, **22b**) were found to be stable toward reductive elimination even at elevated temperatures and in the presence of excess PR_3. The complexes $(PMe_3)_2Ni(Ar)(phthal)$, **7**, (Ar= Ph, **7a**; 3-Me-Ph, **7b**; 2,5,-Me_2-Ph, **7c**), $(PMe_3)_2Ni(Me)(phthal)$, **10**, and $(PMe_3)_2Ni(CH_2SiMe_3)(phthal)$, **14**, did lead to the formation of Ni(0) species at room temperature in the presence of PR_3, but no C-N bond formation was observed in these reactions. The implication of these results has been discussed and compared to the reductive elimination in the analogous $L_2Pd(R)(NR_2)$ system.

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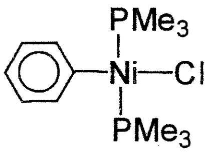
NMR:	nuclear magnetic resonance
δ:	chemical shift in ppm
ppm:	parts per million
Hz:	hertz
J:	coupling constant in Hz
s:	singlet
d:	doublet
t:	triplet
TLC:	thin layer chromotography
IR:	infrared
Eq:	equation
equiv:	equivalent
mmol:	millimole
mL:	milliliter
kcal:	kilocalorie
THF:	tetrahydrofuran
Et_2O:	ether
M:	metal atom
L:	neutral ligand, donor of one pair of electrons
R:	organic group (alkyl, acyl, etc.)

Me:	methyl
Bu:	n-butyl
Ph:	phenyl, $C_6H_5^-$
Ar:	aryl group
PMe_3:	trimethylphosphine
PPh_3:	triphenylphosphine
PCy_3:	tricyclohexylphosphine
DPPE:	1,2-bis(diphenylphosphino)ethane
DMPE:	1,2-bis(dimethylphosphino)ethane
DPPP:	1,2-bis(diphenylphosphino)propane
DPPF:	1,1'-bis(diphenylphosphino)ferrocene
BINAP:	2,2'-bis(diphenylphophino)-1,1'-binaphtyl
COD:	1,5-cyclooctadiene
dba:	dibenzylidene acetone
Mes:	mesityl, 2,4,6-$Me_3C_6H_2$
Phthal:	phthalimidate group (deprotonated phthalimide)
acac:	acetylacetonate (deprotonated 2,4-pentanedione)

Complexes synthesized

Intermediate complexes

1a



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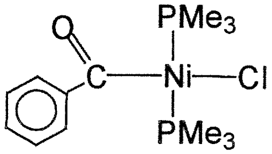

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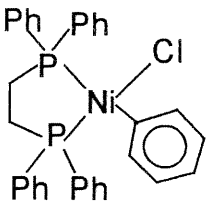

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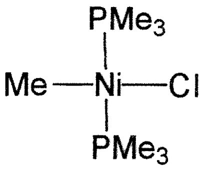

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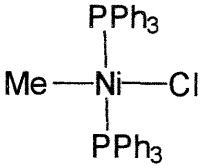

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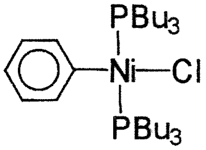
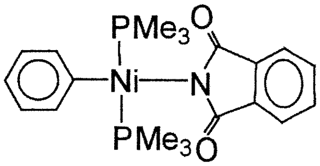


Phthalimidato derivatives

7a



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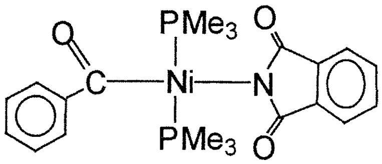
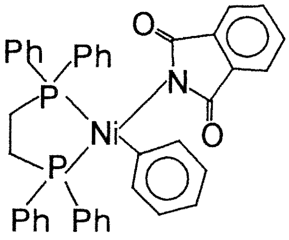


9a



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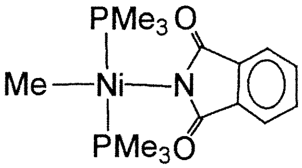

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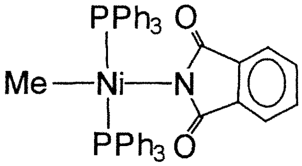

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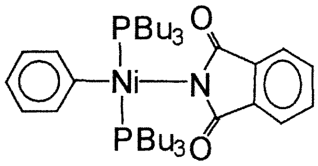

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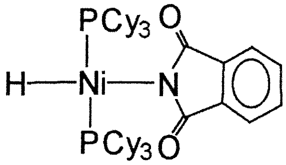
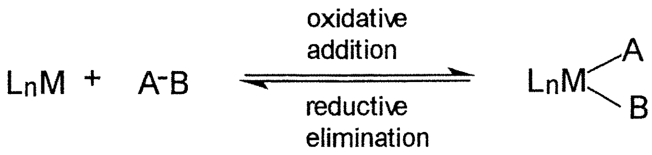


CHAPTER 1

Introduction

Transition metal-mediated reactions that form and cleave various bonds in organic molecules are the foundation of homogeneous catalysis. Such bond cleavage and formation reactions often occur by oxidative addition and reductive elimination steps, respectively.[1] As shown in Equation 1, these two reactions are essentially the same processes in opposite directions: oxidative addition increases the oxidation state of the metal by two (i. e., decreases the d-electron count by two), while reductive elimination causes the opposite two-electron changes. Thermodynamic factors dictate whether a complex might ultimately undergo reductive elimination (Eq. 1, right to left) or if organic species oxidatively add to the metal fragment (Eq. 1, left to right).

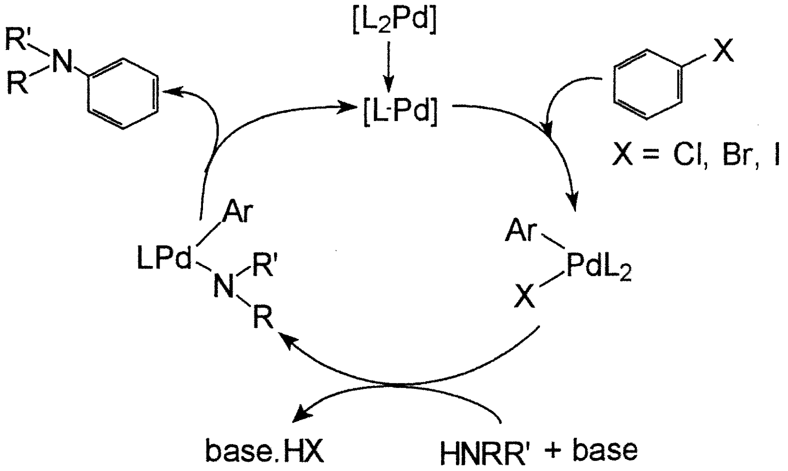


(1)

The chemistry of late transition metal amide complexes has been the subject of extensive research in recent years.[2,3] The main motivation for the study of these compounds is their potential to facilitate C-N bond formation through catalytic[4] or stoichiometric[5] reactions. The relatively slow development of the chemistry of late-transition-metal-amide complexes has been attributed to the inability of the electronically saturated, soft late metal centers to accommodate π-donation from the lone-pair electrons of the hard amide moiety.[6] The absence of this interaction should result in a relatively weak M-N bond, thereby making it reactive towards unsaturated organic molecules. Although the synthesis and characterization of amide complexes involving late transition metals is established,[7,8] the factors that influence the stability and reactivity of the M-NR_2 bonds are still poorly understood. One example of a fundamental transformation that could be of vital importance to the development of metal-amide complexes as catalysts or stoichiometric reagents is the reductive elimination from complexes containing the MR(NR'_2) group to generate a product having a C-N bond.

Over the years, a number of useful methods for aryl C-N bond formation have been reported.[9] Aromatic amines play a key role in pharmaceuticals,[10a] agrochemicals[10b], photography[10c], xerography,[10d] pigments[10e] and electronics materials[10f]. All these methods have different drawbacks, some requiring very harsh reaction conditions, while others have a lack of generality and dependability. Also, many of these methods are not cost effective. Only in the last several years have a number of palladium and nickel metal complexes been discovered that catalyze the synthesis of arylamines from the reaction of aryl halides with primary or secondary amines. A catalytic cycle for these reactions, which is supported by detailed mechanistic studies,[11] is shown in Scheme 1.

Scheme 1

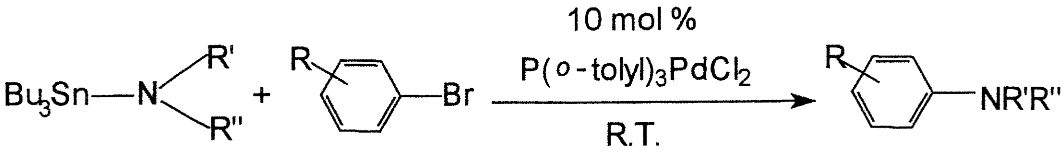


Given the importance of catalytic C-N bond formations to our studies, the following sections will give a brief summary of the recent developments in this area of study. This summary places a particular emphasis on the mechanistic findings which have helped to improve our understanding of the factors influencing these reactions.

1.1 C-N bond formation catalyzed by palladium amide complexes

1.1.1 Tin-promoted aminations

In 1983, Kosugi et al. reported that palladium complexes catalyzed the formation of arylamines from amides and aryl halides[12]. These authors showed that the reaction of tri-*n*-butyltin diethylamide $Bu_3Sn\text{-}NEt_2$ with aryl bromides catalyzed by $PdCl_2(o\text{-}tolyl_3P)_2$ results in the formation of N,N-diethylanilines as shown in Equation 2. However, this reaction is only limited to dialkylamides and electron-neutral aryl halides, such that aryl halides with nitro, acyl, methoxy, and dimethylamino substituents gave poor yields. Table 1 shows that: a) the best catalyst was $PdCl_2(o\text{-}tolyl_3P)_2$, b) chlorobenzene and iodobenzene did not react, c) bromobenzene, *m*- and *p*-methylbromobenzene, and *p*-chlorobromobenzene were better substrates, while the reaction with bromobenzene having other substituents gave rather poor yields.



(2)

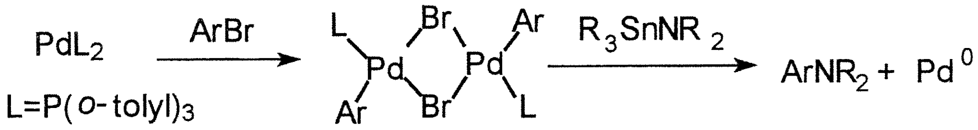
Table 1. Pd-Catalyzed Aromatic Amination by N,N-diethylamino-tributyltin[12]

Aryl Halide R-	-X	Catalyst	Yield of $RC_6H_4NEt_2$ (%)[a)]
H-	-Br	None	(0)
H-	-Br	$Pd(Ph_3P)_4$	(5)
H-	-Br	$PdCl_2(Ph_3P)_2$	(7)
H-	-Br	$PdCl_2(o\text{-tolyl}_3P)_2$	(87), 81, (35)[b)]
H-	-Br	$PdCl_2(o\text{-}ClC_6H_4)_3P)_2$	(21)
H-	-I	$PdCl_2(o\text{-tolyl}_3P)_2$	(0)
H-	-Cl	"	(0)
o-Me-	-Br	"	33
m-Me-	-Br	"	61
p-Me-	-Br	"	(80), 79
p-MeO-	-Br	"	(44), 39
p-Cl-	-Br	"	55
p-Br-	-Br	"	(34), 30
p-MeCO-	-Br	"	16
p-O_2N-	-Br	"	24
p-Me_2N-	-Br	"	36

a) Isolated yields based on aryl bromide; GLC yields in parentheses.

b) Upon addition of 10 mol% of *p*-dinitrobenzene.

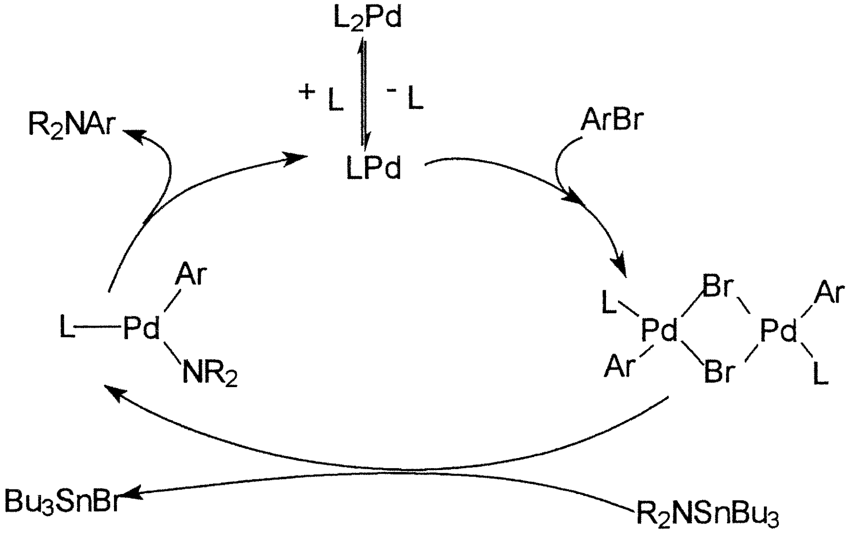
In 1994, John Hartwig's group reported that the palladium complex (o-tolyl$_3$P)PdX$_2$ (X= Cl, Br) catalyzes the hetero coupling of Bu_3SnNMe_2 and bromobenzene or *p*-alkylphenylbromides at 90-100 °C to form N, N,-dimethylanilines in 75-85% yield.[13] They showed that the active catalyst was [Pd{P(*o*-tolyl$_3$}$_2$] and that the oxidative addition of the aryl halides gave the dimeric aryl halide complexes shown in equation 3.



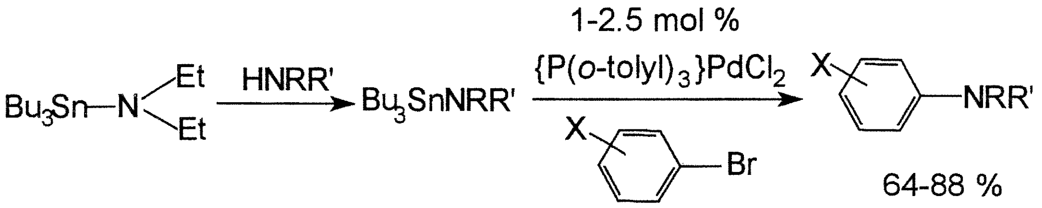
(3)

The mechanism proposed by Hartwig for this reaction is shown in Scheme 2, these dimers are reacted with tin amides to form arylamines.

Scheme 2



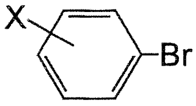
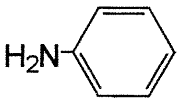
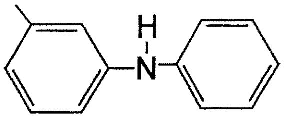
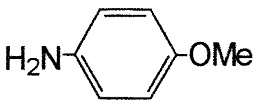
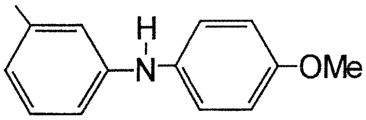
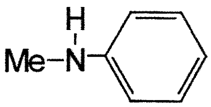
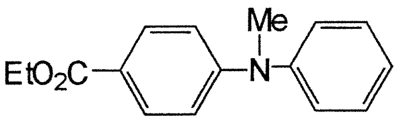
Concurrently with Hartwig's report, Buchwald and co-workers showed that when the tin amide was generated in situ, aryl halides bearing alkoxycarbonyl, amino, and alkoxo groups could be used for the formation of a wide range of arylamines (Eq. 4).[14] However, reactions that proceeded with 80% or greater yields were still limited to tin amides derived from secondary amines, as shown in Table 2. The lower reactivity of aminostannanes derived from aniline can be ascribed to their decreased nucleophilicity.



(4)

$X = CO_2R'', NR''_2, OR'', R''$

Table 2. Pd-catalyzed Aromatic Aminations with in-situ Generated Aminostannanes[14]

 X=	Amine	Aryl Amine	Yield (%)
m-Me			66
m-Me			64
p-CO_2Et			83

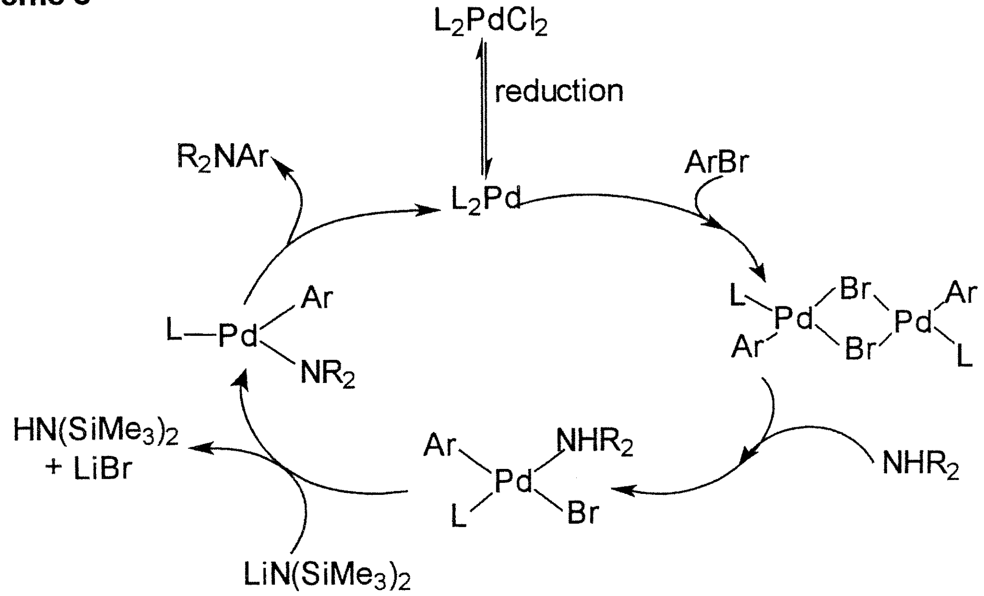
1.1.2 Tin-free aminations

Tin amides provided a convenient source for NR_2 groups in the palladium catalyzed C-N bond formation reactions. However, the toxicity of tin amides and the disposal problem with large scale reactions severely limited the application of this chemistry. These limitations drove Hartwig and Buchwald groups to develope a catalytic synthesis of arylamines in the absence of tin reagents. Thus, instead of using preformed tin reagents, or generating them in-situ, Hartwig et al. reported that the amination reaction can be carried out by reacting an aryl halide with amine and an amide base (Eq. 5).[15]

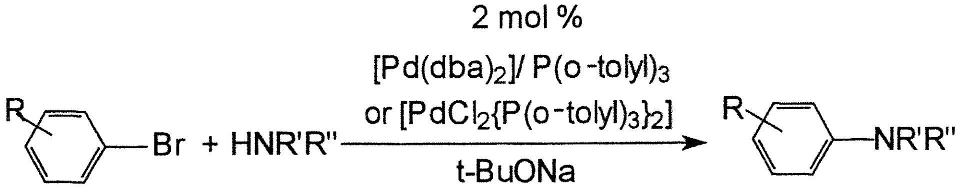
$$\mathrm{ArBr} + \mathrm{HNRR'} \xrightarrow[\substack{\mathrm{LiN(SiMe_3)_2} \\ \mathrm{L = P(}o\text{-}\mathrm{tolyl)_3}}]{\substack{5\ \mathrm{mol}\ \% \\ \mathrm{L_2Pd\ or\ L_2PdCl_2}}} \underset{70\text{-}90\%}{\mathrm{ArNRR'}} \qquad (5)$$

This tin-free, Pd-catalyzed aryl amination reaction most likely begins by the addition of aryl halide to tri-(*o*-tolyl)phosphine palladium(0) to give the dimeric aryl bromide complexes as shown in Scheme 3. These compounds are then cleaved in the presence of amine to form monomeric aryl halide complexes. The enhanced acidity of the amine, when coordinated to palladium, facilitates the deprotonation of the N-H bond with $LiN(SiMe_3)_2$. The resulting amido complexes undergo rapid reductive elimination of arylamine at room temperature to produce {tri-(o-tolyl)phosphine}$_2$Pd(0). The sequence of oxidative addition of aryl bromide to L_2Pd, coordination and deprotonation of secondary amine, and reductive elimination of tertiary arylamine provides an efficient catalytic route to arylamine in the absence of tin reagents. The catalytic cycle is believed to involve $L_2Pd(0)$ that is formed by reduction of L_2PdCl_2, and the reduction of Pd(II) to Pd(0) is clearly slower than the actual catalytic cycle.

Scheme 3



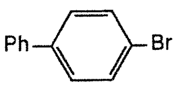
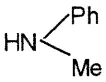
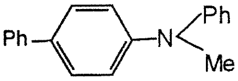
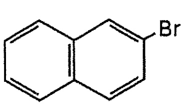
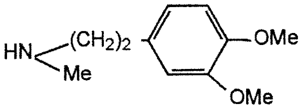
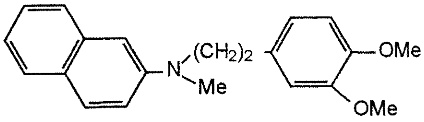
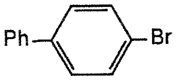
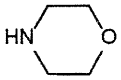
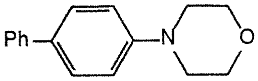
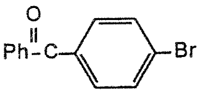
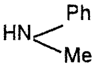
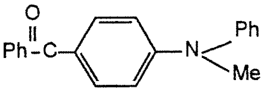
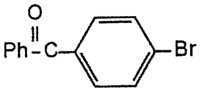
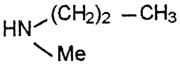
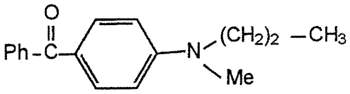
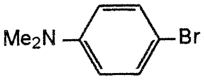
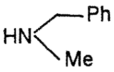
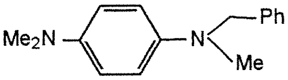
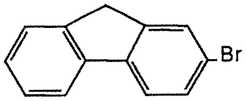
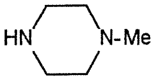
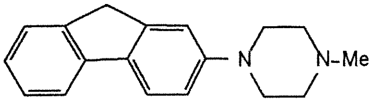
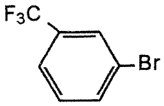
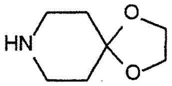
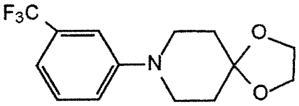
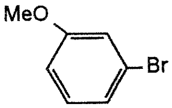
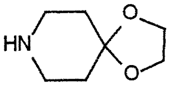
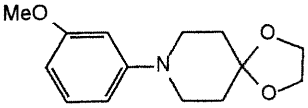
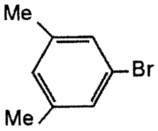
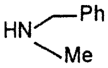
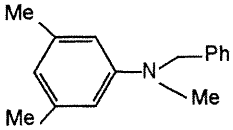
Buchwald et al reported similar results by using alkoxide bases (Eq. 6).[16] Using this approach, aryl bromides with both electron-withdrawing and electron-donating substituents react efficiently with both primary and secondary amines; thus, the Pd-catalyzed aryl amination reaction provides a general route to a variety of arylamines as illustrated in Table 3. This reaction is tolerant to aryl bromides containing acid-sensitive functional groups, but not to those containing base-sensitive functional groups.



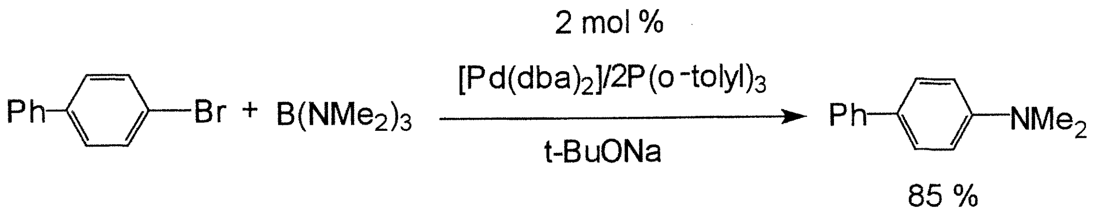
(6)

dba=dibenzylidene acetone

Table 3. Palladium-catalyzed reactions of arylbromides and amines[16]

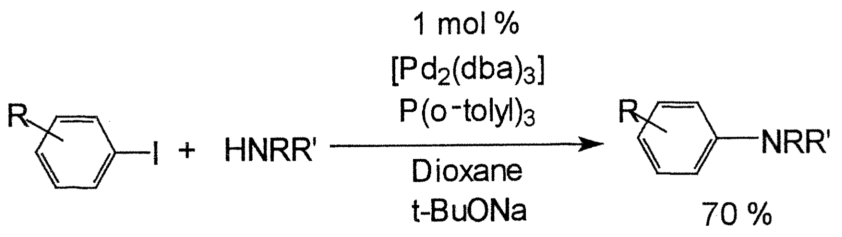
Entry	Aryl bromide	Amine	Arylamine	Yield (%)
1				88
2				78
3				86
4				89
5				72
6				71
7				79
8				67
9				81
10				84

This report also showed that $B(NMe_2)_3$ can serve as a precursor for the transfer of amines. For example, tris(dimethylamino)borane, $B(NMe_2)_3$, reacts with 4-bromobiphenyl in the presence of $[Pd(dba)_2]/2\ P(o\text{-tolyl})_3$ and sodium t-butoxide to afford the corresponding arylamine (Eq. 7).



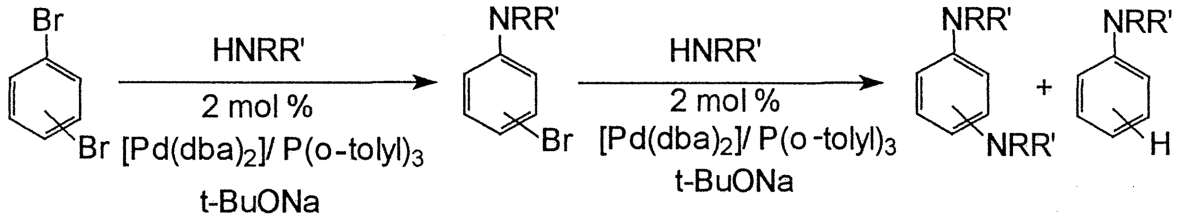
(7)

Complexes other than those containing $P(o\text{-}C_6H_4Me)_3$ ligands have now been shown to catalyze amination of aryl iodides in high yields (Eq. 8); running the reaction in dioxane was the key to the success of this reaction.[17] This method works with both electron-rich and electron-deficient aryl iodides. In contrast with results observed with aryl bromides, secondary amines are more efficient than primary amines and aniline.



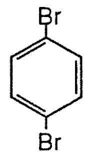
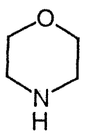
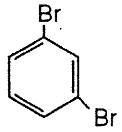
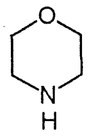
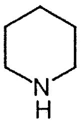
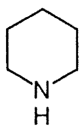
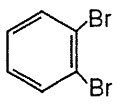
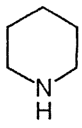
(8)

In 1999, palladium-catalyzed amination of aryl dibromides with secondary amines was reported (Eq. 9).[18] Table 4 shows the yields of the double amination reaction. The study of this reaction has shown that the formation of reductive dehalogenation products occurs according to two independent ways. The first one proceeds via the well-known β-hydride elimination from amido-coordinated palladium complexes. The second one involves the formation of hydrido palladium complexes from amino-coordinated derivatives. This report also gave the results of a detailed examination of the origins of the reductive dehalogenation pathway which limits the usefulness of the catalytic amination of aryl halides, particularly in the case of aryl dihalides.

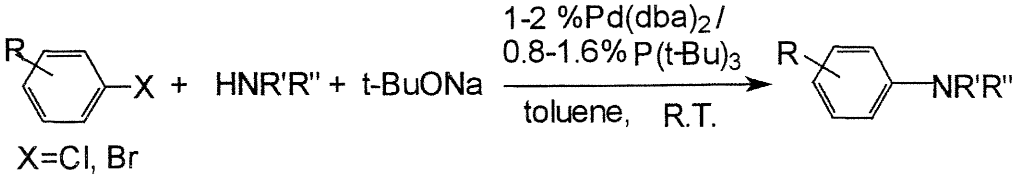


(9)

Table 4. Double amination of *m*- and *p*-dibromobenzenes with secondary amines[18]

	Aryl dibromide	Amine	Yield (%) of aryldiamine		Aryl dibromide	Amine	Yield (%) of aryldiamine
1			76	4			82
2	''		63	5	''		65
3	''	HNEt$_2$	45	6	''	HNEt$_2$	58
				7			-

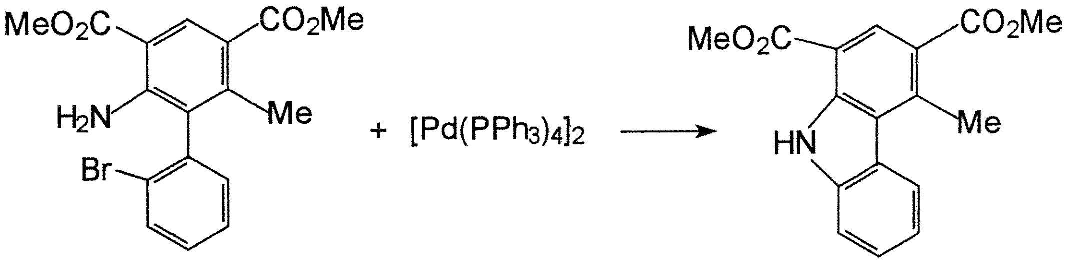
Hartwig et al have studied the room temperature palladium-catalyzed amination of aryl bromides and chlorides, thereby extending the scope of aromatic C-N bond formation with the commercially available ligands which are shown in Equation 10.[19] They showed that conditions can be found for the amination of aryl bromides with arylamines and with secondary alkylamines at room temperature using commercially available $P(t\text{-}Bu)_3$. Moreover, this ligand allows for similar aminations to be conducted with unactivated aryl chlorides at 70°C and in one case at room temperature.



(10)

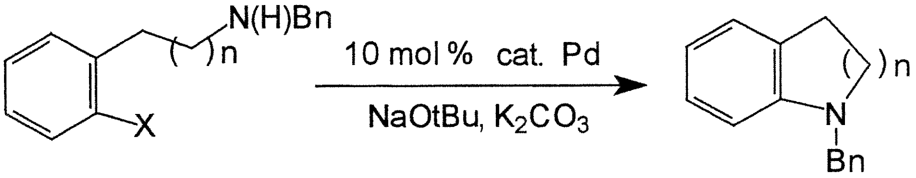
1.1.3 Intramolecular aminations

N-heterocycles are very important organic building blocks for the synthesis of natural products. Boger has shown that N-heterocycles can be formed by palladium-catalyzed intramolecular aryl halide aminations.[20] These reactions were carried out with stoichiometric amounts of $[Pd(PPh_3)_4]$ as shown in Equation 11.



(11)

By applying the base-mediated palladium-catalyzed amination to this type of cyclization, Buchwald's group has developed a method for the intramolecular amination of aryl halides (Eq. 12).[16,21] A combination of NaO*t*Bu and K_2CO_3 bases was used. Although both aryl bromides and aryl iodides can be used for the intermolecular aryl halide amination, aryl iodides and $Pd(PPh_3)_4$ give the best results in the intramolecular amination. Screening of a variety of combinations of phosphine ligands and Pd precursors showed that chelating ligands such as 1,1'-bis-(diphenylphosphino)ferrocene (DPPF) or $Ph_2P(CH_2)_nPPh_2$ (n= 2-4) gave good yields of cyclized product, but $Pd(PPh_3)_4$ was a better precatalyst.



(12)

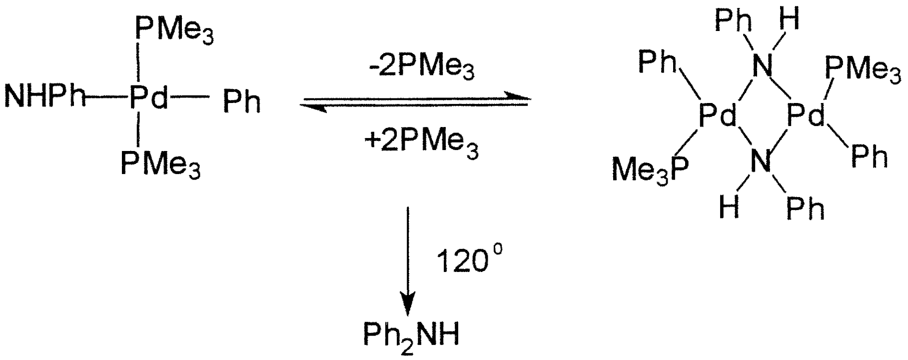
Cat Pd = $Pd(PPh_3)_4$ or $[PdCl_2P(o\text{-tolyl})_3]_2$
X = Br or I

n=1 87 %
n=2 72 %
n=3 61 %

1.1.4 Thermolysis of the amination reactions

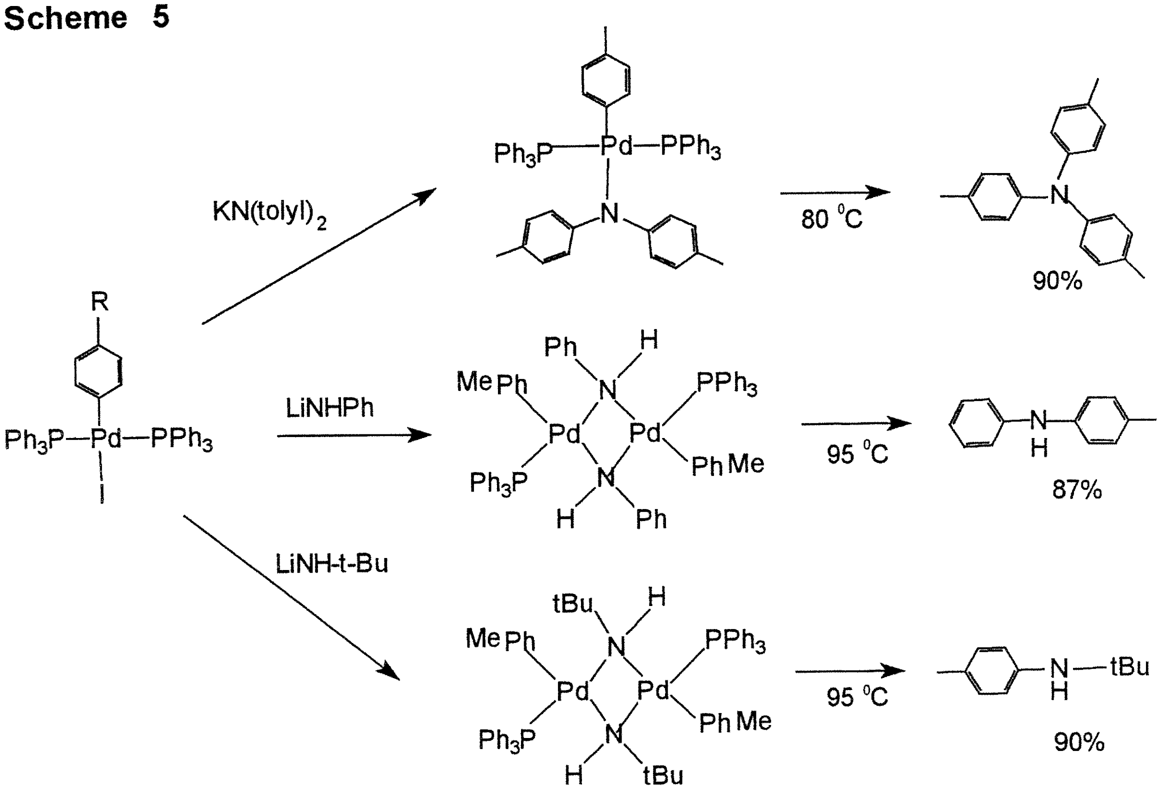
Boncella and co-workers have reported C-N bond forming reductive elimination of arylamines upon thermolysis of the Pd(II) amide complexes *trans*-$(PMe_3)_2Pd(R')(NRPh)$ (R = H, Me; R' = Ph, Me) which dimerized upon thermolysis.[22] It is known that late transition-metal amide complexes tend to dimerize due to the coordination of the lone pair electrons on the nitrogen atom of amides to the second metal. Prolonged heating of the dimers results in C-N bond formation via reductive elimination as shown in Scheme 4.

Scheme 4



By using the transmetallation of metal amides, Hartwig's group has isolated several stable palladium amido aryl complexes.[23,24] The syntheses and reactivity of both monomeric and dimeric amide complexes are shown in Scheme 5. Upon thermolysis and in the presence of PPh_3 serving as a trapping agent, both monomeric and dimeric palladium amide complexes underwent reductive elimination of arylamine in high yields. Mechanistic studies on the reductive elimination reactions of the monomeric PPh_3-ligated amido complexes indicated the presence of two competing pathways for the formation of amines.[14] At low triphenylphosphine [PPh_3], reductive elimination occurs via prior phosphine dissocation to form a three-coordinate intermediate; as [PPh_3] is increased, reductive elimination from a four-coordinate complex becomes dominant. In the case of the dimeric palladium amide complexes, studies indicated that the reductive elimination of amine proceeds via a dimer dissociation to generate a three-coordinate intermediate analogous to those formed by the PPh_3-ligated monomeric amido complexes. The reductive elimination reactions are accelerated by electron-withdrawing groups on the Pd-bound aryl group and by electron-donating groups on the amide ligands.

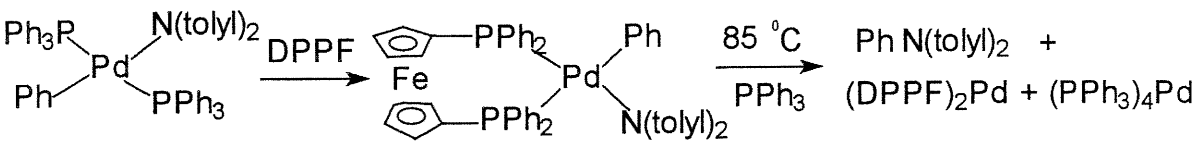
Scheme 5



1.1.5 Chelating ligands in amination reactions

The catalytic amination of aryl halides using palladium complexes with chelating ligands has been developed since 1994. Many of the catalysts used for intermolecular aminations contain tri-*o*-tolylphosphine as the auxiliary ligand and the importance of this ligand was attributed to its steric bulk which is believed to hinder the formation of the relatively inactive bis(phosphine) palladium intermediates.[13] The catalysts bearing P(o-tol)$_3$ give high yields with secondary amines and aryl bromides, but poor results are obtained for the cross coupling of primary amines with aryl bromides due to β-hydride elimination from Pd-amide intermediates.[16] The observations that i) reductive elimination of arylamine can occur from a four-coordinate palladium amido complex[23] and ii) the use of chelating bis(phosphine) ligands inhibits β-hydride elimination, prompted both Hartwig's[25] and Buchwald's[26] groups to seek the synthesis of palladium amido complexes possessing cis-chelating phosphine ligands. Such cis-chelated complexes would allow the C-N bond forming reductive elimination in the absence of competing processes such as phosphine dissociation and cis/trans isomerization.

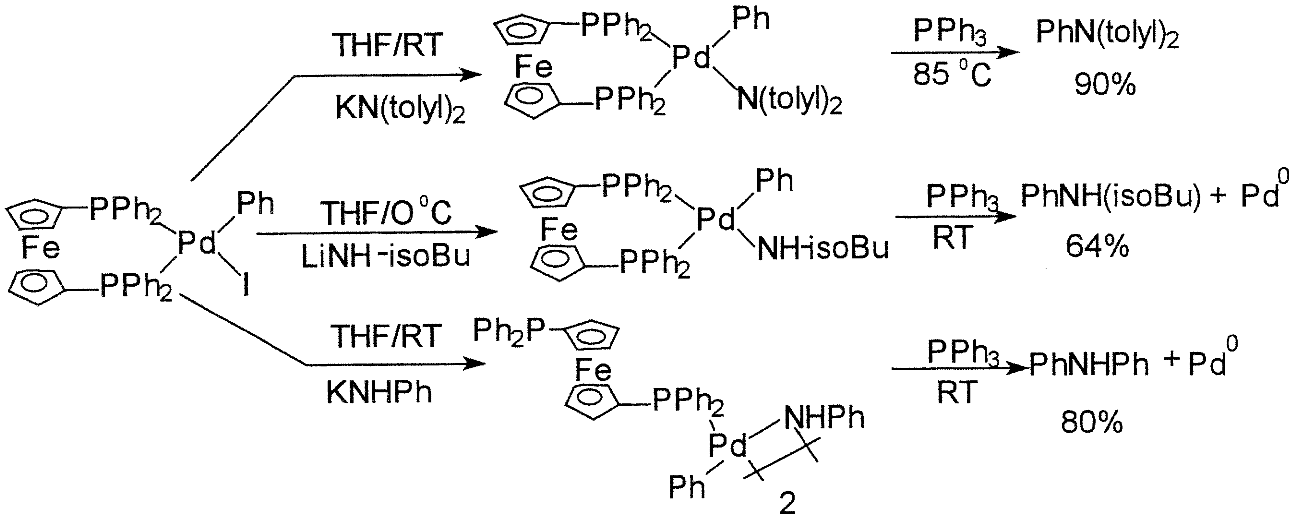
Hartwig's group found two routes for the isolation of amido complexes containing the DPPF ligand [DPPF=1,1'–bis(diphenylphosphino)ferrocene]. As shown in (Eq. 13), addition of DPPF to $(PPh_3)_2Pd(Ph)[N(tolyl)_2]$ generated $(DPPF)Pd(Ph)[N(tolyl)_2]$ in 54% yield, and this complex underwent reductive elimination of the amine when warmed to 85°C in the presence of free PPh_3.[25]



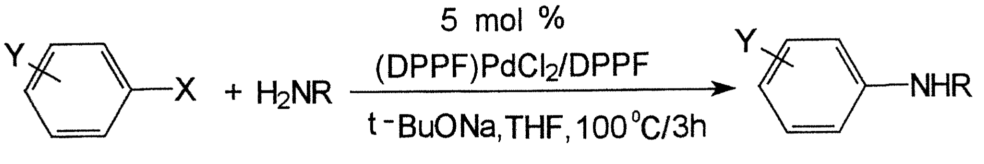
(13)

Hartwig's group has also made chelating bisphospine palladium amide complexes bearing different amido ligands by the direct amination of the Pd-I bond, as shown in Scheme 6. Both monomeric and dimeric palladium amide complexes have been synthesized.

Scheme 6



The observation of these facile reductive elimination reactions led Hartwig's group to test DPPF–ligated palladium complexes as catalysts for the formation of aromatic amines. Reactions of aryl bromides and iodides with both aryl and alkyl primary amines catalyzed by 5 mol% (DPPF)PdCl$_2$ provided a general route to a variety of aryl amines in high yield as shown in Equation 14. Aryl halides bearing electron donating or electron withdrawing and hindered or unhindered groups reacted effectively with anilines to form aryl amines in high yields.

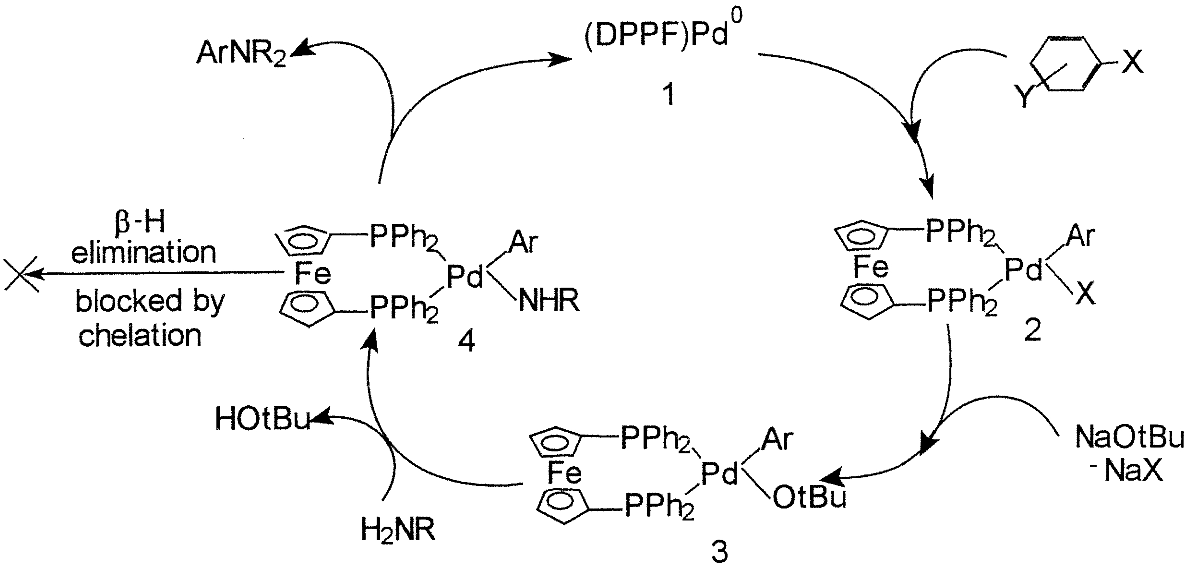
 (14)

X = Br, I
Y = *o*-, *p*-OMe, Me, Ph, CN, C(O)Ph, C(O)NEt$_2$
R = aryl, alkyl

60-92 %

Scheme 7 shows a mechanism for the amination of aryl halides catalyzed by DPPF-palladium complexes.[23] The reductive elimination proceeds directly from the 16-electron, four-coordinate complex 4, in contrast to the reductive elimination from the mono-phosphine, 14-electron, three-coordinate amido complex containing the P(*o*-tolyl)$_3$ ligand. The selectivity for the reductive elimination for the DPPF-palladium complexes is better than that with P(o-$C_6H_4Me)_3$ palladium complexes because the chelating ligands block phosphine dissociation and hence block a pathway for β-hydrogen elimination from 14-electron, three-coordinate species.

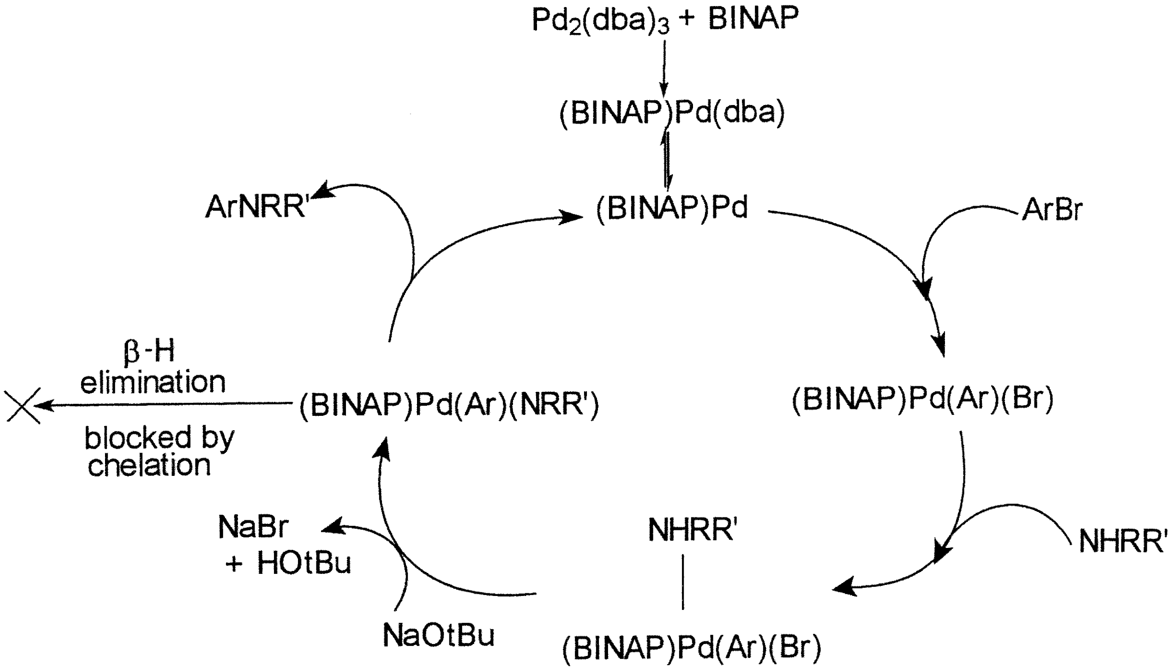
Scheme 7



Buchwald's group has reported the amination reaction with palladium complexes containing BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) ligand as catalysts.[26] The combination of $Pd_2(dba)_3$ and BINAP in the presence of NaO*t*Bu constitutes a superior catalyst system for the formation of amination by the reaction between primary amines and aryl bromide (Eq. 15). The use of BINAP as the ligand for the amination reaction gives much better yields than when P(*o*-tolyl)$_3$ is used as the ligand.

$$\mathrm{ArBr} + \mathrm{HNRR'} \xrightarrow[\substack{\text{NaOtBu} \\ \text{toluene, } 80\ ^{\circ}\text{C}}]{\substack{0.5\text{ mol \%} \\ \text{cat. } \mathrm{Pd_2(dba)_3/BINAP}}} \underset{88\ \%}{\mathrm{ArN(R)R'}} \tag{15}$$

Scheme 8

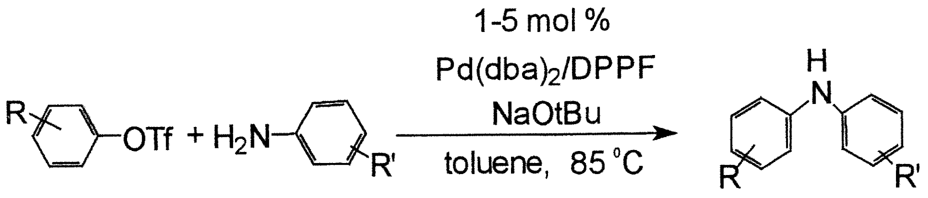


Scheme 8 shows a mechanism for the amination of aryl bromide catalyzed by the BINAP-palladium complex.[26] This catalytic cycle is similar to what Hartwig proposed for the DPPF-palladium catalyzed amination reaction. β-Hydrogen elimination is presumably inhibited due to the inaccessibility of a three-coordinate, 14-electron mono-phosphine intermediate. The difference between the two proposed mechanisms is that Buchwald has proposed that the coordination of the amine to (BINAP)Pd(Ar)(Br) gives a pentacoordinate (BINAP)Pd(Ar)(Br)(NHRR'), followed by the deprotonation of the coordinated amine (by NaO*t*Bu) which gives (BINAP)Pd(Ar)(NRR'). According to Hartwig's proposal, NaO*t*Bu reacts with the Pd-X bond first (X=Br, I) and then exchange of the base NaO*t*Bu with H_2NR forms (DPPF)Pd(Ar)(NHR). Both mechanisms proposed reductive elimination directly from the four-coordinate 16-electron complexes.

1.1.6 Aryl triflate aminations

Palladium complexes with chelating ligands have been reported to undergo more effective C-C bond formation with aryl triflates than those with monodentate ligands.[27,28] Hartwig and Buchwald have reported that the amination of aryl triflates is also catalyzed more effectively by palladium complexes bearing chelating ligands.

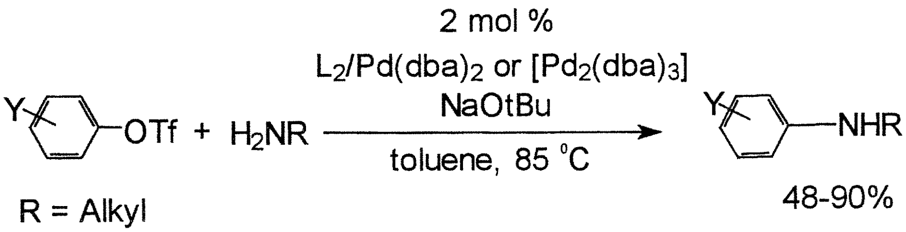
The reaction of electron rich or electron poor aryl triflates with aniline in the presence of NaO*t*Bu and a combination of $Pd(dba)_2$ and a chelating ligand like DPPF in toluene gave high yields of the mixed diarylamines as shown in Equation 16.[29]



(16)

R = MeO, Ph, Me or ArOTf = 2-naphthyl triflate 80-94%

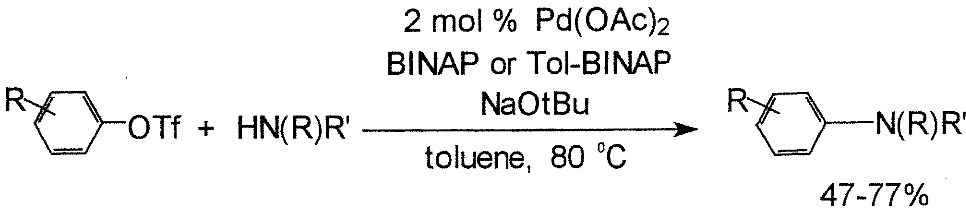
The reaction of alkyl amines with aryl triflates catalyzed by a combination of $Pd(dba)_2$ and DPPF or BINAP also gave good yields of the mixed N-alkylamines as shown in Equation 17.



(17)

R = Alkyl
Y = *o*-, *m*-, or *p*-alkyl, CN, C(O)Ph, OMe, Ph
L_2 = DPPF or BINAP

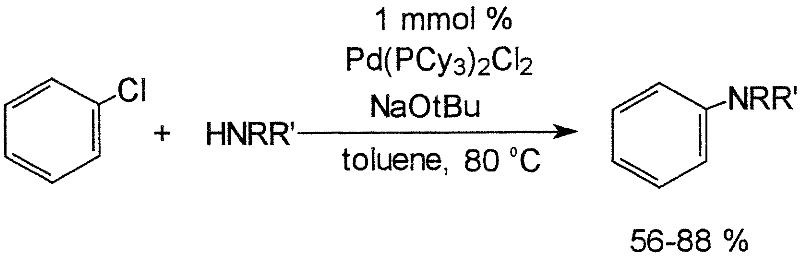
Buchwald's group reported that a combination of $Pd(OAc)_2$ and BINAP or Tol-(BINAP) can be used to catalyze the amination of aryl triflates with amines (Eq. 18).[30] A possible catalytic cycle for the amination of aryl triflates was proposed which is very similar to Scheme 8. The reaction of BINAP with $Pd(OAc)_2$ forms $(BINAP)Pd(OAc)_2$ which is then reduced to (BINAP)Pd(0). Oxidative addition of aryl triflate to this species forms the palladium aryl cation and the coordination of amines gives $[(BINAP)Pd(Ar)(NHRR')]^+OTf^-$ which is deprotonated by NaO*t*Bu to afford the palladium amide complex (BINAP)Pd(Ar)(NRR'). Reductive elimination yields the arylamine.



(18)

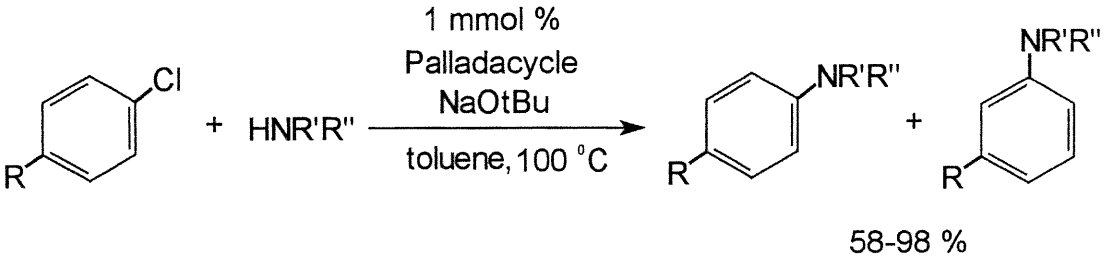
1.1.7 Aryl chloride aminations

Considering the greater availability and lower price of aryl chlorides, a catalytic system for the amination of aryl chlorides is of practical importance. Catalytic systems based on the $P(o\text{-tolyl})_3$, DPPF or BINAP ligands cannot promote the amination of aryl chlorides since the reactivity of the C-Cl bonds is much lower than those of C-Br or C-I. Based on the fact that a metal center coordinated to bulky and electron-rich phosphine ligands such as PCy_3 (Cy = cyclohexyl) can effectively cleave C-Cl bonds of aryl chlorides,[31] Tanaka et al. reported the palladium catalyzed amination of aryl chlorides with the use of tricyclohexylphosphine as shown in Equation 19.[32]



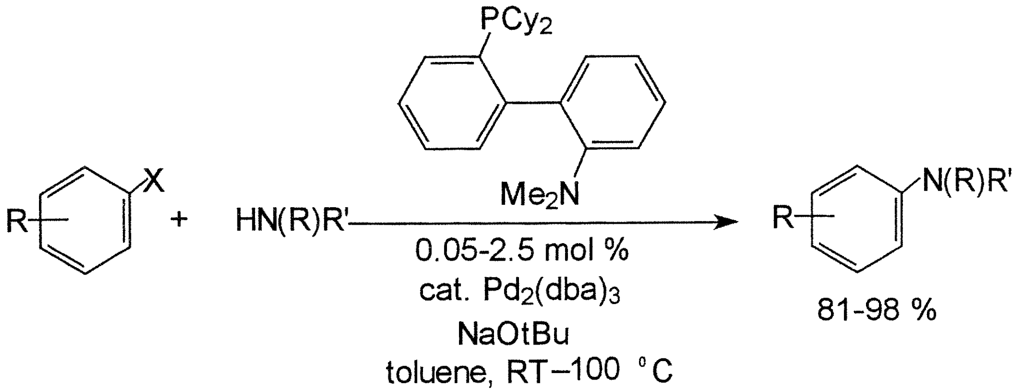
(19)

Similarlly, Beller et al. reported that the palladacycle {*trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)} and additional bromide ions as co-catalysts can catalyze amination of aryl chlorides with amines (Eq. 20).[33]



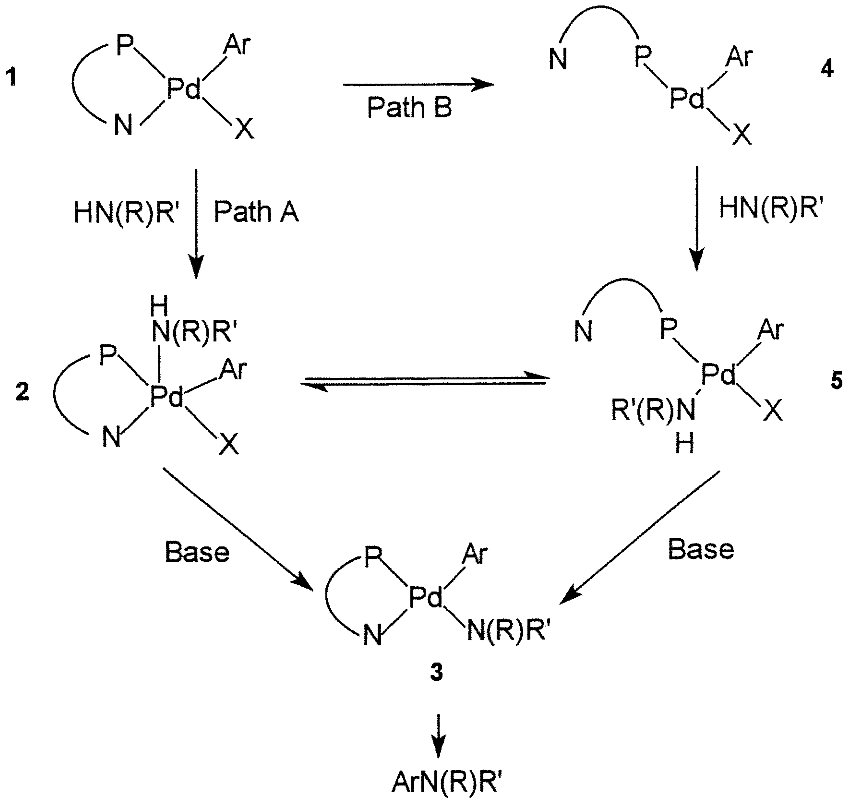
(20)

The amination reactions of aryl bromides catalyzed by BINAP/$Pd(OAc)_2$ suggested that the oxidative addition step was rate limiting.[34] For aryl chlorides, oxidative addition can be anticipated to be even more sluggish. To facilitate this slow step, Buchwald's group has prepared electron-rich bidentate aminophosphine ligands to expand the scope of palladium-catalyzed aryl chloride transformations as shown in Equation 21.[35]



(21)

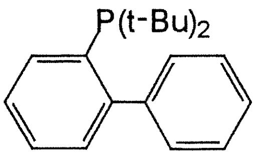
Scheme 9



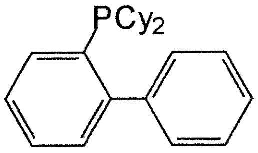
The mechanism shown in Scheme 9 has been proposed by Buchwald for the amination of unactivated aryl chlorides using palladium complexes with aminophosphine ligands. The reaction involves binding of the amine to the four-coordinate complex **1**, followed by the deprotonation of the resulting five-coordinate complex **2** to give **3** (path A). Alternatively, coordination of the amine substrate may occur after the initial dissociation of the dimethylamino moiety of the ligand, followed by nucleophilic attack of the amine substrate on the three-coordinate complex **4** to give **5**. Deprotonation of **5** is followed by rapid recomplexation of the amine moiety of the ligand to give **3** (path B). This result indicates that the reaction of aryl chlorides in Pd-catalyzed processes need not be limited by the rate of the oxidative addition step.

1.1.8 Room temperature aminations

Palladium-catalyzed C-N bond-forming reactions have evolved into a versatile and efficient synthetic methodology.[33-35] However, high reaction temperatures are often required. Recently, Buchwald also reported palladium complexes supported by (o-biphenyl)P(t-Bu)$_2$ (A) or (o-biphenyl)PCy$_2$ (B) ligands which are efficient catalysts for the catalytic amination of aryl chloride at room temperature.[36] Interestingly, ligands A and B are air-stable. Their effectiveness is believed to be due to a combination of steric and electronic properties that promote oxidative addition, Pd-N bond formation, and reductive elimination.



A

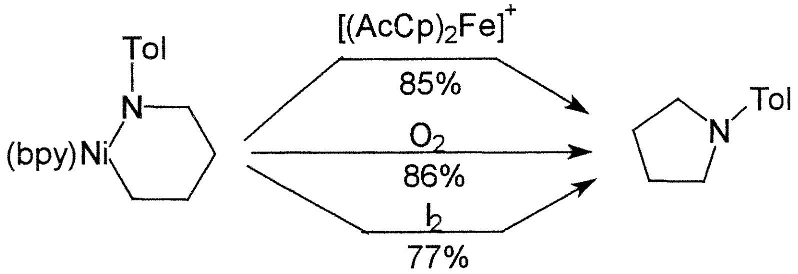


B

1.2 C-N bond formation catalyzed by nickel amide complexes

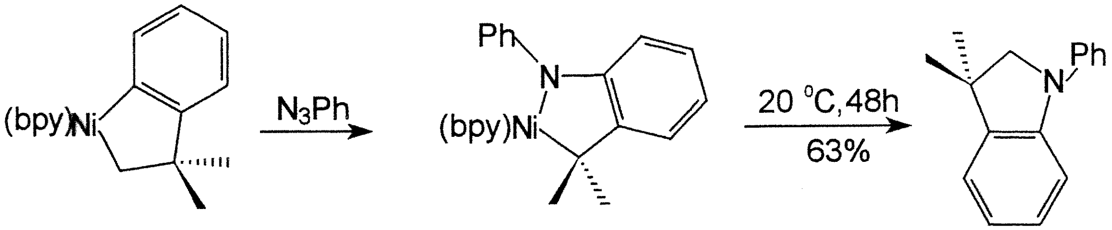
Hillhouse's group has shown that C-N bond forming reductive elimination of amines can also occur from nickel amido complexes.[37] Thus, the reaction of (bpy)Ni[N(Tol)$(CH_2)_4$] with either O_2 or I_2 at ambient temperature affords high yields of N-*p*-tolylpyrrolidine. This product was also obtained by the reaction with the one-electron oxidant 1,1'-diacetylferrocenium tetrafluoroborate as shown in Scheme 10.

Scheme 10



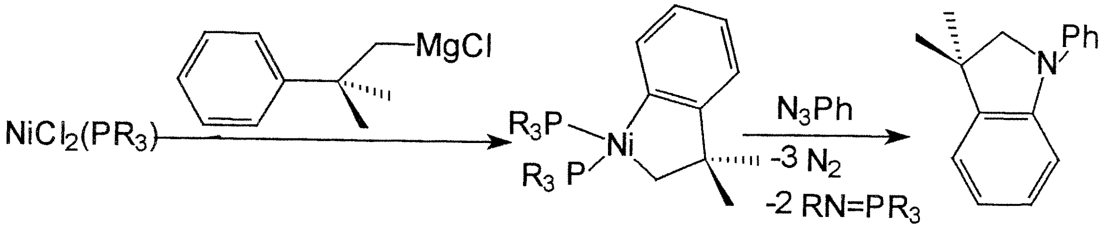
Nickel catalyzed C-N bond formation was also observed by thermal reductive elimination.[38] Thus, the reaction of (bpy)Ni(CH_2CMe_2-o-C_6H_4) with N_3Ph at ambient temperature gives the NPh insertion product. This azametallacycle is thermally unstable and gives an N-phenyl indoline by C-N reductive elimination as shown in Scheme 11.

Scheme 11



Phosphine-ligated nickel complexes are also reported by Hillhouse et al as shown in Scheme 12.[39] A nitrogen heterocycle was formed upon addtion of N_3Ph to the phosphine-ligated Ni complex.

Scheme 12

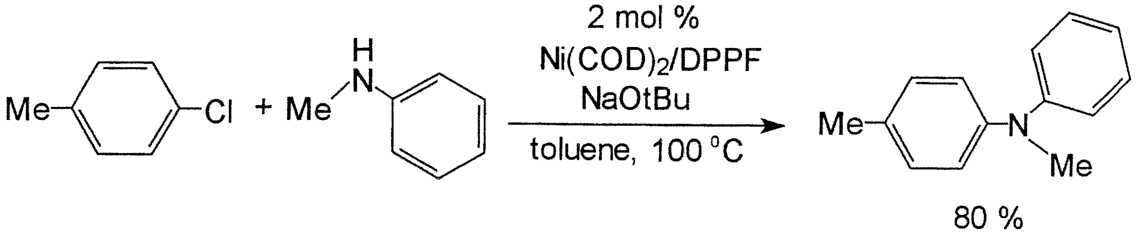


These Ni promoted C-N bond formations are different from the Pd catalyzed C-N bond formations in that the latter involve elimination between amides and aryl ligands while the former reactions are stoichiometric and involve amide and alkyl ligand.

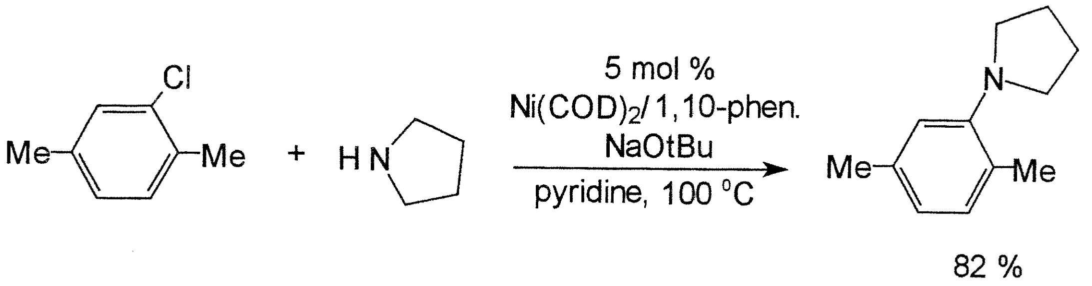
Buchwald's group[40] recently reported that aryl chlorides can be converted to aniline derivatives using catalytic amounts of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) and DPPF or 1, 10-phenanthroline in the presence of sodium tert-butoxide as shown in Equation 22.[40] Electron-rich and electron-poor aryl chlorides, as well as chloropyridine derivatives, can be combined with primary and secondary amines to give the desired aryl amine products in moderate to excellent yields.

$$\mathrm{Ar{-}Cl} \quad + \quad \mathrm{HNRR'} \xrightarrow[\text{toluene, } 70\text{–}100\ ^\circ\mathrm{C}]{\substack{\text{2-5 mol \%} \\ \mathrm{Ni(COD)_2/DPPF} \\ \mathrm{NaOtBu}}} \underset{\text{50-96 \%}}{\mathrm{Ar{-}NRR'}} \qquad (22)$$

Two examples of these reactions are given in Equation 23 and Equation 24. This system constitutes the first nickel-catalyzed amination of aryl chlorides, which allows for the coupling of a wide variety of substrates under relatively mild conditions and gives higher yields compared to the palladium-catalyzed amination of aryl chlorides.



(23)



(24)

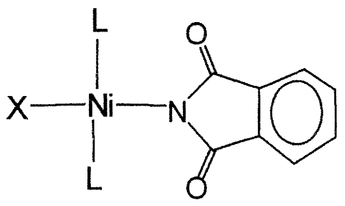
1.3 Summary

The palladium and nickel catalyzed amination reactions presented above constitute very useful methods for the construction of a wide variety of important substrates. For the past several years, many researches have worked on the development of new ligand systems and the careful optimization of reaction conditions and reagents. A general, reliable, and practical methodology for the formation of aromatic carbon-nitrogen bonds has been developed. Mechanistic studies have revealed a great deal about the mechanism of Pd and Ni-catalyzed amination reactions.

Although palladium catalyzed aminations are well-developed, nickel catalyzed amination remains less developed. There are only a few publications on nickel catalyzed amination.[32-35] Generally speaking, there are several advantages in using nickel complexes over palladium complexes. Nickel is less expensive than palladium and, in some cases, the nickel complexes have greater reactivity than the analogous palladium complexes. Nickel amide complexes have been prepared before,[41-44] and nickel complexes are known to catalyze cross-coupling, C-C bond forming processes through mechanisms not likely to occur with palladium complexes.[45,46] This prompted us to investigate nickel catalyzed amination. The following section outlines the objectives of the present study.

1.4 Objectives

Our research interests have been directed towards the preparation of Ni-NR_2 model complexes (where NR_2 is the phthalimidate moiety) and the study of the C-N bond forming reductive elimination of these compounds. We have set out to prepare a series of complexes of the type $L_2Ni(X)$(phthalimide) (Figure 1) with the aim of studying the differences in their structures as a function of geometry (*cis, trans*), type of X (*trans* influence) and nature of L ligands (donor capacity, size, etc.).

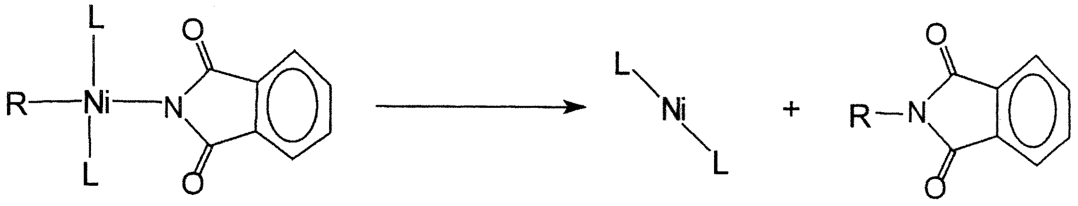


X=Ar, Me, Cl, Br, H, C_2Cl_3, CH_2SiMe_3

L=PPh_3, PMe_3, PCy_3, PBu_3, DPPE

Figure 1. The nickel imidato complexes under study

In addition to these structural studies, we were also interested in studying the ease of reductive elimination of the phthalimidato and R ligands (Eq. 25) and to compare these to the corresponding reactions with the Ni-NR_2 and Pd-NR_2 systems reported in the literature. Finally, we hope to use the findings from these studies to develope a catalytic system (Scheme 13) for the preparation of aryl imidato complexes.

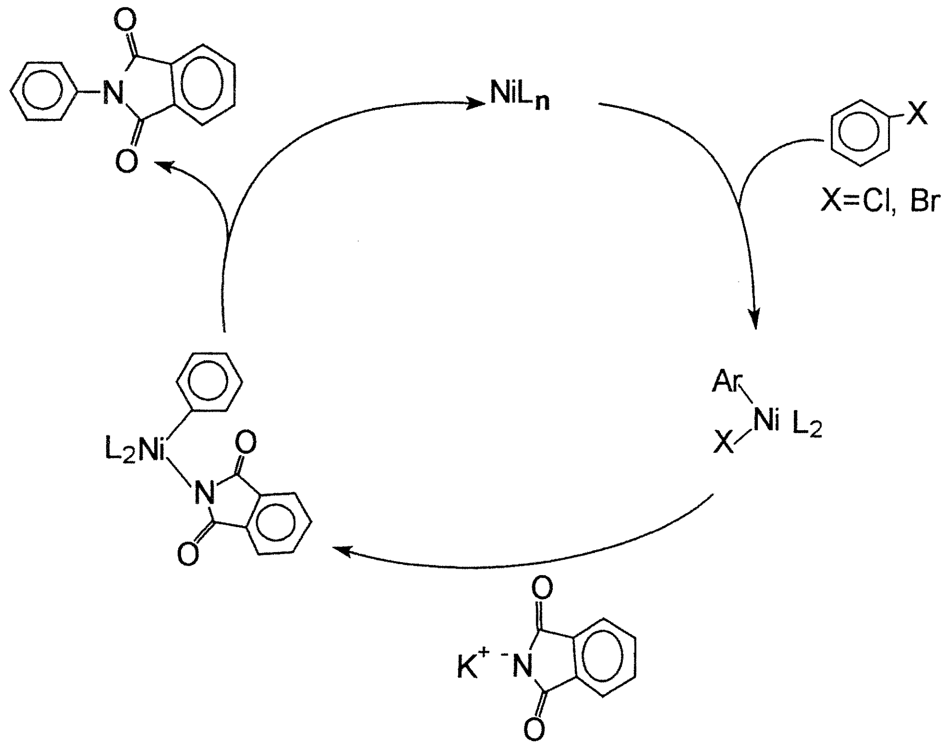


(25)

R= Ar, CH_3, CH_2SiME_3

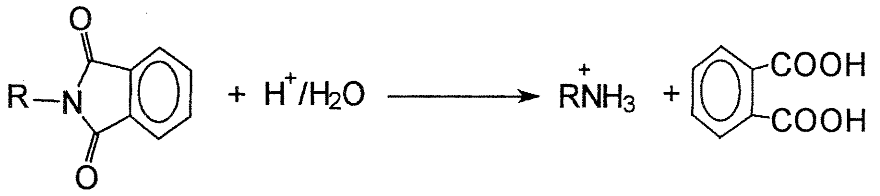
L= PMe_3, PPh_3, PBu_3, DPPE

Scheme 13



L= PPh_3, PMe_3, PCy_3, PBu_3, DPPE

There are two main reasons for choosing phthalimidato ligands for these studies. The first reason is related to the utility of the phthalimide group as a protected form of the NH_2 moiety. Since R-phthalimide is often less reactive than the R-NH_2, R-phthal can be considered as a protected analogue of R-NH_2. The amine form can be obtained by hydrolysis of R-phthal (Eq. 26)[47] or by the reaction of the substituted phthalimide with hydrazine (Eq. 27).[48]



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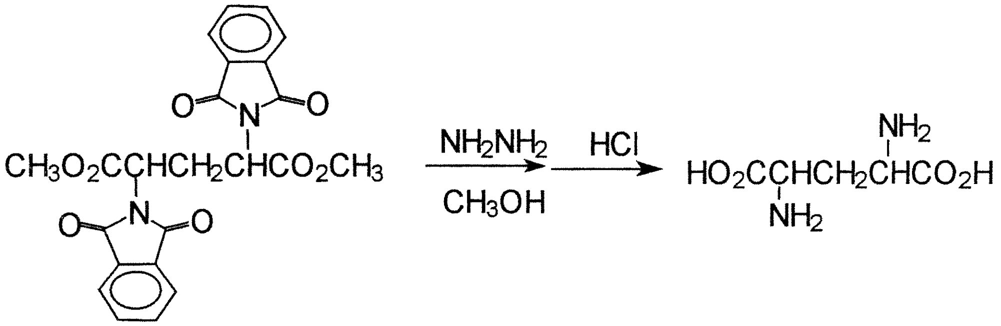


(27)

The second reason for our interest in phthalimides is that the phthalimide moiety is present in a number of compounds which have biological activity as drugs. Thus, access to compounds which contain the phthalimide group might have some practical applications. As shown in Figure 2, the bioactive molecules A[49] and B[50] bearing the phthalimide group have therapeutic properties.

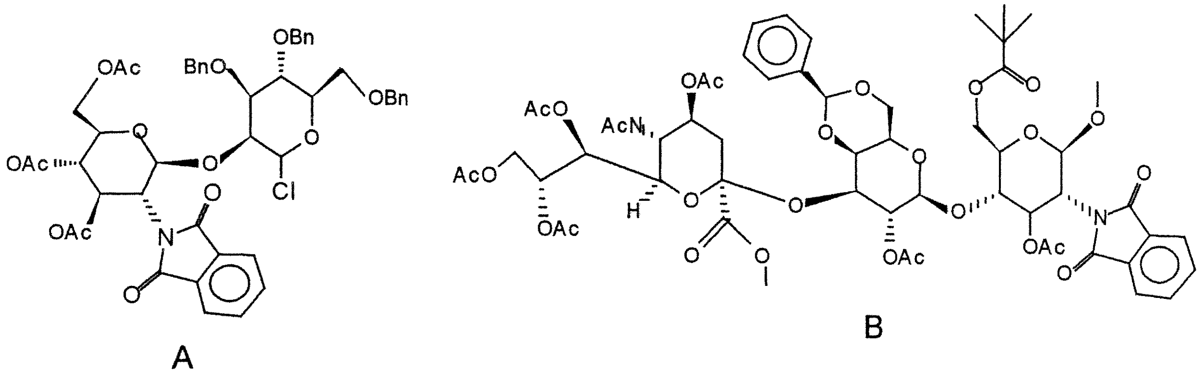
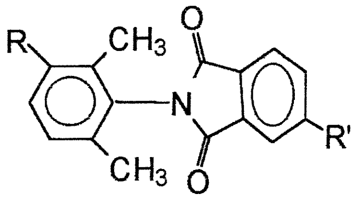


Figure 2. Bioactive molecules bearing the phthalimide group

We are specifically interested in developing a route to aryl-phthalimides since many organic molecules containing aryl-phthalimide moieties have biological activity. The compound, in Figure 3, exhibits anticonvulsant and neurotoxic properties.[51a] Moreover, some systems containing substituted anilines are of interest in various applications such as polymers,[51b] photography, materials,[51c] etc.

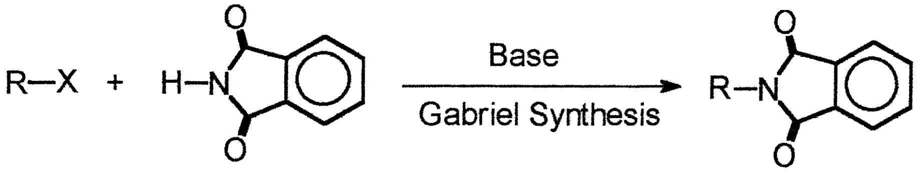


$R = H, NO_2, NH_2$

$R' = H, NO_2, NH_2, OH, Cl$

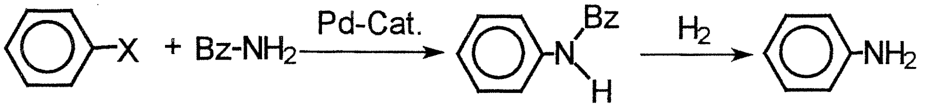
Figure 3. Bioactive molecule bearing the aryl-phthalimide group

Alkylamines or alkylphthalimide are easily prepared by conventional methods such as the Gabriel synthesis (Eq. 28), which is a nucleophilic substitution not needing catalysis.

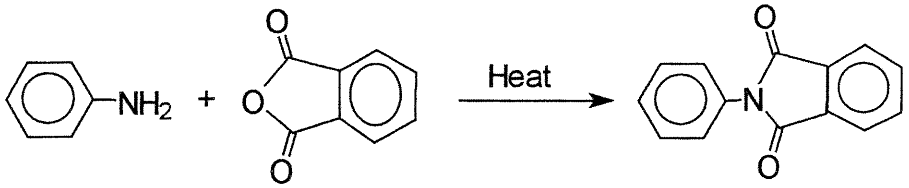


(28)

However, there is no direct method to convert aryl-halides to anilines or aryl-phthalimides. As shown in Equation 29, the preparation of anilines needs a Pd-catalyzed amination followed by hydrogenation, while one way for preparing aryl-phthalimides without catalysis is to react them with phthalic anhydride under reflux condition instead of going through the Gabriel synthesis as shown in Equation 30.

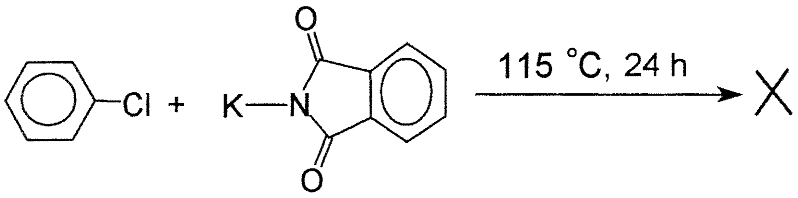


(29)



(30)

The direct reaction of arylchloride with potassium phthalimide does not produce arylphthalimide even when heated to 115°C for 24 h (Eq. 31).



(31)

The difficulty in driving this reaction to completion is not thermodynamic ($\Delta G^0 < 0$), but rather kinetic because the C-Cl and K^+N^- interactions are very stable. Therefore, a catalyst is required to facilitate the cleavage of these bonds and the formation of the C-N and K^+Cl^- bonds.

This project presents a number of challenges, the most important being the fact that little is known about nickel phthalimide complexes, their stability, and their propensity to undergo reductive elimination. The phthalimide group is like a pseudo-halogen which should resist reductive elimination; this is because the two carbonyl groups which are strongly electron-withdrawing groups can delocalize the nitrogen lone pair, thereby reducing the electron density on the N and enhancing the overall stability of the resulting M-N bond.

Our strategy is to prepare a series of Ni-phthalimide complexes in order to study the Ni-N interaction as a function of auxiliary ligands L (*cis* vs. *trans*, chelating vs. monodentate, bulky vs. less bulky, etc.) and to test the reductive elimination of R-N. The results of these studies are described in the following two chapters.

Virtual Coupling

Prior to presenting the results of our studies, it is necessary to introduce the phenomenon of virtual coupling, which relates to the analysis of the ^{1}H NMR spectra for the complexes *trans*-$(PMe_3)_2Ni(X)(Y)$. This phenomenon has been described by Jesson for some organometallic complexes (J. P. Jesson, "Stereochemistry and Stereochemical Nonrigidity in Transition Metal Hydrides", in Transition Metal Hydrides, ed. E. L. Muetterties, New York, Marcel Dekker Inc., 1971, pp. 85-87)[51d]. Virtual coupling applies to situations in which there is such strong spin-spin coupling between a set of magnetically nonequivalent nuclei that they act with respect to other nuclei as though they were magnetically equivalent. For complexes in which two PMe_3 groups are *trans* with respect to each other, this phenomenon results in the observation of a triplet (instead of a doublet) for the P-C-*H* signal. This arises from the fact that the chemically equivalent but magnetically nonequivalent P nuclei are so strongly coupled to each other that the values of $^2J_{P\text{-}H}$ and $^2J_{P'\text{-}H'}$ become equal. This equivalence gives rise to an apparent coupling constant which is roughly equal to half the "true" value (i.e., the value normally observed in the absence of strongly coupled *trans*-PMe_3 groups). This type of virtual triplets have been observed for the *trans*-PMe_3 groups in some of our complexes; it should be noted, however, that in some instances the poor resolution of the spectrum results in the detection of a singlet resonance.

CHAPTER 2

Synthesis and Characterization of Nickel Imidato Complexes

The number of routes available for the incorporation of amido units (NR_2) onto a transition metal are numerous,[52] but four main methods appear to have been utilized[3] for late transition metals. General equations for these procedure are given below:

1. Transmetallation with an alkali metal amide, of which the lithium salts are common;

$$L_nM\text{-}X + LiNRR' \rightarrow L_nM\text{-}NRR' + LiX \qquad (32)$$

2. Elimination of HY, where Y is a basic ligand such as OH^- or an alkyl, from $Y\text{-}M\text{-}NHR_2$;

$$L_nM\text{-}Y + HNRR' \rightarrow L_nM\text{-}NRR' + HY \qquad (33)$$

3. Deprotonation of a coordinated amine;

$$L_nM(NHRR')^+ + B^{\bullet} \rightarrow L_nM\text{-}NRR' + BH^+ \qquad (34)$$

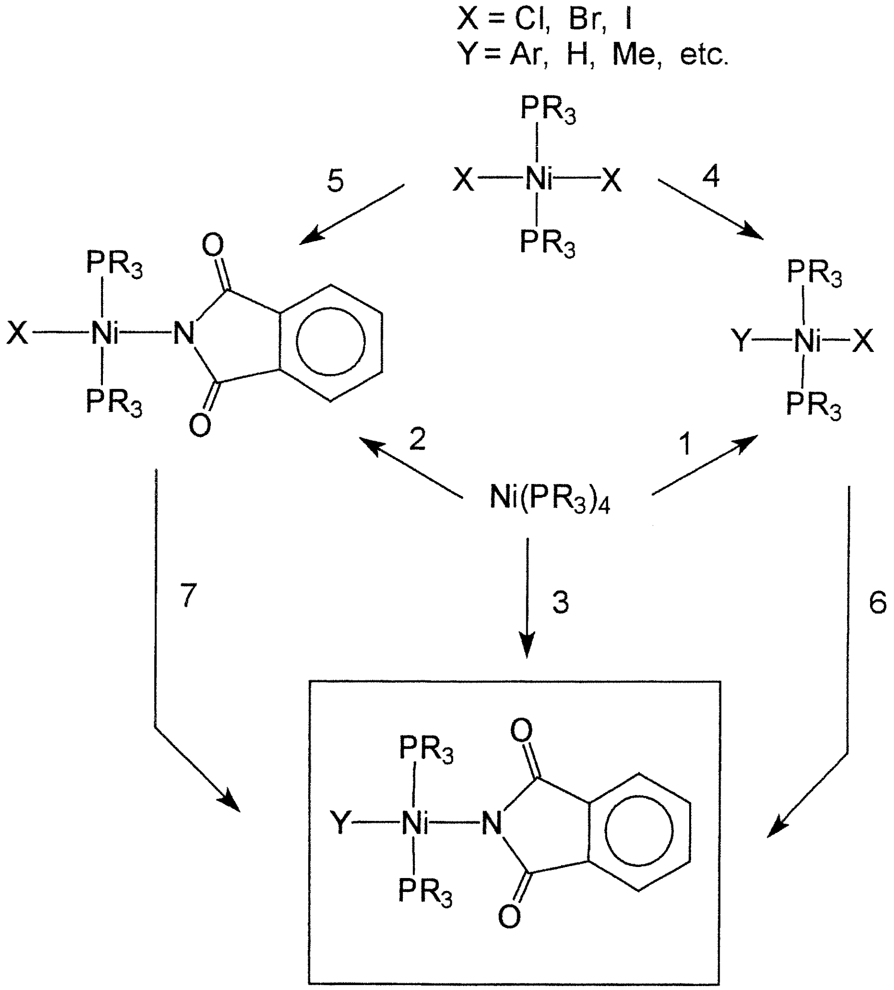
4. Hydride addition across an organic azide or a related, unsaturated, nitrogen-containing substrate.

$$L_nM\text{-}H + RN_3 \rightarrow L_nM\text{-}NHR + N_2 \qquad (35)$$

The most general procedure appears to be transmetallation, although care must be taken since reduction in lieu of metathesis is a common side reaction for late metals, especially for nickel.

The synthetic routes we selected for the preparation of our target complexes are shown in scheme 14. We have found that the nature of the phosphine ligand in the target complexes has a strong influence on the facility of the oxidative addition of aryl chlorides to form $(PR_3)_2Ni(Ar)Cl$. Some Ni(0) complexes can undergo facile oxidative addition with aryl chlorides, thus allowing the use of route 1, whereas for other compounds routes 4 and 5 were dictated by the difficulty in the oxidative addition step (1). Therefore, the best route depends on the nature of the phosphine ligands.

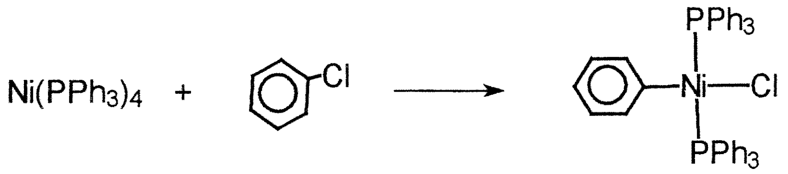
Scheme 14



2.1 Synthesis and characterization of intermediate complexes

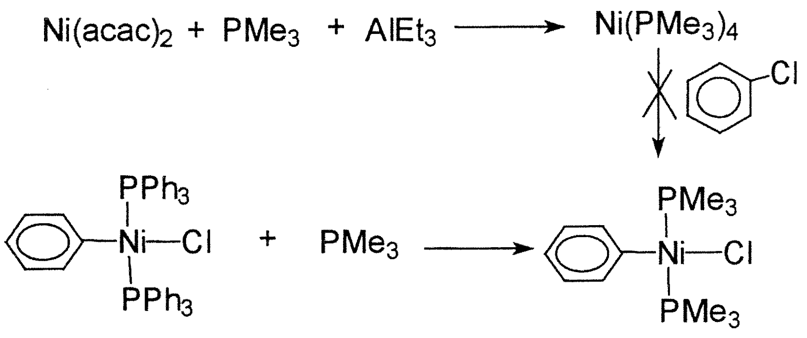
The nickel phthalimide complexes $L_2Ni(Y)(phthal)$ cannot be prepared directly from Ni(0) precursors as shown in Scheme 14 (path 3), so the intermediate compound $(PR_3)_2Ni(Y)(X)$ (Y= Ph, 3-Me-Ph, 2,5-Me_2-Ph, Me) (X= Cl, Br, I) must be prepared through the routes 1 and 4.

The rate and extent of dissociation of a phosphine from $Ni(PR_3)_4$ is a key step in the reaction of oxidative addition because the loss of PR_3 can open up a vacant site at the metal. In addition, the dissociation of PR_3 ligands is more facile for bulky ligands.[53] This phenomenon is best illustrated by the observation that $Ni(PPh_3)_4$ undergoes oxidative addition of Ph-Cl while $Ni(PMe_3)_4$ does not promote this reaction. Thus, we prepared $(PPh_3)_2Ni(Ph)Cl$ from Ni(0) as shown in Equation 36, and used this compound to prepare the PMe_3 analogues by ligand substitution (Scheme 15).



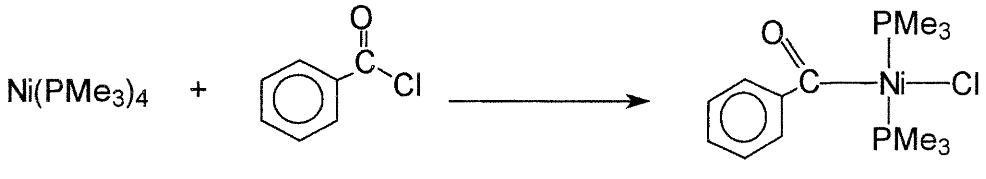
(36)

Scheme 15



1a

Complex $(PMe_3)_2Ni(Ar)Cl$ **1** (Ar = Ph, **1a**; 3-Me-Ph, **1b**; 2,5-Me_2-Ph, **1c**) was obtained as an orange crystalline solid. These complexes were characterized readily on the basis of their singlet peaks in the $^{31}P\{H\}$ spectra: –14.7 ppm (**1a**), -14.8 ppm (**1b**), -13.9 ppm (**1c**).



(37)

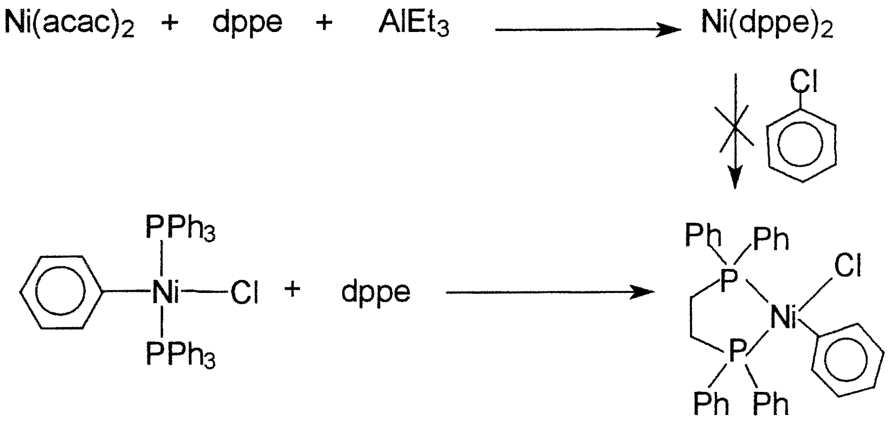
2

In contrast to chlorobenzene, benzoyl chloride reacts with $Ni(PMe_3)_4$ to give the product $(PMe_3)_2Ni\{Ph\text{-}(C{=}O)\}Cl$ **2** (Eq. 37). The reason why benzoyl chloride undergoes oxidative addition is that the C-Cl bond of benzoyl chloride is weaker and more prone to attack by nucleophiles and to oxidative addition onto transition metals. Complex **2** has been characterized by $^{31}P\{H\}$, $^{13}C\{H\}$ and ^{1}H NMR spectra. One singlet was observed at –16.43 ppm in the $^{31}P\{H\}$ NMR spectrum. The $^{13}C\{H\}$ NMR spectrum showed one more signal (C=O) at 193.18 ppm compared to complex $(PMe_3)_2Ni(Ph)Cl$, the rest of the signals were similar.

In order to evaluate the influences on the Ni-imidato complexes of *cis* vs *trans* geometries, we chose DPPE to prepare the *cis* intermediate compound. Because $Ni(DPPE)_2$ does not undergo oxidative addition with chlorobenzene, we used the same route as that for the PMe_3 complex to prepare (DPPE)Ni(Ar)Cl **3** (Ar= Ph, **3a**; 3-Me-Ph, **3b**; 2,5-Me_2-Ph, **3c**) (Scheme 16). A yellow solid was obtained in 70% yield. Because the two phosphines are not equivalent, we observed two doublet signals in $^{31}P\{H\}$ NMR spectra at 55.3 ppm (d, $^{2}J_{P\text{-}P}$=17.8) and 35.5 ppm (d, $^{2}J_{P\text{-}P}$=17.8) (**3a**), 56.8 ppm (d, $^{2}J_{P\text{-}}$

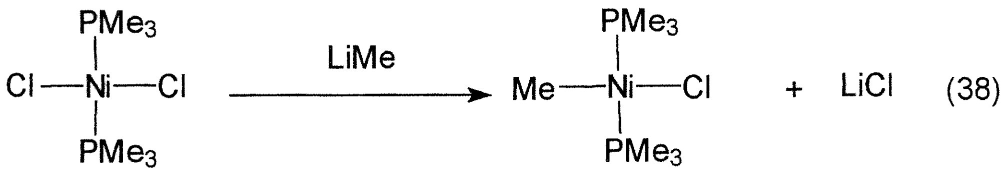
${}_{P}$=17.8) and 34.9 ppm (d, ${}^{2}J_{P\text{-}P}$=17.8) (**3b**), 32.2 ppm (d, ${}^{2}J_{P\text{-}P}$=15.3) and 52.8 ppm (d, ${}^{2}J_{P\text{-}P}$=15.3) (**3c**).

Scheme 16



3a

We chose to prepare a nickel-phthalimide complex with Y=Me in order to compare the influences on the Ni-N bond of different carbon groups such as the differences between alkyl and aryl groups. The transmetallation method was used to prepare the product $(PMe_3)_2Ni(Me)Cl$ **4** as shown in Equation 38. This compound has been characterized by ${}^{31}P$ {H} and ${}^{1}H$ NMR spectroscopy. The presence of the PMe_3 ligands was confirmed from the singlet at –14.76 ppm in the ${}^{31}P\{H\}$ NMR spectrum, and a singlet at 0.98 ppm in the ${}^{1}H$ NMR spectrum; a singlet at –0.53 ppm in the ${}^{1}H$ NMR spectrum confirmed the presence of the methyl group attached to the metal center.



$$Cl-\underset{PMe_3}{\overset{PMe_3}{Ni}}-Cl \xrightarrow{LiMe} Me-\underset{PMe_3}{\overset{PMe_3}{Ni}}-Cl + LiCl \quad (38)$$

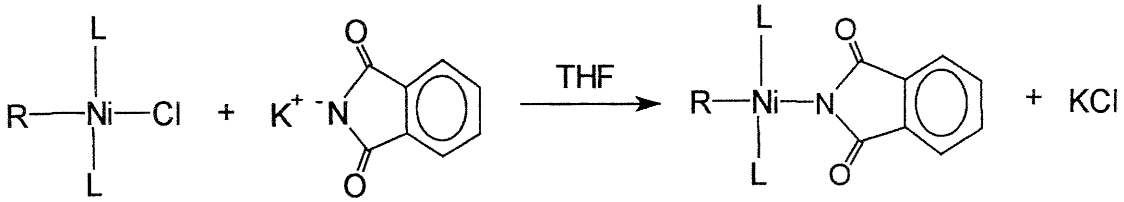
4

By using the same route as Equation 38, we prepared the intermediate complex $(PPh_3)_2Ni(Me)Cl$ **5** which has been characterized by $^{31}P\{H\}$ and ^{1}H NMR spectra. The synthesis must be carried out at –78°C because the solution of the complex **5** is not stable at room temperature, but the solid isolated from the solution is stable. This compound was characterized by $^{31}P\{H\}$ and ^{1}H NMR spectroscopy: we observed a singlet at 23.4 ppm in $^{31}P\{H\}$ NMR spectrum, and a broad singlet at –1.15 ppm in ^{1}H NMR spectrum assigned to the proton of methyl group about the metal center.

By the same route as Scheme 15, we also prepared $(PBu_3)_2Ni(Ph)Cl$, **6**, which has been characterized by $^{31}P\{H\}$ and ^{1}H NMR spectra: a singlet at 4.43 ppm in the $^{31}P\{H\}$ NMR spectrum was observed. The presence of PBu_3 group was confirmed in the ^{1}H NMR spectrum by a triplet at 0.89 ppm ($^{2}J_{H\text{-}H}$ = 5.6) which was assigned to the CH_3 group, a multiplet signal at 1.21 ppm which was assigned to the $P\text{-}CH_2\text{-}CH_2$ and a broad singlet at 1.39 ppm which was assigned to $P\text{-}CH_2$.

2.2 Synthesis and characterization of phthalimide derivatives

The most general route, salt metathesis, was used to synthesize the phthalimide derivatives. As shown in Equation 39, THF was used for this procedure; most of the syntheses were done at room temperature, but some were done at low temperature (-78°C) when the *cis* or *trans* intermediate complex $L_2Ni(R)Cl$ was not stable at room temperature.

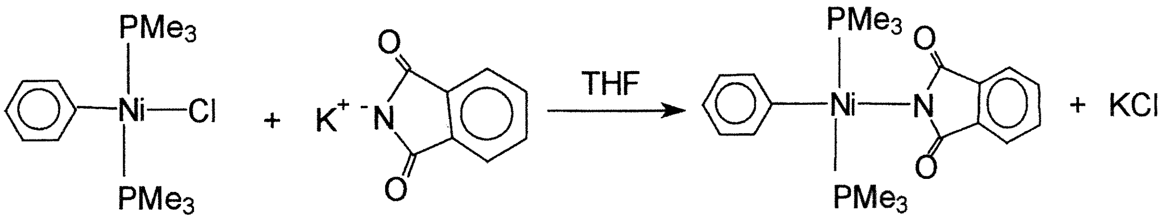


(39)

L=PMe$_3$, R=Ar, Me, Ph$\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}$ L=PCy$_3$, R=H   L=PBu$_3$, R=Ar

L=PPh$_3$, R=Ar, Me   L=DPPE, R=Ar

The synthesis of complex **7** (Eq. 40) was achieved by reacting the intermediate complex $(PMe_3)_2Ni(Ar)Cl$, **1**, (Ar = Ph, **1a**; 3-Me-Ph, **1b**; 2,5-Me$_2$-Ph, **1c**) with a small excess of potassium-phthalimide in THF at room temperature. Complexes **7** were obtained in pure yellow powder which was stable to air and water. These complexes were characterized by $^{31}P\{H\}$, $^{13}C\{H\}$ and ^1H NMR spectroscopy, elemental analysis and by single crystal X-ray analysis. One singlet was observed at –13.7 ppm (**7a**), -13.7 ppm (**7b**), -13.0 ppm (**7c**) in the $^{31}P\{H\}$ NMR spectrum. For complex **7a**, the ^{13}C {H} NMR spectrum showed a signal at 177.60 ppm due to the CO group of the phthalimide ligand. The PMe$_3$ groups appear as triplets ($^2J_{P\text{-}H}$=3.5 Hz) in the ^1H NMR spectra. This multiplicity is due to the phenomenon of virtual coupling (see introduction).



1a   **7a**   (40)

Crystallographic data of complex $(PMe_3)_2Ni(Ph)(phthal)$, **7a**, can be found in Table 5. The intensity data were collected on a Bruker CCD SMART diffractometer at low temperature (173K) and the structure was solved in space group P-1. Selected bond lengths and angles are found in Table 6. The ORTEP drawings (1), (2) and (3) of the three independent molecules of $(PMe_3)_2Ni(Ph)(phthal)$ are shown in the unit cell (Figure 4, 5 and 6). There is a rotational disorder for PMe_3. The structure of **7a** shows square planar coordination around the nickel center with the phosphines *trans* to one another. The P1-Ni-P2 angle is nearly linear (ca. 174° in the three independent molecules), the plane of phthalimide group is tilted by ca. 80-90° about the coordination plane defined by P1, P2, N, and C_{ph}, while the phenyl ring is oriented ca. 70° about the plane of the molecule. The significance of some structural parameters such as Ni-N bond length will be discussed later.

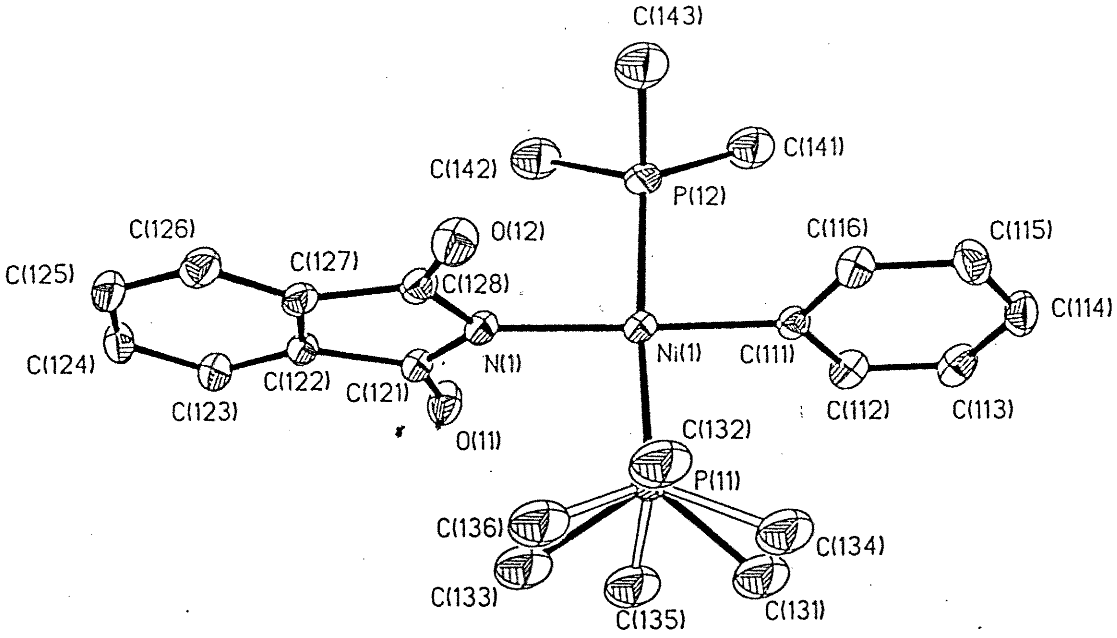


Figure 4. ORTEP drawing (1) of $(PMe_3)_2Ni(Ph)(phthal)$ **7a**

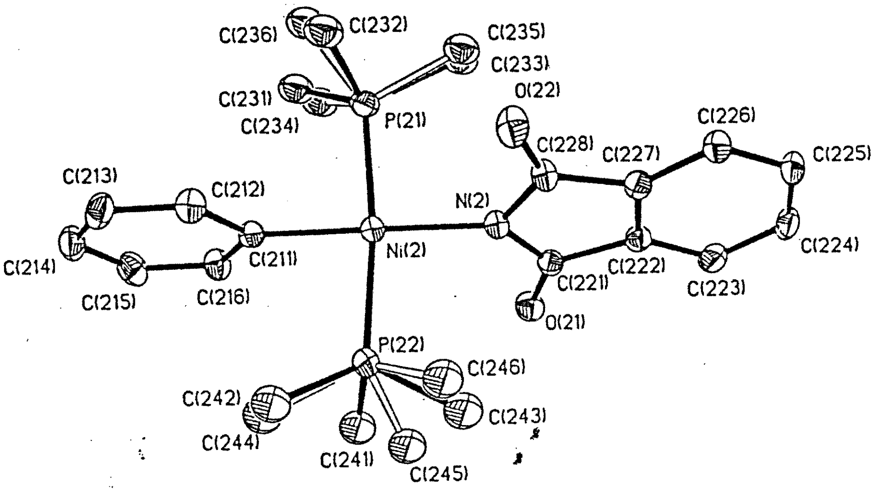


Figure 5. ORTEP drawing (2) of $(PMe_3)_2Ni(Ph)(phthal)$ **7a**

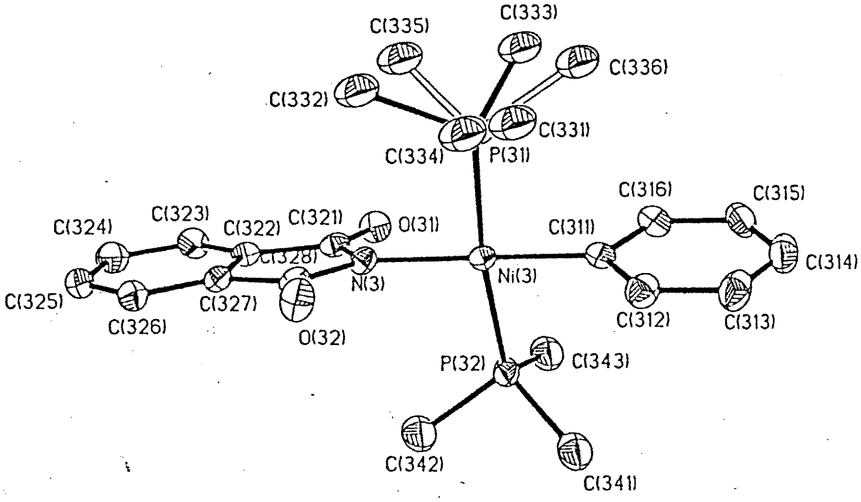


Figure 6. ORTEP drawing (3) of $(PMe_3)_2Ni(Ph)(phthal)$ **7a**

Table 5. Crystallographic Data for $(PMe_3)_2Ni(Ph)(phthal)$ **7a**

Formula	$C_{20}H_{27}NNiO_2P_2$
Formula weight	434.08
Space group	P-1
a, Å	9.4499(5)
b, Å	15.3923(8)
c, Å	23.1843(11)
β, deg.	95.8000(10)
Volume, $Å^3$	3247.3(3)
λ, Å	0.71070
Z	6
Temperature, K	173(2)
μ, mm^{-1}	1.057
Independent reflections	16693
Measured reflections	38916
Range of hkl	$-12 \leq h \leq 12$
	$-20 \leq k \leq 20$
	$-31 \leq l \leq 31$
R(I>2σ(I))	0.0464
wR2	0.1132
S	1.269

$$R = \Sigma (\| F_0 | - | F_c \|) / \Sigma (| F_0 |)$$

$$wR2 = \{ \Sigma [w (F_0^2 - F_c^2)^2] / \Sigma (F_0^2)^2 \}^{1/2}$$

$$S = \{ \Sigma [w (F_0^2 - F_c^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.}) \}^{1/2}$$

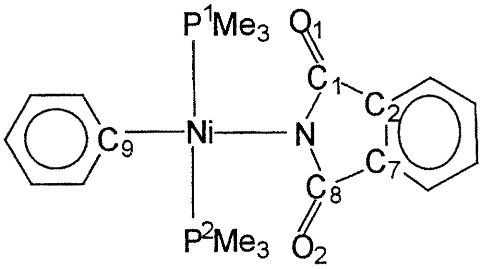
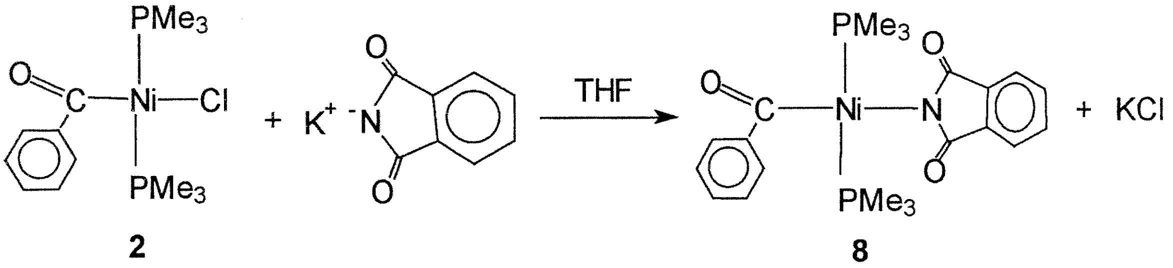


Figure 7. Complex $(PMe_3)_2Ni(Ph)(phthal)$ **7a**

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $(PMe_3)_2Ni(Ph)(phthal)$ **7a**

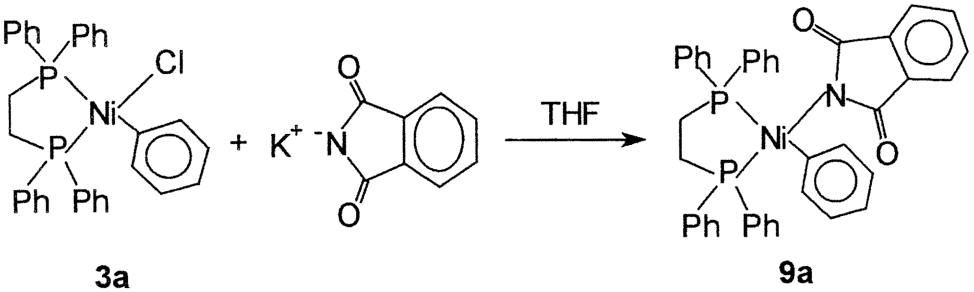
Molecule	1	2	3
Ni-N	1.9317(18)	1.9353(18)	1.9375(19)
Ni-P1	2.1839(7)	2.1882(7)	2.1947(7)
Ni-P2	2.1919(7)	2.1893(7)	2.1954(7)
Ni-C9	1.899(2)	1.892(2)	1.903(2)
N-C1	1.375(3)	1.386(3)	1.373(3)
N-C8	1.381(3)	1.377(3)	1.379(3)
C1-C2	1.503(3)	1.497(3)	1.498(3)
C7-C8	1.494(3)	1.499(3)	1.501(3)
P1-Ni-P2	173.81(3)	174.79(3)	173.07(3)
P1-Ni-N	92.70(6)	92.14(6)	93.60(6)
P1-Ni-C9	86.93(7)	87.73(7)	87.25(7)
P2-Ni-N	93.49(6)	91.75(6)	93.24(6)
P2-Ni-C9	86.88(7)	86.16(7)	85.90(7)
C9-Ni-N	179.34(8)	176.58(9)	178.85(9)
Ni-N-C1-O1	-1.4(4)	-3.0(4)	-0.9(4)
Ni-N-C8-O2	0.2(4)	1.4(4)	3.4(4)

Complex $(PMe_3)_2Ni(Ph\text{-}C{=}O)(phthal)$, **8**, was prepared from the reaction of $(PMe_3)_2Ni(Ph\text{-}C{=}O)Cl$, **2**, with excess potassium phthalimide at room temperature (Eq. 41). Complex **8** is stable to air and has been characterized by $^{31}P\{H\}$, $^{13}C\{H\}$ and ^1H NMR spectroscopy. The $^{13}C\{H\}$ NMR spectrum displayed one more signal than complex **7** $(PMe_3)_2Ni(Ph)(phthal)$, a triplet at 193.18 ppm ($^2J_{P\text{-}C}$=4.4) assigned to the carbonyl group of benzoyl. The signal for the two equivalent carbonyl groups of the phthalimide moiety was observed at 182.33 ppm; a triplet at 9.89 ppm was assigned to the methyl group of PMe_3, and the rest of the signals were similar to complex **7a**. A singlet at –14.58 ppm in the $^{31}P\{H\}$ NMR spectrum and a triplet at 0.74 ppm in the ^1H NMR spectrum were assigned to the PMe_3 ligand.



(41)

Reacting the complex (DPPE)Ni(Ar)Cl (Ar= Ph, **3a**; 3-Me-Ph, **3b**; 2,5-Me_2-Ph, **3c**), with an excess of potassium phthalimide in THF for two hours (Eq. 42) gave the air-stable complexes (DPPE)Ni(Ar)(phthal), **9** (Ar= Ph, **9a**; 3-Me-Ph, **9b**; 2,5-Me_2-Ph, **9c**) as yellow powders. This complex has been characterized by $^{31}P\{H\}$, $^{13}C\{H\}$ and ^1H NMR spectra, elemental analysis and by single crystal X-ray analysis. The two non-equivalent phosphine groups give rise to two doublet signals in the $^{31}P\{H\}$ NMR spectrum: at 50.0 and 45.5 ppm (d, $^2J_{P\text{-}P}$=17.8) (**9a**); 50.2 and 44.9 ppm (d, $^2J_{P\text{-}P}$=16.5) (**9b**); 46.6 and 41.5 ppm (d, $^2J_{P\text{-}P}$=15.3) (**9c**). The ^{13}C {H} NMR spectrum of **9a** showed a signal at 176.10 ppm for the CO group of the phthalimide ligand.



(42)

X-ray structures of complexes (DPPE)Ni(Ph)(phthal), **9a**, and (DPPE)Ni(3-Me-Ph)(phthal), **9b**, were obtained. Experimental details are given in the Experimental Section (X-ray Crystallography). Details of the intensity data collections and refinements are given in Table 7, the ORTEP drawings are in Figure 8 and 9, and the structural parameters are listed in Table 8. A complete listing of all structural parameters is given in Appendix III.

The structure of complex (DPPE)Ni(Ph)(phthal), **9a**, was solved in the space group C2/c. The coordination geometry around the Ni atom is square planar. The phthalimide and phenyl groups are oriented nearly perpendicular (86.8° for phthalimide and 79.2° for phenyl) to the plane of the molecule.

The structure of complex **9b** was solved in the space group $P2_1/n$. The phthalimide and tolyl groups are oriented almost perpendicular (89.9° and 86.1°, respectively) to the plane of the molecule. The value of the R factor (0.0675) is a little higher than we expected because there are two rotational disorders. One source of disorder arises from the two positions of the methyl groups on the phenyl ring (65%) and the other from the two positions of the phenyl groups on the phosphine (35%). The significance of some other structural parameters such as the Ni-N bond lengths will be discussed later.

Table 7. Crystallographic Data for

(DPPE)Ni(Ph)(phthal) **9a** and (DPPE)Ni(3-Me-Ph)(phthal) **9b**

	9a	**9b**
Formula	$C_{40}H_{33}NNiO_2P_2$	$C_{41}H_{35}NNiO_2P_2$
Formula weight	680.324	694.350
Space group	*C 2/c*	*P* 2_1/*n*
a, Å	36.6410(2)	12.4274(1)
b, Å	9.9030(1)	14.7898(1)
c, Å	21.4137(1)	19.5204(1)
β, deg.	118.92(1)	92.167(1)
Volume, Å^3	6800.98(5)	3585.26(4)
λ, Å	1.54178	1.54178
Z	8	4
Temperature, K	293(2)	293(2)
μ, mm^{-1}	1.990	1.898
Independent reflections	6633	7081
Reflections collected	39967	35478
Range of hkl	$-45 \leq h \leq 44$	$-14 \leq h \leq 15$
	$-12 \leq k \leq 12$	$-17 \leq k \leq 18$
	$-26 \leq l \leq 26$	$-23 \leq l \leq 23$
R(I>2σ(I))	0.0434	0.0675
wR2	0.1210	0.1575
S	1.036	0.943

$R = \Sigma (|| F_0 | - | F_c ||) / \Sigma (| F_0 |)$

$wR2 = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / \Sigma (F_0{}^2)^2 \}^{½}$

$S = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.}) \}^{½}$

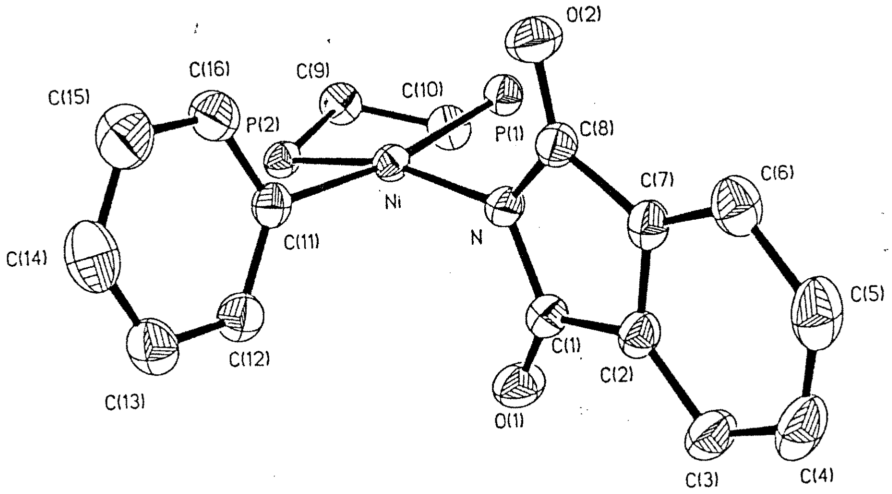


Figure 8. ORTEP drawing of (DPPE)Ni(Ph)(phthal) **9a**, the Ph groups on DPPE have been omitted.

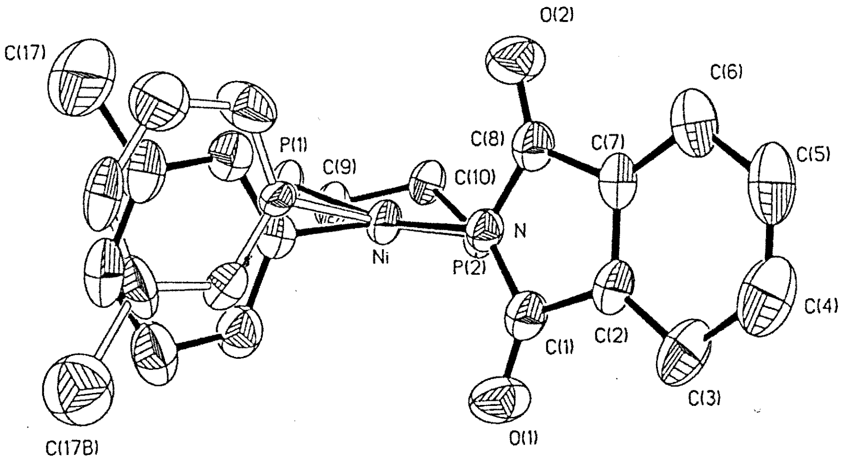
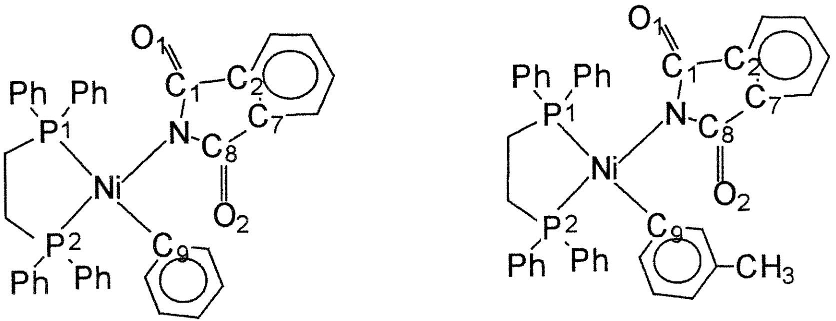


Figure 9. ORTEP drawing of (DPPE)Ni(3-Me-Ph)(phthal) **9b**, the Ph groups on DPPE have been omitted.



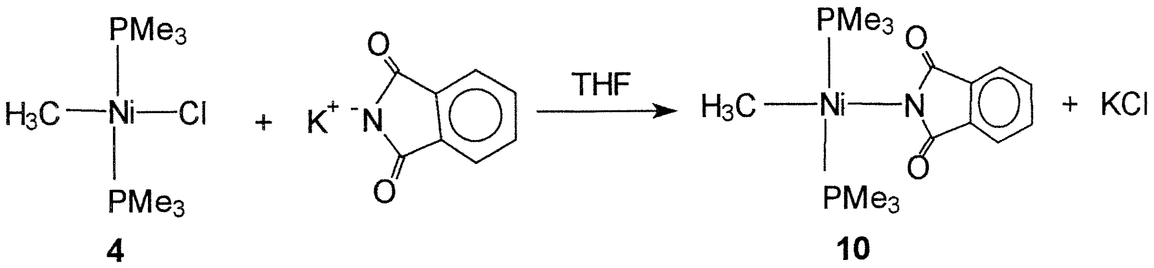
9a **9b**

Figure 10. Complexes (DPPE)Ni(Ar)(phthal) **9**

Table 8. Selected Bond Lengths (Å) and Angles (deg) for (DPPE)Ni(Ph)(phthal) **9a** and (DPPE)Ni(3-Me-Ph)(phthal) **9b**

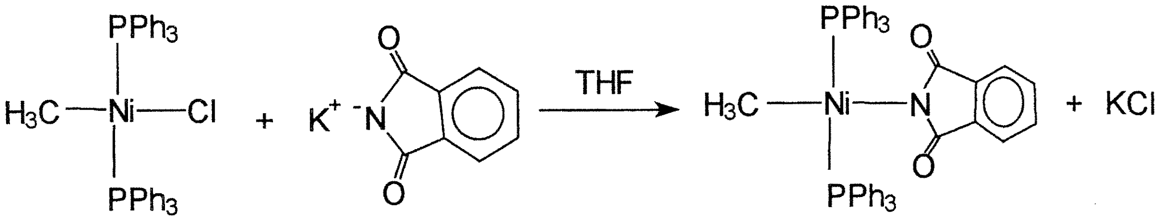
	9a	**9b**
Ni-N	1.9272(15)	1.930(3)
Ni-P1	2.2060(6)	2.2173(10)
Ni-P2	2.1261(5)	2.1266(10)
Ni-C9	1.9210(19)	1.911(4)
N-C1	1.363(2)	1.376(5)
N-C8	1.372(2)	1.360(4)
C1-C2	1.497(3)	1.505(5)
C7-C8	1.496(3)	1.506(5)
P1-Ni-P2	87.15(2)	86.70(4)
P1-Ni-N	96.72(5)	96.08(8)
P1-Ni-C9	169.88(6)	164.5(2)
P2-Ni-N	165.81(5)	166.9(9)
P2-Ni-C9	88.25(5)	86.6(3)
C9-Ni-N	89.91(7)	93.6(3)
Ni-N-C1-O1	-1.8(3)	0.2(6)
Ni-N-C8-O2	3.0(3)	-1.0(6)

The reaction of complex $(PMe_3)_2Ni(Me)Cl$, **4**, with potassium phthalimide affords the complex **10**, $(PMe_3)_2Ni(Me)(phthal)$, as yellow crystals which are thermally stable but air-sensitive (Eq. 43). Complex **10** has been characterized by ^1H, $^{13}C\{H\}$ and $^{31}P\{H\}$ NMR spectroscopy and elemental analysis. Singlet signals at 0.81 ppm in the ^1H spectrum and at –11.67 ppm in the $^{31}P\{H\}$ NMR spectrum are assigned to PMe_3. The ^1H NMR spectrum also displays a broad singlet at –0.61 ppm which confirms the presence of the Ni-Me group. Interestingly, the coupling of the methyl protons of Ni-CH_3 with the two phosphines was not observed, perhaps because of slow exchange of the PMe_3 group on the NMR time scale. We did not observe the signal for Ni-CH_3 in the $^{13}C\{H\}$ NMR spectrum perhaps because of the exchange of the PMe_3 ligands which broadens and hence weakens this signal.



(43)

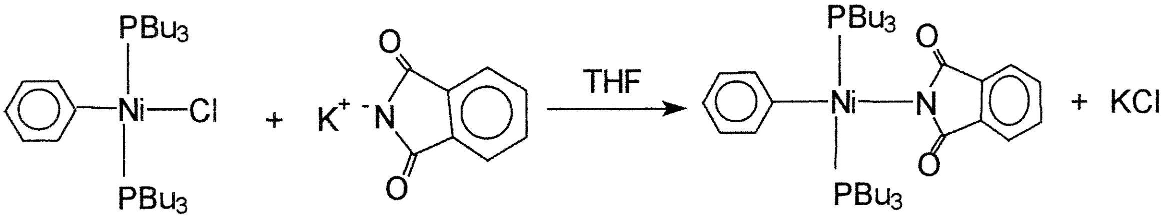
Since the intermediate compound $(PPh_3)_2Ni(Me)(Cl)$, **5**, is not stable at room temperature, compound $(PPh_3)_2Ni(Me)(phthal)$, **11**, was synthesized by reacting **5** with excess potassium phthalimide at –78°C (Eq. 44). The solution of complex **11** is not stable at room temperature, but the isolated solid is stable but air-sensitive. Complex $(PPh_3)_2Ni(Me)(phthal)$, **11**, has been characterized by $^{31}P\{H\}$ and ^1H NMR spectroscopy. A singlet resonance at 22.11 ppm in the $^{31}P\{H\}$ NMR spectrum and a singlet at 0.79 ppm in the ^1H NMR spectrum were assigned to the PMe_3 ligand; a broad singlet at –0.41 ppm in ^1H NMR spectrum was assigned to Ni-CH_3. As in the complex **10**, the broad signal might imply that there is a slow exchange of the PPh_3 ligands on the NMR time scale.



5 11

(44)

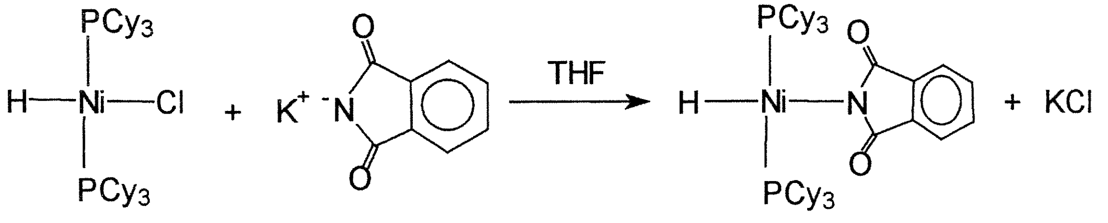
The complex $(PBu_3)_2Ni(Ph)(phthal)$, **12**, was obtained from the reaction of $(PBu_3)_2Ni(Ph)Cl$, **6**, with potassium phthalimide at room temperature (Eq. 45). A yellow powder was obtained in 52% yield, and has been characterized by $^{31}P\{H\}$ and ^{1}H NMR spectra. A singlet at 4.78 ppm in the $^{31}P\{H\}$ NMR spectrum was observed.



6 12

(45)

The hydrido phthalimidato complex **13** was prepared by reacting the intermediate complex $(PCy_3)_2Ni(H)Cl$ with excess potassium phthalimide (Eq. 46). Complex $(PCy_3)_2Ni(H)(phthal)$, **13**, has been characterized by $^{31}P\{H\}$, $^{13}C\{H\}$ and ^{1}H NMR spectra, elemental analysis and X-ray diffraction studies. A doublet at 34.7 ppm ($^{2}J_{P\text{-}H} = 57.8$) in the $^{31}P\{H\}$ NMR spectrum confirmed the coupling of the equivalent PCy_3 groups to Ni-H. Accordingly, the ^{1}H NMR spectrum of complex $(PCy_3)_2Ni(H)(phthal)$ displays a triplet at –22.9 ppm ($^{2}J_{P\text{-}H}=76.0$) which confirms that the hydride is coupled with two equivalent phosphorus nuclei about the metal center. The difference in the $^{2}J_{P\text{-}H}$ values obtained in the ^1H and ^{31}P {H} spectra is due to the incomplete decoupling of the proton-phosphine spins in the $^{31}P\{H\}$ spectra.



13

(46)

The crystal structure of complex $(PCy_3)_2Ni(H)(phthal)$, **13**, was solved in space group P-1. The full experimental details are given in the Experimental Section (X-ray Crystallography) and a complete listing of the structural parameters is given in Appendix IV. A summary of the data collection parameters and selected bond lengths and angles are found in Table 9 and Table 10, respectively. Complex **13** has two independent molecules in the unit cell. The value of R factor is higher that the value we expected (0.0823) because the size of the crystal used was too small. The ORTEP drawings of complex **13** are shown in Figure 11 and Figure 12. The expected *trans* square-planar geometry about nickel was observed, and the hydride ligand was located. The P1-Ni-P2 angle is ca. 156° which is much smaller than 180° because of the minimum steric requirements of the hydride group. The phthalimide group is rotated ca. 67° about the plane of the molecule. The significance of some other structural parameters such as the Ni-N bond lengths will be discussed later.

Table 9. Crystallographic Data of $(PCy_3)Ni(H)(phthal)$ **13**

Formula	$C_{44}H_{71}NNiO_2P_2$
Formula weight	766.67
Group space	P-1
a, Å	13.776(3)
b, Å	18.666(4)
c, Å	19.985(4)
β, deg.	104.37(3)
Volume, $Å^3$	4320.7(16)
λ, Å	1.54178
Z	4
Temperature, K	293(2)
μ, mm^{-1}	1.602
Independent reflections	16376
Measured reflections	16376
Range of hkl	$-16 \leq h \leq 16$ $0 \leq k \leq 22$ $-24 \leq l \leq 22$
$R(I>2\sigma(I))$	0.0823
wR2	0.1915
S	1.060

$$R = \Sigma (|| F_0 | - | F_c ||) / \Sigma (| F_0 |)$$

$$wR2 = \{ \Sigma [w (F_0^2 - F_c^2)^2] / \Sigma (F_0^2)^2 \}^{½}$$

$$S = \{ \Sigma [w (F_0^2 - F_c^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.}) \}^{½}$$

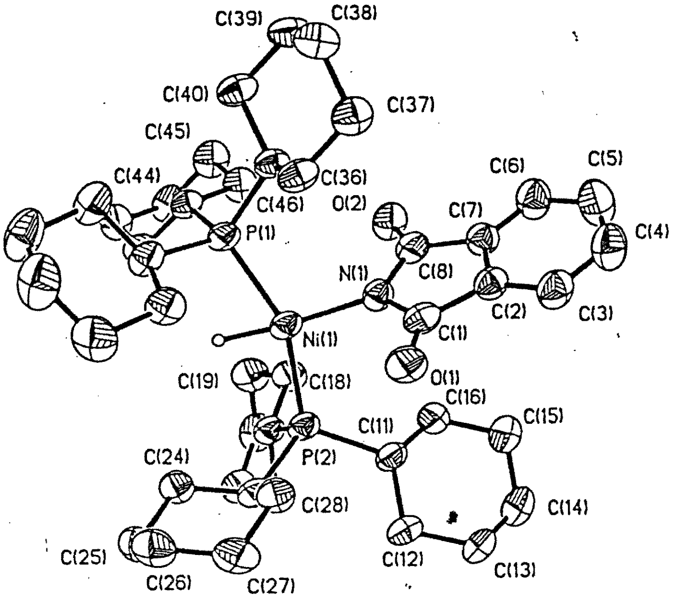


Figure 11. ORTEP drawing (1) of $(PCy_3)_2Ni(H)(phthal)$ **13** (molecule 1)

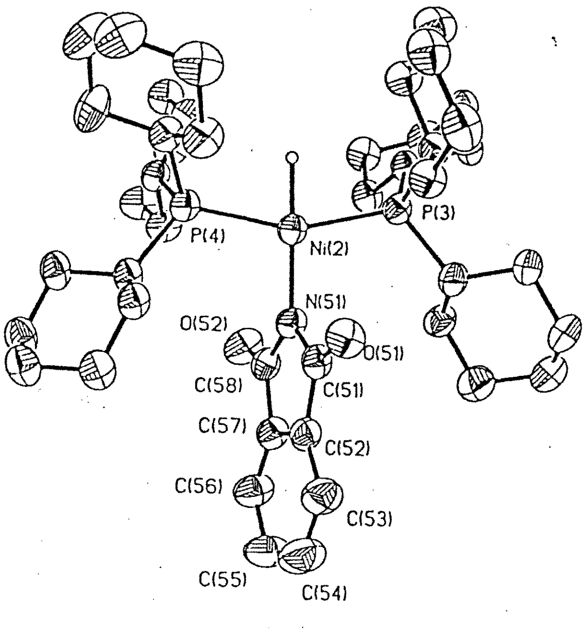


Figure 12. ORTEP drawing (2) of $(PCy_3)_2Ni(H)(phthal)$ **13** (molecule 2)

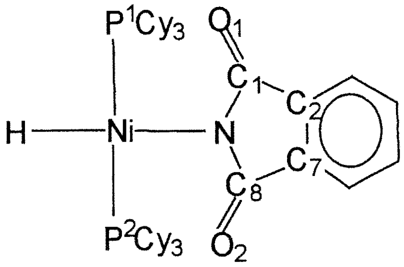


Figure 13. Complex $(PCy_3)_2Ni(H)(phthal)$ **13**

Table 10. Selected bond lengths (Å) and angles (deg) for $(PCy_3)_2Ni(H)(phthal)$ **13**

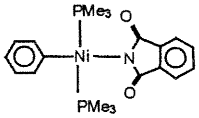
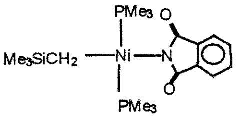
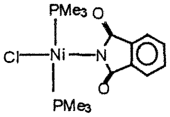
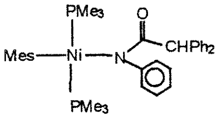
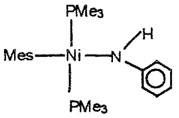
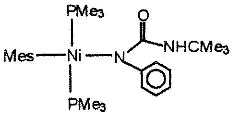
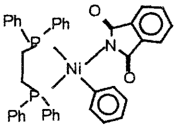
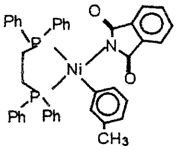
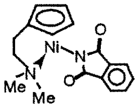
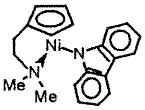
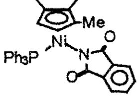
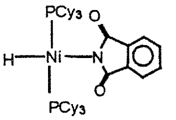
Molecule	1	2
Ni-N	1.925(4)	1.927(4)
Ni-P1	2.1765(17)	2.1779(16)
Ni-P2	2.178(2)	2.1798(16)
Ni-H	1.39(4)	1.48(4)
N-C1	1.377(6)	1.382(5)
N-C8	1.384(6)	1.385(6)
C1-C2	1.481(7)	1.484(7)
C7-C8	1.490(7)	1.469(7)
P1-Ni-P2	155.97(7)	155.55(7)
P1-Ni-N	101.85(13)	102.15(12)
P1-Ni-H	73.7(17)	77.0(17)
P2-Ni-N	102.18(13)	102.29(12)
P2-Ni-H	82.3(17)	78.5(17)
H-Ni-N	174.7(17)	179.1(17)
Ni-N-C1-O1	-0.6(7)	-0.5(7)
Ni-N-C8-O2	-0.3(8)	2.9(7)

2.3 Structural comparisons for the complexes $L_2Ni(R)(phthal)$

The reactivity of late transition metal amides is generally linked to the lability of the Ni-N bond as predicted by both the Hard-Soft-Acid-Base concept (a soft, late transition metal coordinating a hard amido ligand) and the expected destabilizing π-interactions between the amide ligand and the filled orbitals of the low-valent, electron-rich metal center.[41,3] Another approach to understanding the M-NR_2 bond is in terms of an electrostatic versus covalent bonding model which balances ionic and covalent σ-interactions and neglects π-effects.[54] Bergman et al.[55] have reported that the Ni-NR_2 bonds possess a strong electrostatic component and the stability of the various species depends strongly on the stablization of the negative charge on the NR_2 ligand. In the case of our Ni-imidato complexes, one reason for the enhanced stability of the Ni-N bond is the possibility of a Ni→N back bonding which appears feasible due to the energetically low-lying imidato-π^* orbital which makes π-back bonding from Ni to imidato possible.[56] Such stabilizing π-back bonding would strengthen the Ni-N bond and render it rather inert. The enhanced stability for transition metal complexes with anionic nitrogen ligands bearing electron-withdrawing groups and a planar spatial arrangement around the nitrogen to allow for an efficient delocalization of the lone pair was further proven with the structures of complexes **14**,[57] **15**,[57] **16**,[58] **17**,[59] **18**,[60] **19**,[61] **20**,[61] **21**[62] shown below. The Ni-N bond lengths in these nickel complexes are listed in Table 11.

Recall that the trans influence of a ligand weakens the bond trans to itself, and that usually the stronger σ-interaction a ligand has, the higher the trans influence is. On the other hand, certain ligands facilitate the replacement or the substitution of the ligand *trans* to themselves, and those ligands which are more effective at this type of labilization are said to have a higher *trans* effect.[53,]

Table 11. Ni-N Bond Lengths for Various Nickel Imidato Complexes

Complex		Ni-N(Å)	Reference
	**7a**	1.9317(18) 1.9353(18) 1.9375(19)	present work
	**14**	1.961(5)	57
	**15**	1.875(6)	57
	**16**	1.974(3)	58
	**17**	1.932(3)	59
	**18**	1.978(6)	60
	**9a**	1.9272(15)	present work
	**9b**	1.930(3)	present work
	**19**	1.907(3)	61
	**20**	1.898(5)	61
	**21**	1.895(4)	62
	**13**	1.925(4) 1.924(4)	present work

By comparing Ni-N bond lengths of complexes **7a**, **14** and **15** which have different *trans*-ligands (Ph, CH_2SiMe_3 and Cl) but the same PMe_3 and phthalimide ligands we find that the *trans*-influence of the different X groups on the Ni-N follows the order:

$$Cl < Ph < CH_2SiMe_3$$

These observations confirm the above-mentioned importance of the *trans* influence of the ligands in the lengthening of the M-ligand bonds.

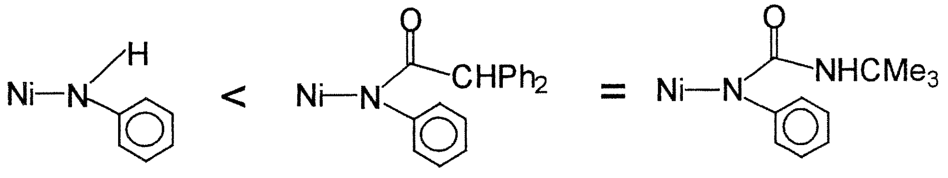
The value of Ni-N bond length in the nickel hydrido phthalimide complex **13** indicates that the hydride ligand has an intermediate *trans*-influence on Ni-N bond in contrast to the complexes **7a**, **14** and **15** which can be observed in Table 11.

The comparison of the Ni-N bond lengths can be extented to other Ni-phthal complexes. For example, compounds **7a** and **9a** both have the same phenyl and phthalimide groups, but different phosphine ligands (PMe_3-*trans* vs. DPPE-*cis*). We have noted that the trans influence of the aryl group in **7a** (Ni-N=1.935(2) Å) is somewhat greater than that of the phosphine in **9a** (Ni-N=1.927(2) Å). Thus, if we assume a direct relationship between the Ni-N bond length (a thermodynamic parameter) and the rate of C-N reductive elimination (a kinetic parameter), we can propose that the relative rates of the reductive elimination reactions should follow the order shown below. This assertion will be tested in the studies of reductive elimination reactions (see chapter 3).

$(PMe_3)_2Ni(CH_2SiMe_3)(phthal)$ **14** > $(PMe_3)_2Ni(Ph)(phthal)$ **7a** >

$(DPPE)_2Ni(3\text{–}Me\text{–}Ph)(phthal)$ **9b** = $(DPPE)_2Ni(Ph)(phthal)$ **9a**

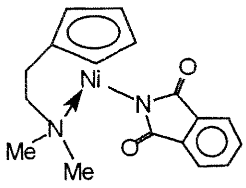
An unexpected observation was made when we compared the Ni-N bond lengths in complexes **16**, **17** and **18** all of which have the same trans-ligand (Mes) but different amido ligands. The order of the Ni-N bond lengths is shown below:



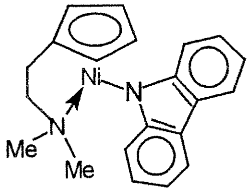
17 **16** **18**

As stated earlier, the presence of electron withdrawing groups on amide ligands should increase their stabilities. For instance, the relatively strong (i.e., short) Ni-N bonds in our nickel-imidato complexes (in which there are two highly electron withdrawing groups on the N atom) are due to the possibility of a Ni→N back bonding which would strengthen the Ni-N bond. According to this logic, the presence of only one electron-withdrawing group on the amido N should cause a weakening (i.e., lengthening) in the Ni-N bond length. Contrary to this expectation, the NHPh ligand in **17** forms a shorter Ni-N bond than the ligands [N(Ph)C(O)CHPh$_2$] in **16** and [N(Ph)C(O)N(H)CMe$_3$] in **18**. The cause of this anomalous observation is not known at this stage.

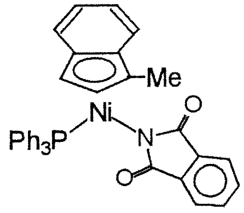
Complexes **19** and **20** have the same Cp^N group but different N-ligated, phthalimido and carbazolato ligand. From Table 11 we see that both complexes have very similar Ni-N bond lengths. This comparison indicates that nitrogen ligands bearing two carbonyl or phenyl groups have the same efficiency in enhancing the stability of the Ni-N bond.



Cp^{N}Ni(phthal) **19**



Cp^{N}Ni(carbazolato) **20**



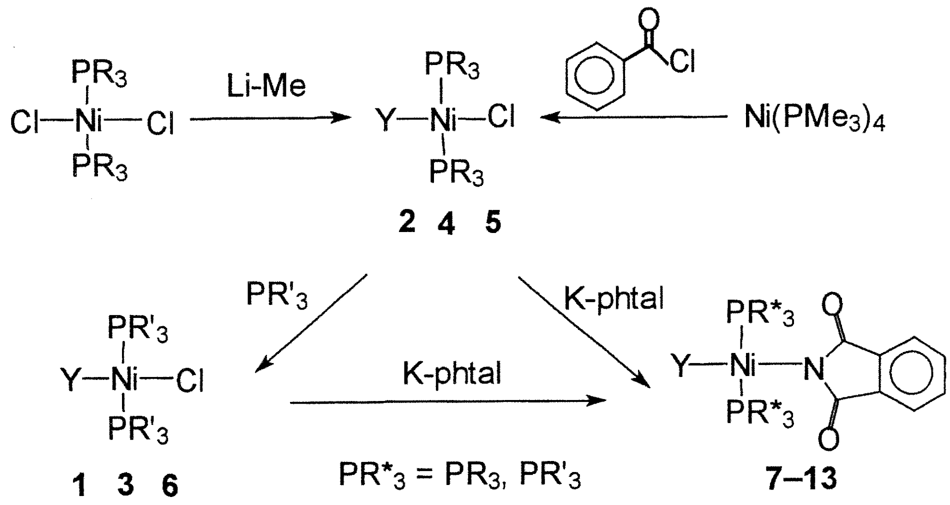
(1-Me-Ind)Ni(PPh$_3$)(phthal) **21**

Next we compare the Ni-N bond length in phthalimido complexes with different auxiliary ligands in order to determine their influence on the Ni-N bond. Let us take, for instance, complexes **19**, **21**, **7a**, and **13** which have the phthalimido ligand in common but while the first two have fairly similar auxiliary ligands and structures, complexes **7a** and **13** have a different set of ligands. It is interesting to note that the Ni-N bond lengths are only marginally different in **19** (1.907(3) Å) and **21** (1.895(4) Å), while the Ni-N bond is significantly longer in **7a** (1.9348(18) Å) and **13** (1.925(4) Å). This "discrepancy" demonstrates, once again, the importance of the trans influence of the auxiliary ligands, which seems to follow the order Cp or Ind < H < Ph, although it is evident this comparison is not completely legitimate because the remaining auxiliary ligands (e.g., PMe$_3$, PCy$_3$, Cp, Ind) are not identical. These results indicate, perhaps, that the target complexes such as **7** might be more susceptible to C-N reductive elimination reactions because of their longer Ni-N bonds. (Here, we are assuming again that the thermodynamic parameters such as bond lengths can be reflected in kinetic parameters such as bond strengths and labilities.) This point is pursued in the following chapter which describes the studies of the reductive elimination reactions involving complexes **7**, **9**, **10**, **11**, **13**, **14**, and **22**.

2.4 Summary

We have prepared six precursor complexes and seven nickel-phthalimide complexes using the routes shown in Scheme 17. All intermediate complexes are air-sensitive, but putting phthalimide on Ni makes them more air-stable. Thus, the phthalimide complexes **7**, **8**, **9**, **13** are stable to air, and **10**, **11**, **12** are only somewhat air-sensitive.

Scheme 17



PR*$_3$ =	PMe$_3$,	PMe$_3$,	DPPE,	PMe$_3$,	PPh$_3$,	PBu$_3$,	PCy$_3$
Y =	Ar,	Ph$^-$(C=O),	Ar,	Me,	Me,	Ph,	H
	7	**8**	**9**	**10**	**11**	**12**	**13**

Complexes **1-13** have been characterized by NMR spectroscopy, while complexes **7a**, **9a**, **9b** and **13** have also been characterized by X-ray diffraction studies.

The structural data obtained have been compared to other nickel-imidato and nickel-amido complexes in order to evaluate the importance of the N-substituents and the trans influence of the auxiliary ligands on the Ni-N bond lengths. The following chapter aims to determine whether these thermodynamic parameters can be used to assess kinetic questions such as the rate of C-N reductive elimination reactions in these complexes.

CHAPTER 3

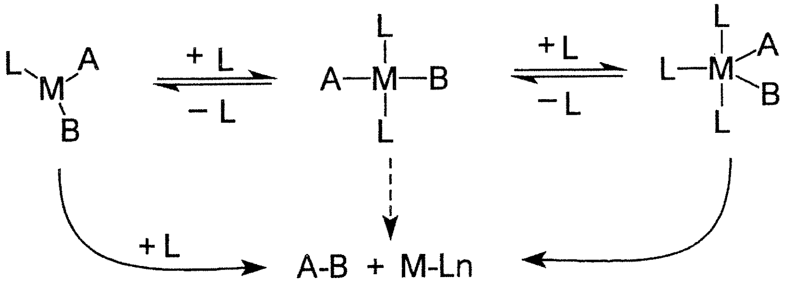
Studies of Reductive Elimination (C-N Bond Formation)

Low-valent late-transition-metal (Ni and Pd) amido complexes are highly reactive molecules involved in some catalytic reactions such as the palladium and nickel-catalyzed amination of aryl halides.[30,40] The C-N bond-forming reductive elimination reaction is essential for the further development of the latter catalytic processes. Hartwig has reported that C-N bond forming reductive elimination reactions are accelerated by electron-withdrawing groups on the Pd-bound aryl group and by electron-donating groups on the amido ligand, suggesting that the aryl group acts as an electrophile and the amido ligand acts as a nucleophile.[23] Since the phthalimide group we are studying bears electron-withdrawing groups on the N atom, the phthalimide ligand should resist reductive elimination. This point will be demonstrated in the following sections.

3.1 Attempts at catalysis

As we mentioned in chapter 2, $Ni(PPh_3)_4$ readily undergoes oxidative addition reactions because the dissociation of a PPh_3 ligand is facile for this bulky ligand. In contrast, $Ni(PMe_3)_4$ does not promote oxidative addition since PMe_3 is less bulky and more strongly bound to the Ni than PPh_3. In the case of reductive elimination reactions, literature reports have shown that 16-electron, d^8 complexes undergo reductive elimination reactions more easily from 3- or 5-coordinate intermediates[63] as shown in Scheme 18. Therefore, it is reasonable to conclude that the reductive elimination of Ar-phthal in our system is likely to proceed from a 3-coordinate species of the type LNi(Ar)(phthal) when L is the bulky PPh_3, while five-coordinate species of the type $L_3Ni(Ar)(phthal)$ are likely to be involved when L is the smaller PMe_3 ligand.

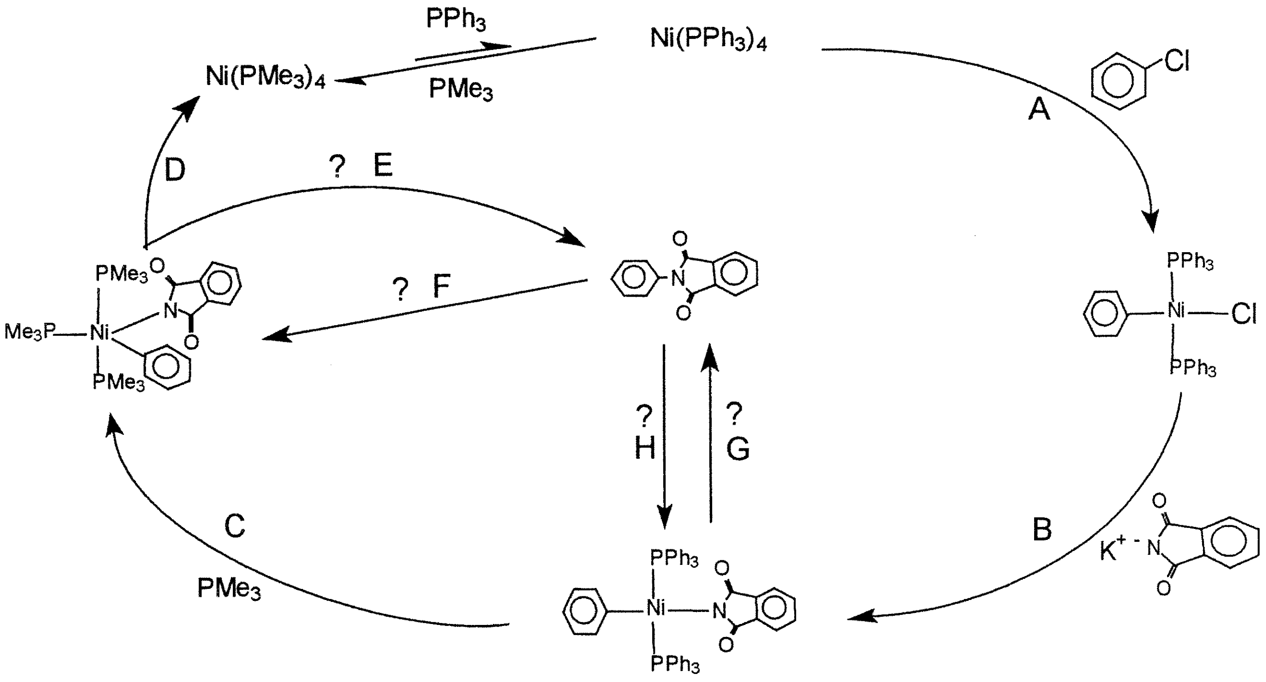
Scheme 18

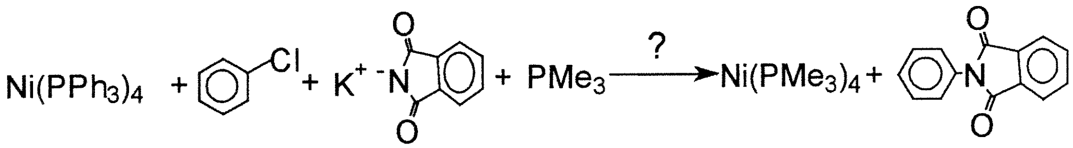


On the basis of the above reasoning, we selected $Ni(PPh_3)_4$ as the starting point for the catalysis in order to facilitate the oxidative addition of phenyl chloride. The putative Ni(II) intermediate arising from the oxidative addition would then react with potassium phthalimide to form the Ni-N bond; subsequently, the excess PMe_3 would serve to replace the PPh_3 ligands from $(PPh_3)_2Ni(Ph)(phthal)$ to give the above-mentioned 5-coordinate species. The latter species would then undergo the reductive elimination reaction as shown in the proposed catalytic cycle depicted in Scheme 19.

The results presented in chapter 2 indicate that the reactions shown in paths A and B (Scheme 19) should work well, but the likelihood that paths C-H would take place was not known. We began studying the feasibility of the catalytic system by testing various ratios of the reactants in order to determine the optimal conditions (Eq. 47). The best ratio of reactants to give Ni(0) species was found to be 1 : 50 : 25 : 60 ($Ni(PPh_3)_4$: Ph-Cl : K-phthal : PMe_3); under these conditions, we could observe the formation of $Ni(PMe_3)_4$ within 2h at room temperature as monitored by $^{31}P\{H\}$ NMR spectroscopy. However, monitoring the organic products of this reaction by TLC and GC did not show the formation of the expected product Ph-phthal; instead we found that only the compound biphenyl (Ph-Ph) had formed.

Scheme 19

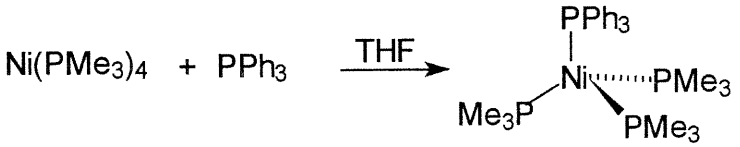




(47)

equiv:	1.0	100	50	5
equiv:	1.0	670	10	2
equiv:	1.0	500	100	4
equiv:	1.0	500	100	20
equiv:	1.0	50	50	20
equiv:	1.0	50	25	60

The absence of the desired product Ph-phthal might be related to the fact that the C-N bond formation is not favoured or that the desired product further reacts under the reaction conditions (e.g., via paths F or H). Another complication in the catalysis is related to the regeneration of the catalyst via the reaction $Ni(PMe_3)_4 + PPh_3 \rightarrow Ni(PPh_3)_4$ which does not go to completion, as shown in Equation 48. The formation of the species $(PMe_3)_3Ni(PPh_3)$ was confirmed by the detection of a quartet at ca. 36 ppm and a doublet at ca. -25 ppm ($^2J_{P-P}$ ca. 26 Hz) in the $^{31}P\{H\}$ spectrum.



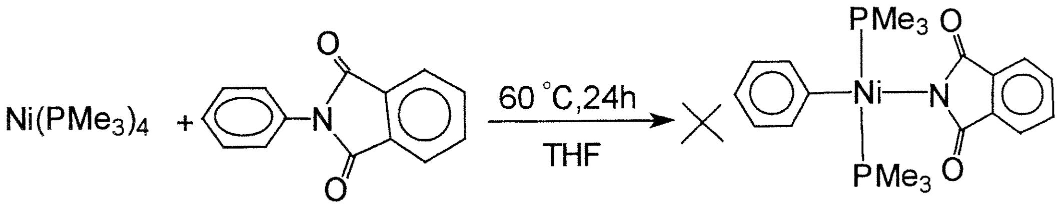
(48)

Therefore, it was evident that the catalytic cycle could not be achieved with the present system. Although the failure to regenerate $Ni(PPh_3)_4$ is important in the long term, the more important problem is the fact that C-N bond formation does not seem to occur. In order to understand the main cause of this problem we set out to study in detail the reaction shown in Equation 47. The following section describes our studies directed at solving this problem.

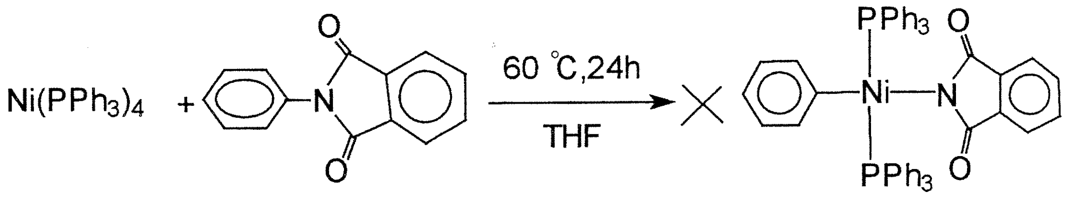
3.2 Mechanistic studies

3.2.1 The potential problem of oxidative addition of aryl-phthalimide

Since aryl halides (Ar-X) can be oxidatively added to some Ni(0) compounds such as $Ni(PPh_3)_n$ and since we consider phthalimide as a pseudo-halogen, we wondered if the oxidative addition of aryl-phthalimide would also be feasible. We carried out some experiments aimed at testing the feasibility of this oxidative addition; if successful, this route would indicate that the reductive elimination reaction is thermodynamically inaccessible, that is to say that path H/F is more likely to occur than path D/E. To examine this question, we reacted $Ni(PMe_3)_4$ or $Ni(PPh_3)_4$ with phenyl-phthalimide but all attempts at inducing the oxidative addition (Eq. 49, 50) failed, indicating that this reaction is either thermodynamically inaccessible (i.e. $\Delta G>0$) or that it has a very large energy of activation. What is important for our catalytic studies is that these results demonstrate that if the aryl-phthalimide is produced in the catalysis, it will be stable and will not undergo oxidative addition of the C-N bond. Thus, the absence of C-N products must be due to the difficulties in the reductive elimination step.



(49)



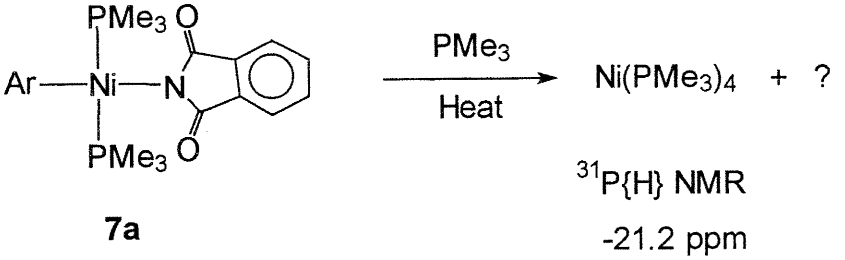
(50)

3.2.2 Examination of the reductive elimination step

With the aryl-phthalimide complexes at hand, we carried out a number of experiments aimed at testing the feasibility of the reductive elimination of aryl-phthalimide compounds. Since the bis(phosphine) complexes $(PR_3)_2Ni(phthal)(Ar)$ do not undergo spontaneous reductive elimination, we need to add excess PR_3 to induce a reductive elimination via 5-coordinate intermediates.[63] The following three sections present the results of these studies with $(PMe_3)_2Ni(R)(phthal)$, (DPPE)Ni(Ar)(phthal), and $(PPh_3)_2Ni(R)(phthal)$.

Reductive elimination reactions of $(PMe_3)_2Ni(R)(phthal)$

Reacting the complexes **7a** (R = Ph), **7b** (R= 3-Me-Ph), and **7c** (R= 2,5-Me_2-Ph) with excess PMe_3 (at room temperature or higher) led to reactions which formed $Ni(PMe_3)_4$ which was detected by ^{31}P NMR spectroscopy. (Eq. 51).



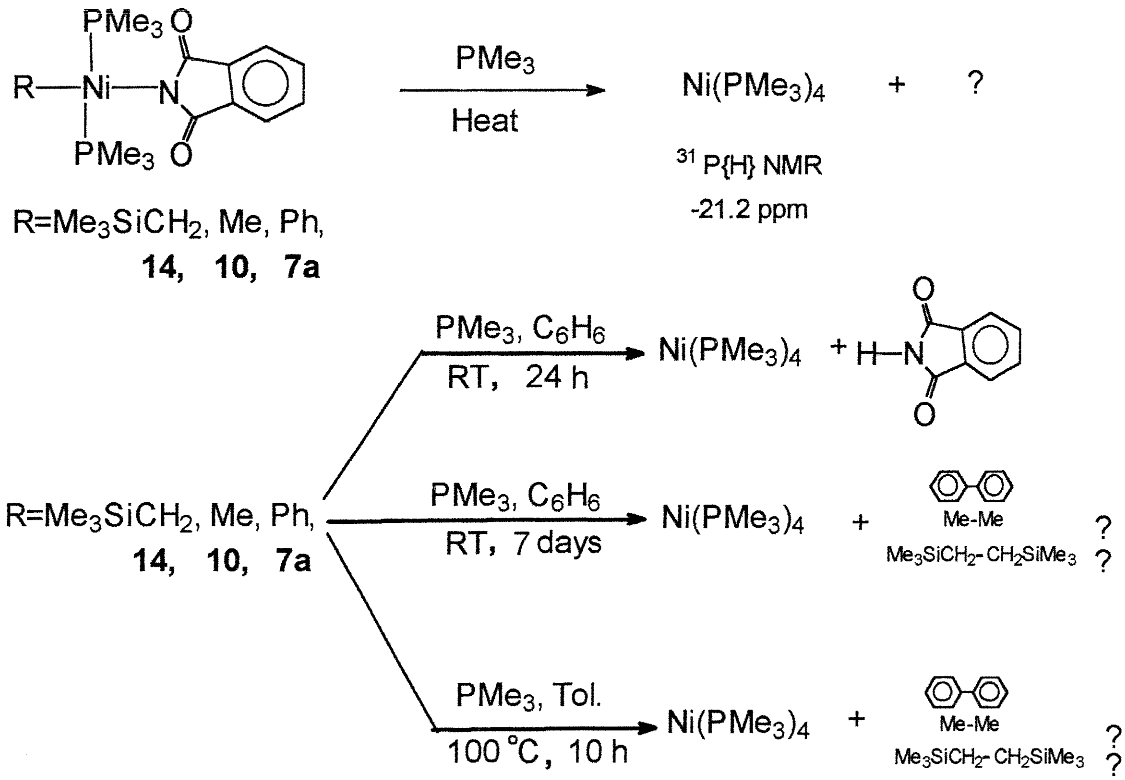
7a

(51)

For instance, 10 equiv. of PMe_3 were added to the solution of $(PMe_3)_2Ni(Ar)(phthal)$ in 20 mL THF, then the reaction was monitored by $^{31}P\{H\}$ NMR spectroscopy over 48 h until $Ni(PMe_3)_4$ was observed. The final mixture was then analyzed by ^1H NMR spectroscopy and TLC and compared to the authentic products Ar-phthal purchased from commercial sources or prepared by us. The organic products of the reaction were then isolated by flash column chromatography and analyzed by GC and mass spectroscopy. In no case were observed products arising from a C-N bond forming step.

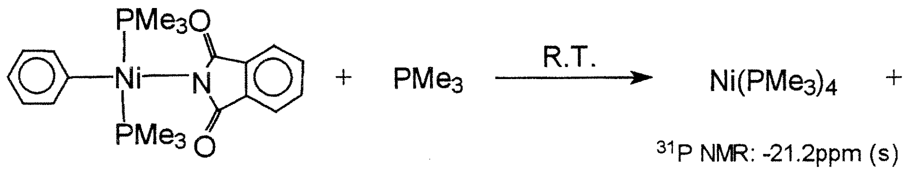
Similar results were obtained from the reactions of the complexes $(PMe_3)_2Ni(R)(phthal)$ (R= Me, CH_2SiMe_3). As before, the identity of the organic products of these reactions was confirmed by monitoring the products of the reactions illustrated in Scheme 20 and by comparing the products to authentic samples purchased from commercial sources, including phenyl-phthalimide, methyl-phthalimide and Me_3SiCH_2-phthalimide. These products have been characterized by NMR, TLC, GC and mass spectrometry.

Scheme 20



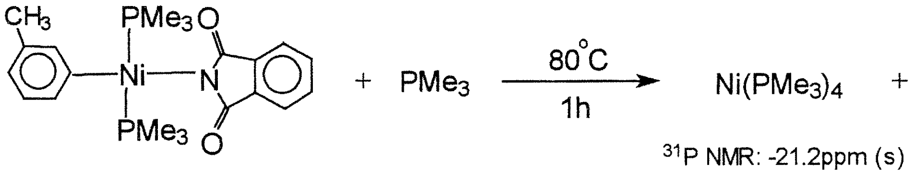
The results have shown us that the reaction of PMe_3 with the nickel-phthalimide compounds studied (**7a**, **10** and **14**) did not give the product of the C-N bond formation reaction from the three complexes. The products arising from H-N and C-C bond formations were observed instead depending on the reaction conditions. For example, within 24 h we obtained phthalimide as the major product (N-H bond formation) whereas after 7 days at room temperature or 10 h at 100°C the product of the reaction of complex **7a** was biphenyl (Scheme 20). We could not confirm the formation of Me_3SiCH_2-CH_2SiMe_3 which might have formed in the reactions of the complexes **14** because we did not have the authentic sample, but the results monitored by TLC showed that the two products are quite like C-C bond formations comparing with biphenyl.

It is interesting to note that the formation of $Ni(PMe_3)_4$ from the complex *trans*-$(PMe_3)_2Ni(Ar)(phthal)$ is slower when the Ar group is a substituted Ph like 3-Me Ph or 2,5-Me_2-Ph. That is, the order of reaction rate is as follows: Ph > 3-Me-Ph > 2,5-Me_2-Ph as shown in Equations 52, 53 and 54.



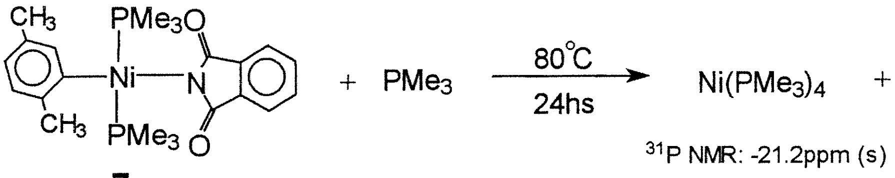
7a

(52)



7b

(53)



7c

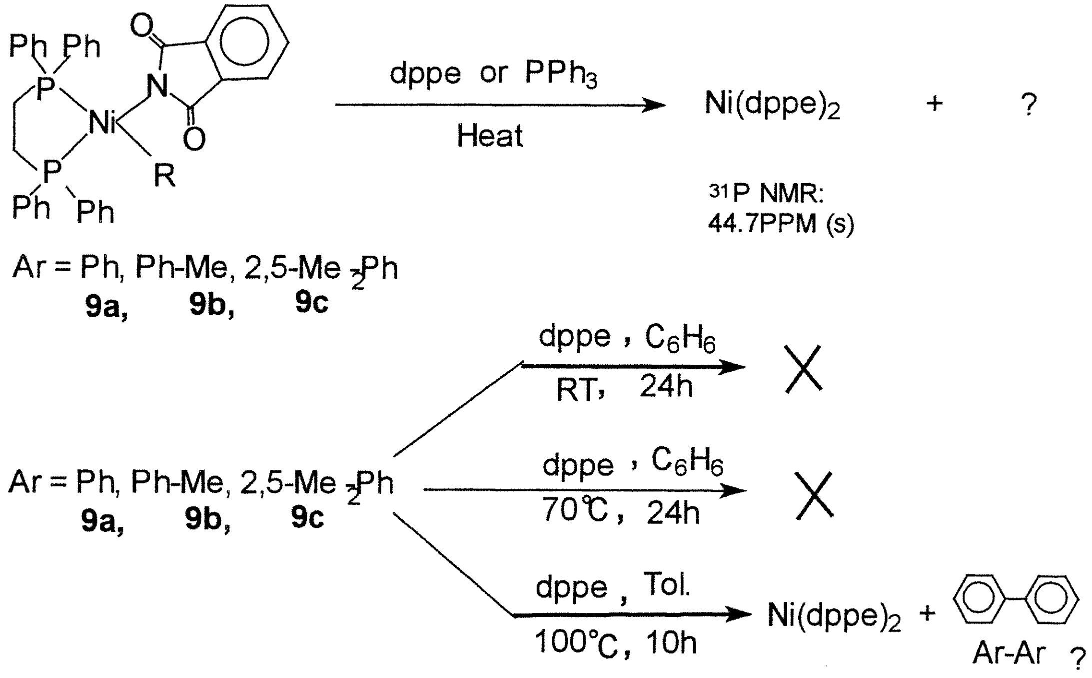
(54)

These relative rates may be explained as follows. If we consider that the reductive elimination step takes place from a 5-coordinate intermediate such as $(PMe_3)_3Ni(Ar)(phthal)$, then the coordination of another ligand is more or less like a substitution reaction. The smaller and the more basic the incoming ligand (e.g., PMe_3), the faster the substitution reaction will take place. On the other hand, the more bulky the ligands around the Ni center, then the coordination of the fifth ligand will be hindered. This would mean that if we use Ph-Me instead of Ph, then the excess PMe_3 has more difficulty approaching the Ni center and so the reductive elimination is slow. So our results indicate that this system undergoes reductive elimination by association of a ligand.

Reductive elimination reactions of (DPPE)Ni(Ar)(phthal)

As shown in Scheme 21, when we heated the mixtures of complex **9** and excess DPPE or PPh_3 at high temperature (T= 100 °C) in the presence of excess DPPE, the complexes underwent reductive elimination to give Ni(0) species. As in the previous reactions, the organic product from the reaction of complex **9a** was always biphenyl, and no C-N bond formation was observed. The organic products from the reactions of complexes **9b** and **9c** also appeared to be Ar-Ar on the basis of a comparison of their TLC traces to that of biphenyl.

Scheme 21

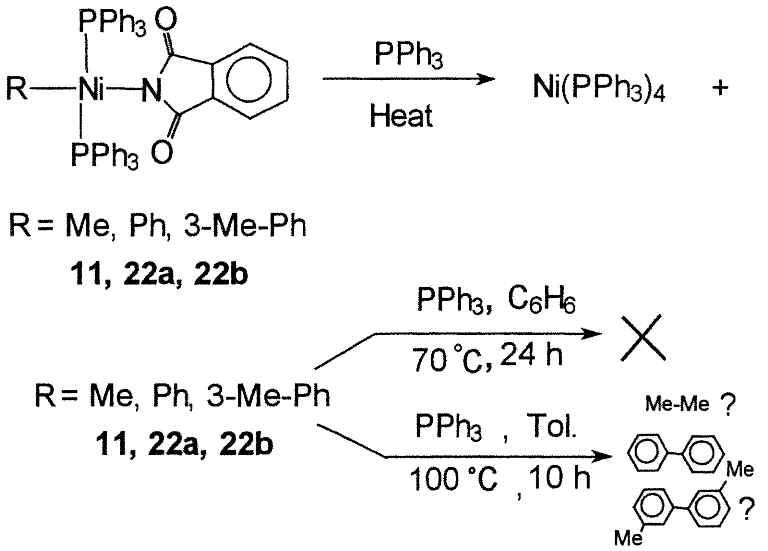


The rate of the reductive elimination from these *cis*-complexes is more sluggish (no reductive elimination occurs unless the mixtures are heated to 100 °C) than with the *trans*-complexes such as $(PMe_3)_2Ni(Ph)(phthal)$ for which the reaction proceeds at room temperature. The reasons for this include the chelating nature and the bulkiness of the DPPE ligand, which would hinder the formation of the 3- and 5-coordinate intermediates. Moreover, the stronger Ni-N bond in the DPPE complex, as reflected in the shorter Ni-N bond, might contribute to the inertness of the complex toward reductive elimination.

Reductive elimination reactions of $(PPh_3)_2Ni(R)(phthal)$

The reductive elimination reactions of complexes **11** and **22** had to be followed by monitoring ($^{31}P\{H\}$ NMR spectroscopy) the disappearance of the Ni(II) starting materials, because the resulting $Ni(PPh_3)_4$ can not be detected (the $^{31}P\{H\}$ NMR signals are lost in the baseline because of the dissociation/exchange of PPh_3). As shown in Scheme 22, here too no reductive elimination takes place below 100 °C. The product of reductive elimination from complex **22a** is once again biphenyl, and the products from complexes **11** and **22b** are presumed to arise from the C-C bond formation reaction.

Scheme 22



3.2.3 Summary

The results of the stoichiometric reactions presented in this chapter show that the PMe_3-ligated nickel-phthalimide complexes are more prone to reductive elimination than the analogous PPh_3- and DPPE-ligated complexes. The relative ease of these reactions allows us to test whether the rates of these reductive elimination reactions are related to the Ni-N bond distances and other factors (e.g., sterics, chelation, etc.). As mentioned in section 2.3, we assumed that the rate of the C-N reductive elimination should be in the order **14** > **7a** > **9b** = **9a**. The results obtained here are in accord with the above assertion regarding the relationship between the rate of reductive elimination reaction and the Ni-N bond lengths even though no C-N bond formation has occurred in the reactions studied.

The reductive elimination reactions we have studied did not give the desired products arising from C-N bond formation; instead, the organic products arise from either H-N or C-C bond; in most cases, we were unable to determine the fate of the phthalimide moiety.

CHAPTER 4

Conclusion

This study has shown that nickel imidato complexes of the type $L_2Ni(X)(phthal)$ (L=PMe_3, PCy_3, ½DPPE, PBu_3; X=Ph, 3-Me-Ph, 2,5-Me_2-Ph, Ph-(C=O), Me, H) can be synthesized by relatively straightforward procedures. The characterization of these compounds by NMR spectroscopy was also straightforward, although in some cases the multiplicities of the signals were not well understood. For instance, the ^1H NMR spectra of complexes $(PMe_3)_2Ni(Me)X$ (X=Cl, **4**; phthal, **10**) showed a singlet resonance for the Ni-CH_3 protons; the absence of $^3J_{P\text{-}H}$ coupling might be due to exchange of PMe_3, but this point has not been clarified in our work. In complexes $(PPh_3)_2Ni(Me)X$ (X=Cl, **5**; phthal, **11**) the signal for Ni-CH_3 is a broad singlet; this broadening might be related to the distorted structure (intermediate between square planar and tetrahedral), but again this point has not been clarified in our studies.

The determination of the solid state structures for four of the new compounds have established the influences of the different R groups and the different phosphine ligands on the Ni-N bond length. In general, the aryl groups seem to exert the highest *trans* influence, even higher than the hydride and phosphine ligands. Comparison of the Ni-N bond lengths obtained from the present studies or those reported for other nickel-imidato complexes has shown that the relationship between the bond length and the nature of the N-substituents is not straightforward. In some cases, electron withdrawing groups have a significant stabilizing effect while in others (e.g., with HNPh vs. phthal) there is no obvious destabilization caused by the absence of strongly electron withdrawing groups. This observation is contrary to the notion that the reason for the enhanced stability of nickel-imidato complexes is the possibility of a Ni→N back bonding which would strengthen the Ni-N bond.

We have tested the reductive elimination reactions of some of the newly prepared nickel-phthalimide complexes in an attempt to develop a method for C-N bond formation reactions. The catalytic tests and the stoichiometric reactions described in chapter 3 have shown that our systems give C-C, as opposed to C-N, reductive elimination and that in a stoichiometric, as opposed to a catalytic fashion. We have observed that PMe_3-ligated nickel-phthalimide complexes are more prone to reductive elimination than the PPh_3 and DPPE analogues; we have put forth (chapter 3) a tentative explanation for this difference in reactivity.

A number of observations about the relative rates of the reductive elimination reactions in our Ni-phthal imply that this system undergoes reductive elimination by the association of a phosphine ligand. This would mean that future work should focus on using bulky ligands such as $P(o\text{-tolyl})_3$, (o-biphenyl)$P(t\text{-Bu})_2$, or (o-biphenyl)PCy_2 which might change the intermediate to a 3-coordinate complex, and this might help the reductive elimination at least for more substituted aryl cases. As well, these ligands have the potential to facilitate the oxidative addition of Ar-Cl because if L is sufficiently large, there will not be $L_4Ni(0)$ but rather $L_3Ni(0)$ or might even $L_2Ni(0)$.

Although we did not succeed in developing a catalytic system for forming C-N bonds, our observations from the stoichiometric reactions and from the structural studies have given us a better understanding of the stabilities of the Ni-phthal complexes. We have confirmed also that the reductive elimination step is the most difficult problem to solve. Future work should focus on studying the conditions under which this step can be facilitated.

CHAPTER 5

Experimental Section

5.1 General

All reactions were performed under an inert atmosphere using standard Schlenk techniques or in an inert atmosphere N_2 glovebox. Diethylether, hexane, benzene, toluene and THF were distilled from purple solutions of sodium and benzophenone under nitrogen.

The syntheses of some of the intermediate complexes such as $(PPh_3)_2Ni(Ar)Cl$,[64] $(PPh_3)_2Ni(Ar)(phthal)$,[57] $(PCy_3)_2Ni(H)Cl$,[65-67] $(PPh_3)_2NiCl_2$,[68] and $(PMe_3)_2NiCl_2$[69] were carried out according to the procedures described in the thesis of Sophie Beaudoin[57].

All NMR spectra were obtained using a Bruker 400 spectrometer. All samples were run in benzene-d_6 in 5 mm NMR tubes. The ^{13}C NMR spectra, both coupled and decoupled, were recorded at 100.6 MHz. $^{31}P\{H\}$ NMR spectra were recorded at 162 MHz using 85% H_3PO_4 (0.00 ppm) as the external standard. The elemental analyses were performed by Laboratoire d'Analyse Élémentaire Université de Montréal.

5.2 X-Ray Crystallography

All X-ray quality crystals were obtained by the slow diffusion of hexane into a concentrated solution of THF. The crystals were then filtered, dried, and examined under a microscope for selection. The crystals to be studied were then attached to a glass fiber and transferred under a stream of nitrogen to the appropriate diffractometer.

The crystal data for **9a** and **9b** were collected on a Bruker AXS SMART 2K diffractometer using graphite-monochromated Cu Kα radiation at 293(2)K (SMART[70] software). The cell refinement and data reduction were carried out using SAINT.[71] The refinement of absorption data were done by using SADABS program.[72]

The crystal data for **13** was collected on an Enraf-Nonius CAD-4 diffractometer. The data was collected with a graphite-monochromated Cu Kα radiation, the refinement of the cell parameters was done using CAD-4 software[73] on 25 standard reflections, and the data reduction used NRC-2 and NRC-2A.[73] The absorption correction was done using ABSORP in NRCVAX.[74]

The data collection for complex **7a** was carried out on a Bruker CCD SMART diffractometer equipped with Mo Kα radiation at 173(2)K.[70] (at National Research Council Ottawa) We chose Mo radiation to analyze complex **7a** because there is a rotational disorder for PMe_3. The peaks for each of the PMe_3 groups were found from the electron density map. The P-C distances were fixed, whereas the C-P-C angles were restrained by fixing the C-C distances. Site occupancies were determined after refinement with isotropic thermal motion parameters fixed at 0.06 $Å^2$. The unit cell data were determined by using standard 60 frames collections. The refinement and absorption correction were done using Bruker empirical SADABS program. [72]

All structures were solved by direct methods using SHELXS97[75] for **7a**, **9a** and **9b**, SHELXS96[76] for **13**, and the refinements were done on F^2 by full–matrix least squares. All non-hydrogen atoms were refined anisotropically, while the hydrogen (isotropic) were constrained to the parent atom using a riding model. Additional crystallographic data on the structural determination of complexes **7a**, **9a**, **9b** and **13** are listed in chapter 2 and appendixes I, II, III and IV.

6.3 Synthesis of complexes

$(PMe_3)_2Ni(Ar)Cl$ (Ar = Ph, **1a**; 3-Me-Ph, **1b**; 2,5-Me_2-Ph, **1c**)

A 250 mL, round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 0.263 mmol of $(PPh_3)_2Ni(Ar)Cl$ **23**[64] (192 mg, **23a**; 195 mg, **23b**; 199 mg, **23c**) and 20 mL of Et_2O. To this yellow suspension was added dropwise 80 mg of PMe_3 (1.0515 mmol, 4.0 equiv.). The resulting clear yellow solution was stirred at room temperature for 1 h, and then evaporated at reduced pressure to half volume. 20 mL of hexane was added to this solution and the resulting yellow precipitate was filtered and washed twice with hexane and vacuum dried. $(PMe_3)_2Ni(Ar)Cl$ was obtained as an orange crystalline solid (yields: **1a**=77%, **1b**=71%, **1c**=70%).

$^{31}P\{H\}$ NMR: **1a:** -14.77(s); **1b:** -14.85(s); **1c:** -13.93(s).

^{1}H NMR: **1a:** 0.87(s, CH_3 of PMe_3), 6.75-7.45(m, 5H of Ar); **1b:** 0.80(s, CH_3 of PMe_3), 2.16(s, CH_3 of 3-Me-Ph), 6.60-7.31(m, 4H of Ar); **1c:** 0.82(s, CH_3 of PMe_3), 2.22 & 2.72(s, CH_3 of 2,5-Me_2-Ph), 6.65-7.38(m, 3H of Ar).

$^{13}C\{H\}$ NMR: **1a:** 9.86(s, 6C of PMe_3), 118.99(s, 1C of Ph), 131.47(s, 2C of Ph), 133.52(s, 2C of Ph), 153.15(s, 1C of Ni-C); **1b:** 9.90(s, 6C of PMe_3), 18.90(s, CH_3 of 3-Me-Ph), 119.92(s, 1C of Ar), 123.89(s, 1C of Ar), 126.47(s, 1C of Ar), 130.58(s, 1C of Ar), 134.05(s, 1C of Ar) 152.82(s, 1C of Ni-C).

$(PMe_3)_2Ni(Ar)(phthal)$ (Ar = Ph, **7a**; 3-Ph-Me, **7b**; 2,5-Me_2-Ph, **7c**)

A 250 mL, round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 343 mg of potassium phthalimide (1.852 mmol, 3.0 equiv.) and 20 mL of THF. To this solution at room temperature was added slowly a yellow solution 0.617 mmol of $(PMe_3)_2Ni(Ar)Cl$ (200 mg, **1a**; 207 mg, **1b**; 214 mg, **1c**) in 20 mL of THF. The reaction was stirred at room temperature for 2 h to give a pale yellow solution which was filtered and evaporated under vacuum. Addition of 15 mL of toluene gave a yellow suspension. Again, the solution was filtered and the toluene was evaporated to dryness. $(PMe_3)_2Ni(Ar)(phthal)$ was obtained as a yellow powder after recrystallization from THF/hexane (1:3) in yields: **7a**=62%, **7b**=60%, **7c**=60%. The analytical and crystallographic samples were obtained by slow diffusion of hexane into a concentrated solution of the yellow solid in THF.

$^{31}P\{H\}$ NMR: **7a:** -13.67(s); **7b:** -13.73(s); **7c:** -13.02(s).

^{1}H NMR: **7a:** 0.66(t, $^{2}J_{P-H}$=3.5, CH_3 of PMe_3), 6.80-7.73(m, 9H of Ar and phthal); **7b:** 0.69(t, $^{2}J_{H-H}$=3.5, CH_3 of PMe_3), 2.17(s, CH_3 of 3-Me-Ph), 6.64-7.75(m, 8H of Ar and phthal); **7c:** 0.66(t, $^{2}J_{H-H}$=3.5, CH_3 of PMe_3), 2.21 & 3.08(s, CH_3 of 2,5-Me_2-Ph), 6.66-7.73(m, 7H of Ar and phthal).

^{13}C NMR: **7a:** 9.69(t, $^{2}J_{P-C}$=13.5, 6C of PMe_3), 117.98(s, 2C of phthal), 119.11(s, 1C of Ar), 123.89(s, 2C of Ar), 128.65(s, 2C of phthal), 133.71(s, 2C of Ar), 135.57(s, 2C of phthal), 153.57(t, $^{2}J_{C-P}$=35.7, 1C of Ni-C), 177.60(s, 2CO).

IR: **7a:** 2962 (CH), 1750 (2CO of phthal), 1385 (CN) cm^{-1}.

X-ray analysis of $(PMe_3)_2Ni(Ph)(phthal)$ **7a** has been done (see chapter 2 and appendix I).

Elemental analysis: **7a:** Calculated for $C_{20}H_{27}NP_2O_2Ni$ (MW):434.10 g/mol, C 55.34%, H 6.27%, N 3.23%; Found: C 55.41%, H 6.64%, N 3.26%.

(DPPE)Ni(Ar)Cl (Ar = Ph, **3a**; 3-Me-Ph, **3b**; 2,5-Me_2-Ph, **3c**)

A 250 mL, round-bottomed Schlenk flask equipped with a magnetic stir bar and capped by a rubber septum was charged with 0.273 mmol of $(PPh_3)_2Ni(Ar)Cl$ **23**[64] (200 mg, **23a**; 203 mg, **23b**; 206 mg, **23c**) and 15 mL of Et_2O. To this suspension at room temperature was added slowly a colorless solution of 109 mg of DPPE (0.273 mmol, 1.0 equiv.) in 15 mL of Et_2O. The reaction was stirred at room temperature for 1 h and the resulting yellow suspension was filtered and evaporated under vacuum. The solid was washed with hexane (3 × 10 mL) and dried under vacuum to give a yellow powder in yields: **3a**=70%, **3b**=64%, **3c**=64%.

$^{31}P\{H\}$ NMR: **3a:** 55.3(d, $^{2}J_{P\text{-}P}$=17.8), 35.3{d, $^{2}J_{P\text{-}P}$=17.8); **3b:** 56.8(d, $^{2}J_{P\text{-}P}$ = 17.8), 34.9(d, $^{2}J_{P\text{-}P}$=17.8); **3c:** 52.8(d, $^{2}J_{P\text{-}P}$=15.3), 32.2(d, $^{2}J_{P\text{-}P}$=15.3).

^{1}H NMR: **3a:** 1.54-1.78(m, 4H of CH_2-CH_2), 6.72-8.12(m, 25H of Ph); **3b:** 1.55-1.80(m, 4H of CH_2-CH_2), 1.96(s, CH_3 of 3-Me-Ph), 6.58-8.11(m, 24H of Ph); **3c:** 2.10-2.63(m, 4H of CH_2-CH_2), 2.10(s, CH_3 of 2,5-Me_2-Ph), 2.63(s, CH_3 of 2,5-Me_2-Ph), 6.65-8.29(m, 23H of Ph).

(DPPE)Ni(Ar)(phthal) (Ar = Ph, **9a**; 3-Me-Ph, **9b**; 2,5-Me_2-Ph, **9c**)

A 250 mL, round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 294 mg of potassium phthalimide (1.587 mmol, 3.0 equiv.) and 20 mL of THF. To this solution at room temperature was added slowly a yellow solution 0.529 mmol of (DPPE)Ni(Ar)Cl (301 mg, **3a**; 308 mg,**3b**; 314 mg, **3c**) in 20 mL of THF. The mixture solution was stirred at room temperature for 2h and the resulting yellow solution was filtered and evaporated under vacuum. Addition of 15 mL of toluene gave a yellow suspension. This was filtered again and the filtrate was evaporated to dryness. (DPPE)Ni(Ph)(phthal) was obtained as a yellow powder after recrystallization from THF/hexane (1:3) in yields: **9a**=61%, **9b**=57%, **9c**=59%. Samples for elemental analysis and X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of the yellow solid in THF.

$^{31}P\{H\}$ NMR: **9a:** 50.0(d, $^{2}J_{P\text{-}P}$=17.8), 45.5(d, $^{2}J_{P\text{-}P}$=16.5); **9b:** 50.2(d, $^{2}J_{P\text{-}P}$ =16.5), 44.9(d, $^{2}J_{P\text{-}P}$=16.5); **9c:** 46.5(d, $^{2}J_{P\text{-}P}$=15.3), 41.5(d, $^{2}J_{P\text{-}P}$=15.3).

^{1}H NMR: **9a:** 1.65-1.70(m, 4H of CH_2-CH_2), 6.59-7.95(m, 24H of Ph and phthal); **9b:** 1.66-1.70(m, 4H of CH_2-CH_2), 1.87(s, CH_3 of 3-Me-Ph), 6.43-7.95(m, 23H of Ph and phthal); **9c:** 1.54-1.75(m, 4H of CH_2-CH_2), 1.97(s, CH_3 of 2,5-Me_2-Ph), 2.98(s, CH_3 of 2,5-Me_2-Ph), 6.51-8.88(m, 22H of Ph and phthal).

^{13}C NMR: The limited solubility of this compound in C_6D_6 resulted in a very dilute sample and hence very weak intensities for the signals. The signals for some of the nuclei which are coupled to ^{31}P were not detected. **9a:** 64.96, 117.36, 119.46, 124.07, 125.83-128.45(m), 130.93, 131.06, 133.98, 135.93, 156.83, 176.10(s, 2CO).

IR: **9a:** 3050 (CH), 1648 (2CO of phthal), 1375 (CN) cm^{-1}.

X-ray analyses of (DPPE)Ni(Ar)(phthal) (**9a** and **9b**) have been done (see chapter 2 and appendix II & III).

Elemental analysis: **9a:** Calculated for $C_{40}H_{33}NP_2O_2Ni$ (MW):680.37 g/mol,
C 70.62%, H 4.89%, N 2.06%; Found: C 70.53%, H 4.91%, N 2.07%.

$(PMe_3)_2Ni(Me)Cl$ 4

To a purple-red solution of $(PMe_3)_2NiCl_2$ (1.0 g, 3.550 mmol) in 20 mL of THF at -78°C was added 2.50 mL of methyl lithium (3.550 mmol of a 1.4 M solution in Et_2O, 1.0 equiv.) to give a dark-brown solution. The rmixture solution was stirred at –78°C for 30 min and at room temperature for 1 h and then filtered. The resulting brown solution was evaporated under vacuum to dryness. A brown solid was obtained (750 mg, 81% yield).

$^{31}P\{H\}$ NMR: -14.76 ppm (s); ^1H NMR: -0.53(s, CH_3 of Ni-CH_3, no coupling because of the exchange of PMe_3), 0.98(s, CH_3 of PMe_3); ^{13}C NMR: 12.85(s, 6C of PMe_3), (C of Ni-CH_3 was not observed because of the exchange of PMe_3).

$(PMe_3)_2Ni(Me)(phthal)$ 10

To a white suspension of 180 mg of potassium phthalimide (0.972 mmol, 3.0 equiv.) in 20 mL of THF was added a yellow solution of 85 mg of $(PMe_3)_2Ni(Me)Cl$ (0.325 mmol, 1.0 equiv.) in 20 mL of THF. The mixture solution was stirred at room temperature for 2 h. The resulting brown-yellow solution was filtered and evaporated under vacuum. Addition of 15 mL of hexane gave a yellow suspension which was filtered and the filtrate was

evaporated to dryness. $(PMe_3)_2Ni(Me)(phthal)$ was obtained as a yellow powder (650 mg, 60% yield) after recrystallization from THF/hexane (1:2).
$^{31}P\{H\}$ NMR: -11.39(s); ^{1}H NMR: -0.61(s, CH_3 of Ni-CH_3, no coupling because of the exchange of PMe_3), 0.80(s, CH_3 of PMe_3), 7.02-7.73(m, 4H of phthal).
^{13}C NMR: 9.73(s, 6C of PMe_3), 117.85(s, 2C of phthal), 128.54(s, 2C of phthal), 135.67(s, 2C of phthal), 177.92(s, 2CO). (C of Ni-CH_3 was not observed).
Elemental analysis: **10:** Calculated for $C_{15}H_{25}NP_2O_2Ni$ (MW):372.01 g/mol, C 48.43%, H 6.78%, N 3.76%; Found: C 48.43%, H 7.17%, N 3.70%.

$(PPh_3)_2Ni(Me)Cl$ 5

To a dark-green suspension of $(PPh_3)_2NiCl_2$ (1.0 g, 1.528 mmol) in 20 mL of THF was added 1.10 mL of methyl lithium (1.528 mmol of a 1.4 M solution in Et_2O) to give a black-red solution. The mixture solution was stirred at –78°C for 30 min and evaporated under vacuum to dryness. A black-red solid was obtained (770 mg, in 80% yield).
$^{31}P\{H\}$ NMR: 23.37ppm (s); ^{1}H NMR: -1.15(s, broad, CH_3 of Ni-CH_3, no coupling because of the exchange of PPh_3), 6.88-7.44(m, H of PPh_3)

$(PPh_3)_2Ni(Me)(phthal)$ 11

To a white suspension of potassium phthalimide (585 mg, 3.158 mmol) in 20 mL of THF was added a yellow solution of 1000 mg of $(PPh_3)_2Ni(Me)Cl$ (1.578 mmol) in 20 mL of THF. The mixture solution was stirred at –78°C for 2 h and at room temperature for 1 h. The resulting dark-brown solution was filtered, and THF was evaporated under vacuum. $(PPh_3)_2Ni(Me)(phthal)$ was obtained as a brown powder (700 mg, 60% yield).
$^{31}P\{H\}$ NMR: 22.1(s); ^{1}H NMR: -0.41(s, broad, CH_3 of Ni-CH_3, no coupling because of the exchange of PPh_3), 6.99-8.69 (m, 30H of PPh_3); ^{13}C NMR: 131.87(s, 2C of phthal), 132.63(s, 2C of phthal), 132.75(s, 2C of phthal), 134.09(m, 3C of Ph), 135.47(m, 3C of Ph), 172.50(s, 2CO). (C of Ni-CH_3 was

not observed because of the exchange of PMe_3).

$(PMe_3)_2Ni(Ph\text{-}C{=}O)Cl$ 2

To a clear beige solution of $Ni(PMe_3)_4$ (200 mg, 0.551 mmol) in 20 mL of benzene was added 627 mg of benzoyl chloride (4.460 mmol, 8.0 equiv.) to give a yellow suspension. The mixture solution was stirred at room temperature for 20 min, and then filtered immediately. The resulting yellow suspension was evaporated under vacuum to dryness. A yellow solid was obtained (63 mg, 35% yield).

$^{31}P\{H\}$ NMR: -16.43(s);

^{1}H NMR: 0.80(s, CH_3 of PMe_3), 6.80-7.74(m, 5H of Ph);

^{13}C NMR: 13.37(t, $^{2}J_{C\text{-}p}$=13.6, 6C of PMe_3), 127.21(s, 1C of Ph), 131.81(s, 2C of Ph), 131.99(s, 2C of Ph), 132.92(s, 1C of Ph), 188.46(s, CO).

$(PMe_3)_2Ni(Ph\text{-}C{=}O)(phthal)$ 8

A 250 mL, round-bottomed Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 168 mg of potassium phthalimide (0.905 mmol, 3.0 equiv.) and 20 mL of THF. To this solution at room temperature was added slowly a yellow solution of $(PMe_3)_2Ni(Ph\text{-}C{=}O)Cl$ (100 mg, 0.302 mmol, 1.0 equiv.) in 20 mL of THF. The mixture solution was stirred at room temperature for 2h and then filtered and evaporated under vacuum. Addition of 15 mL of toluene gave a yellow suspension which was filtered again and evaporated to dryness. $(PMe_3)_2Ni(Ph\text{-}C{=}O)(phthal)$ was obtained as a yellow powder, 87 mg in 65% yield after recrystallization from THF/hexane (1:3). $^{31}P\{H\}$ NMR: -14.58(s);

^{1}H NMR: 0.74(t, $^{2}J_{H\text{-}p}$=3.7, CH_3 of PMe_3), 6.84-7.74(m, 9H of Ph and phthal).

^{13}C NMR: 9.89(t, $^{2}J_{C\text{-}P}$=13.6, 6C of PMe_3), 118.06(s, 2C of phthal), 121.11(s, 1C of Ph), 127.81(s, 2C of Ph), 128.76(s, 2C of phthal), 131.18(s, 2C of Ph), 131.56(s, 2C of phthal), 135.57(s, 1C of C-CO), 182.33(s, 2CO of phthal),

193.18(t, $^2J_{C\text{-}P}$=4.4, CO of Ph-C=O).
IR: 2962 (CH), 1775 (CO of Ph-C=O), 1745 (2CO of phthal), 1385 (CN) cm^{-1}.

$(PBu_3)_2Ni(Ph)Cl$ 6

To a yellow suspension of $(PPh_3)_2Ni(Ph)Cl$[57] (200 mg, 0.273 mmol) in 20 mL of Et_2O was added 221 mg of tributylphosphine (1.094 mmol, 4.0 equiv.) to give a clear yellow solution. The mixture solution was stirred at room temperature for 1 h, and evaporated at reduced pressure to half volume. 20 mL of hexane were added to this Et_2O solution and the resulting yellow precipitate was filtered and washed twice with hexane and dried in vacuo. $(PBu_3)_2Ni(Ph)Cl$ 100 mg was obtained as a yellow crystalline solid in 50% yield.
$^{31}P\{H\}$ NMR: 4.43(s); ^1H NMR: 0.89(t, $^3J_{H\text{-}H}$=5.6, CH_3 of PBu_3), 1.21(m, CH_2 of PBu_3), 1.39(s, broad, CH_2 of PBu_3), 7.03-7.80(m, 5H of Ph).

$(PBu_3)_2Ni(Ph)(phthal)$ 12

To a white suspension of potassium phthalimide (75 mg, 0.402 mmol, 3.0 equiv.) in 20 mL of THF was added a yellow solution of 100 mg of $(PBu_3)_2Ni(Ph)Cl$ (0.134 mmol, 1.0 equiv.) in 20 mL of THF. The mixture was stirred at 65°C for 2h. The resulting yellow solution was filtered, and THF was evaporated under vacuum. Addition of 15mL of hexane gave a turbid yellow solution which was filtered and evaporated to dryness. $(PBu_3)_2Ni(Ph)(phthal)$ was obtained as a yellow powder, 60 mg in 52% yield after recrystallization from THF/hexane (1:3).
$^{31}P\{H\}$ NMR: 4.78(s); ^1H NMR: 0.90(t, $J_{H\text{-}H}$=7.2, CH_3 of PBu_3), 1.23(sextet, $J_{H\text{-}H}$=3.8, CH_2 of PBu_3), 1.30(t, $J_{H\text{-}H}$=7.4, CH_2 of PBu_3), 6.92-7.64(m).

$(PCy_3)_2Ni(H)(phthal)$ 13

To a white suspension of potassium phthalimide (173 mg, 0.934 mmol, 3.0 equiv.) in 20 mL of THF was added a yellow solution of $(PCy_3)_2Ni(H)Cl$ (200 mg, 0.305 mmol, 1.0 equiv.) in 20 mL of THF. The mixture solution was stirred at room temperature for 2h. The resulting yellow solution was filtered and evaporated under vacuum. Addition of 15 mL of toluene gave a yellow suspension which was filtered again and evaporated to dryness. $(PCy_3)_2Ni(H)(phthal)$ was obtained as a yellow powder in 58% yield after recrystallization from THF/hexane (1:3). The analytical and crystallographic samples were obtained by slow diffusion of toluene into a concentrated solution of the yellow solid in THF. X-ray analysis has been done (see chapter 2 and appendix IV).

$^{31}P\{H\}$ NMR: 34.7(d, J_{H-P}=57.8);

^{1}H NMR: -22.9(t, J_{H-P}=76.0, H of Ni-H), 1.10-2.13(m, 66H of PCy_3), 7.04-7.73(m, 5H of Ph)

^{13}C NMR: 24.12(s, 1C of PCy_3), 25.28(t, J_{C-C}=5.2, 2C of PCy_3), 27.56(s, 2C of PCy_3), 32.36(t, J_{C-C}=10.0, 1C of PCy_3), 117.32(s, 2C of phthal), 128.09(s, 2C of phthal), 136.21(s, 2C of phthal), 177.98(s, 2CO).

Elemental analysis: Calculated for $C_{44}H_{71}NP_2O_2Ni$ (MW): 766.69 g/mol, C 68.93%, H 9.33%, N 1.83%; Found: C 68.83%, H 10.19%, N 1.87%.

5.4 Synthesis of different reactants

m-tolyl phthalimide[77]

Phthalic anhydride (3.0 g, 20.2 mmol, 1.0 equiv.) and 3-methylphenylamine (10.8 g, 101.3 mmol, 5 equiv.) were placed in a 250 mL flask. The flask was placed in an oil bath at 130°C and kept stirring for 15 min, then cooled back to room temperature, filtered and washed with hexane. The pale-purple solid was recrystallized in the minimum chloroform and hexane was added to precipitate the solid. Yield: 70%.

^{1}H NMR: 2.05 (s, CH_3), 6.89-7.21(m, 6H of Ph and phthal), 7.48(quartet, $^{2}J_{H-H}$=2.8, 2H of phthal).

2,5-dimethyl-phenyl phthalimide

The above procedure was followed by using phthalic anhydride (2.0 g, 13.5 mmol, 1.0 equiv.) and 2,5-dimethyl phenyl amine (8.0 g, 67.5 mmol, 5 equiv.). The pale-green solid obtained from this reaction was recrystallized in minimum chloroform and hexane was added to precipitate the solid. Yield: 70%.

^{1}H NMR: 2.01(s, CH_3), 2.03(s, CH_3), 6.83-6.96(m, 5H of Ph and phthal), 7.56(quartet, J_{H-H}=2.8, 2H of phthal).

5.5 Reactivity of different complexes

5.5.1 Reactivities of complex $(PCy_3)_2Ni(H)(phthal)$

Reaction with trimethylphosphine (PMe_3)

To a yellow solution of $(PCy_3)_2Ni(H)(phthal)$ (50 mg, 0.065 mmol) in 20 mL of Et_2O was added PMe_3 (40 mg, 0.263 mmol, 8.0 equiv.).

1) The reaction mixture was unstable at room temperature, the color changed from yellow to red, orange, yellow and white respectively. The resulting white solution was evaporated to dryness.

$^{31}P\{H\}$ NMR: -21.2(s, $Ni(PMe_3)_4$}, 33.4(s, $OPMe_3$), 10.5(s, PCy_3), 15.9(s, ?)

^1H NMR: 0.87(d), 1.15(s), 1.31(m), 1.64(s), 1.70(s), 1.85(d), 6.88(s), 6.96(s), 7.49(s), 7.63(s).

2) The reaction mixture was stable at -78°C, the color changed from yellow to red. The resulting red solution was evaporated to dryness.

$^{31}P\{H\}$ NMR: 33.3(s, $OPMe_3$), 10.5(s, PCy_3), 15.2(s, ?), 46.2(s, $OPCy_3$).

^1H NMR: 1.85(s), 1.21(t), 1.32(t), 1.64(d), 1.86(s), 6.96(s), 7.63(s).

Reaction with 1,2-bis(diphenylphosphino)ethane (DPPE)

To a yellow solution of $(PCy_3)_2Ni(H)(phthal)$ (100 mg, 0.130 mmol) in 20 mL of different solvents (THF, benzene, and toluene) was added DPPE (52 mg, 0.130 mmol, 1.0 equiv.). The reactions were carried out at different temperatures.

1) The reaction mixture was stirred at room temperature for 2 h in THF. The resulting yellow solution was evaporated to dryness. There was no reaction observed from the $^{31}P\{H\}$ NMR spectrum.

2) The reaction mixture was stirred at 60°C for 2 h in THF. The resulting yellow solution was evaporated to dryness.

$^{31}P\{H\}$ NMR: 44.7(s, $Ni(dppe)_2$), 10.5(s, PCy_3), -12.3(s, dppe), 34.3(d, starting material).

3) The reaction mixture was stirred at 90°C for 2 h in benzene. The resulting yellow solution was evaporated to dryness.
$^{31}P\{H\}$ NMR: 44.7(s, Ni(dppe)$_2$), 10.5(s, PCy$_3$), -12.3(s, dppe), 34.3(d, starting material). ^1H NMR: 1.19(q), 1.32(t), 1.64(d), 1.73(d), 1.86(d), 2.13(t), 3.57(s), 6.93-8.11(m)
4) The reaction mixture was stirred at 110°C for 1 h in toluene. The resulting yellow solution was evaporated to dryness.
$^{31}P\{H\}$ NMR: 44.7(s, Ni(dppe)$_2$), 10.5(s, PCy$_3$), -12.3(s, dppe), 34.3(d, starting material). ^1H NMR: 1.10-1.35(m), 1.60-2.10(m), 2.77(s), 6.9-8.1(m).

Reaction with tributylphosphine (PBu$_3$)
To a yellow solution of (PCy$_3$)$_2$Ni(H)(phthal) (150 mg, 0.196 mmol) in 20 mL of THF was added PBu$_3$ (160 mg, 0.787 mmol, 4.0 equiv.). The reaction mixture was stirred at room temperature for 1 h. The resulting yellow mixture was evaporated to dryness.
$^{31}P\{H\}$ NMR: -4.81(s), 3.84(s), 10.45(s, PCy$_3$), 47.52(s, OPCy$_3$), -31.0(s, PBu$_3$), -18.4(s, Ni(PBu$_3$)$_4$?). ^1H NMR: -21.8-77(s), 1.89(s), 1.41(s), 1.70(d), 1.85(s), 3.56(s), 6.86-7.70(m).

5.5.2 Other reactions

Reaction of Ni(PMe$_3$)$_4$ with triphenylphosphine (PPh$_3$)
To a beige solution of Ni(PMe$_3$)$_4$ (100 mg, 0.275 mmol, 1.0 equiv.) in 10 mL of THF was added a colorless solution of triphenylphosphine (108 mg, 0.413 mmol, 1.5 equiv.) in 10 mL of THF. The reaction was stirred at 65°C for 24 h. The resulting pale-yellow solution was evaporated to dryness. (PMe$_3$)$_3$Ni(PPh$_3$) was observed. ^1H NMR: 1.00(s), 1.10(s), 7.07-7.48(m).
$^{31}P\{H\}$ NMR: -4.84(s, PPh$_3$), -24.8(d, $^2J_{P\text{-}P}$=25.4), 36.0(q, $^2J_{P\text{-}P}$=26.4), -21.3(s, Ni(PMe$_3$)$_4$), 31.2(s, OPMe$_3$).

Reaction of $(PPh_3)_2Ni(m\text{-Me-Ph})Cl$ with (PCy_3)

To a yellow solution of $(PPh_3)_2Ni(m\text{-Me-Ph})(Cl)$ (200 mg, 0.269 mmol, 1.0 equiv.) in 20 mL of Et_2O was added a colorless solution of PCy_3 (400 mg, 1.426 mmol, 5.0 equiv.) in 20 mL of Et_2O. The reaction was stirred at room temperature for 1 h. The resulting yellow solution was evaporated to dryness. $^{31}P\{H\}$ NMR: -4.8(s, PPh_3), 10.5(s, PCy_3), 12.9(s), 25.4(s, $OPPh_3$), 46.1(s, $OPCy_3$).

Reaction of $(PPh_3)_2Ni(m\text{-Me-Ph})Cl$ with (PCy_3) and K-phthal

To the resulting yellow solution of the reaction of $(PPh_3)_2Ni(m\text{-Me-Ph})(Cl)$ of (200 mg, 0.269 mmol, 1.0 equiv.) with PCy_3 (400 mg, 1.426 mmol, 5.0 equiv.) in 20 mL of THF was added a white solution of potassium phthalimide of 20 mL of THF. The reaction was stirred at room temperature for 3 h. The resulting yellow solution was filtered and evaporated to dryness. $^{31}P\{H\}$ NMR: -4.8(s, PPh_3), 10.5(s, PCy_3), 25.4(s, $OPPh_3$), 46.1(s, $OPCy_3$). ^1H NMR: 1.08-2.18(m), 3.57(s), 7.03-7.74(m).

Reaction of $(PCy_3)_2Ni(H)(Cl)$ with trimethylphosphine (PMe_3)

To a yellow solution of $(PCy_3)_2Ni(H)(Cl)$ (100 mg, 0.152 mmol, 1.0 equiv.) in 20 mL of Et_2O was added a colorless solution of PMe_3 (46 mg, 0.609 mmol, 4.0 equiv.). The reaction was stirred at room temperature for 10 min. The resulting dark-red solution was filtered and evaporated to dryness. $^{31}P\{H\}$ NMR: 21.2(s, $Ni(PMe_3)_4$), 46.2(s, $OPCy_3$), 10.5(s, PCy_3).

Reaction of $(DPPE)NiCl_2$ with methyl lithium (LiMe)

To a dark-green solution of $(DPPE)NiCl_2$ (200 mg, 0.379 mmol, 1.0 equiv.) in 20 mL of Et_2O was added 0.27 mL of methyl lithium (0.379 mmol of a 1.4 M solution in Et_2O, 1.0 equiv.). The reaction was stirred at -78°C for 30 min. The resulting black solution was evaporated to dryness. There was no signal observed in the $^{31}P\{H\}$ NMR spectrum.

Reaction of 3-methyl-phenyl-chloride with potassium phthalimide

1) To a white suspensive solution of potassium phthalimide (836 mg, 4.513 mmol, 1.0 equiv.) in 5 mL of THF was added a colorless solution of 3-methyl-phenyl-chloride of (1143 mg, 9.029 mmol, 2.0 equiv.). The reaction was stirred at room temperature for 4 h. The resulting white suspensive solution was evaporated to dryness. There was no reaction observed from the ^1H NMR spectrum.

2) To a colorless solution of 3-methyl-phenyl-chloride of (1072 mg, 8.468 mmol, 8.0 equiv.) was added a white solid of potassium phthalimide (200 mg, 1.080 mmol, 1.0 equiv.). The reaction was stirred at 115°C for 24 h. The resulting white suspensive solution was evaporated to dryness. There was no reaction observed from the ^1H NMR spectrum.

Reaction of $Ni(PMe_3)_4$ with phenylphtalimide

To a beige solution of $Ni(PMe_3)_4$ (50 mg, 0.146 mmol, 1.0 equiv.) in 10 mL of THF was added a white suspensive solution of phenylphtalimide (98 mg, 0.439 mmol, 3.0 equiv.) in 10 mL of THF. The reaction was stirred at 60°C for 24 h. The resulting white suspensive solution was evaporated to dryness. There was no reaction observed from the ^1H NMR spectrum.

Reaction of $Ni(PPh_3)_4$ with phenylphtalimide

To a brown solution of $Ni(PPh_3)_4$ (100 mg, 0.0903 mmol, 1.0 equiv.) in 10 mL of THF was added a white suspensive solution of phenylphthalimide (60 mg, 0.269 mmol, 3.0 equiv.) in 10 mL of THF. The reaction was stirred at 60°C for 24 h. The resulting white suspensive solution was evaporated to dryness. There was no reaction observed from the ^1H NMR spectrum.

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APPENDIX I

Table I. 1 Crystal data and structure refinement for $(PMe_3)_2Ni(Ph)(phthal)$

Empirical formula	C20 H27 N Ni O2 P2	
Formula weight	434.076	
Temperature	173(2) K	
Wavelength	0.71070 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 9.4499(5) Å	alpha = 101.31 deg.
	b = 15.3923(8) Å	beta = 95.80 deg.
	c = 23.1843(11) Å	gamma = 97.85 deg.
Volume	3247.3(3) $Å^3$	
Z, Calculated density	6, 1.318 Mg/m^3	
Absorption coefficient	1.057 mm^{-1}	
Crystal size	0.4 x 0.3 x 0.25 mm	
Theta range for data collection	1.37 to 28.74 deg.	
Reflections collected / unique	38916 / 16693 [R(int) = 0.0296]	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.269	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1132	
R indices (all data)	R1 = 0.0719, wR2 = 0.1217	
Largest diff. peak and hole	0.833 and -0.815 $e.Å^{-3}$	

$R = \Sigma (|| F_0 | - | F_c ||) / \Sigma (| F_0 |)$

$wR2 = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / \Sigma (F_0{}^2)^2 \}^{1/2}$

$S = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.}) \}^{1/2}$

Table I. 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for $(PMe_3)_2Ni(Ph)(phthal)$

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

ATOM	Occ.	x	y	z	U(eq)
Ni(1)	1	7542(1)	6389(1)	3502(1)	30(1)
P(11)	1	9338(1)	7161(1)	3202(1)	41(1)
C131a	0.614(3)	11128(6)	7277(5)	3541(3)	80(1)
C132a	0.614(3)	9469(7)	6664(5)	2413(3)	80(1)
C133a	0.614(3)	9098(7)	8279(4)	3129(4)	80(1)
C134b	0.386(3)	10966(10)	6702(7)	3093(5)	80(1)
C135b	0.386(3)	10057(11)	8146(6)	3815(4)	80(1)
C136b	0.386(3)	8960(10)	7664(8)	2603(5)	80(1)
P(12)	1	5823(1)	5507(1)	3768(1)	38(1)
C(141)	1	6235(4)	4861(3)	4321(2)	67(1)
C(142)	1	4374(4)	6034(3)	4046(2)	67(1)
C(143)	1	4969(4)	4638(3)	3140(2)	67(1)
N(1)	1	6209(2)	7139(2)	3259(1)	34(1)
O(11)	1	6240(2)	8220(2)	4110(1)	49(1)
O(12)	1	5652(2)	6359(2)	2284(1)	52(1)
C(121)	1	5819(3)	7889(2)	3585(1)	36(1)
C(122)	1	4756(3)	8234(2)	3194(1)	34(1)
C(123)	1	4036(3)	8957(2)	3309(2)	46(1)
C(124)	1	3081(3)	9080(2)	2843(2)	52(1)
C(125)	1	2881(3)	8504(2)	2291(2)	52(1)
C(126)	1	3636(3)	7786(2)	2177(1)	46(1)
C(127)	1	4570(3)	7668(2)	2643(1)	36(1)
C(128)	1	5514(3)	6974(2)	2685(1)	36(1)
C(111)	1	8819(3)	5610(2)	3695(1)	31(1)
C(112)	1	9685(3)	5769(2)	4239(1)	38(1)
C(113)	1	10625(3)	5196(2)	4365(1)	48(1)
C(114)	1	10716(3)	4439(2)	3950(2)	50(1)
C(115)	1	9882(4)	4261(2)	3412(2)	49(1)
C(116)	1	8949(3)	4843(2)	3286(1)	38(1)
Ni(2)	1	8041(1)	3286(1)	514(1)	29(1)
P(21)	1	6768(1)	4263(1)	931(1)	37(1)
C231a	0.405(18)	7068(13)	4610(10)	1719(4)	51(1)
C232a	0.405(18)	7155(11)	5296(7)	663(7)	51(1)
C233a	0.405(18)	4844(10)	3937(8)	753(7)	51(1)
C234b	0.595(18)	6811(9)	4322(7)	1728(3)	51(1)
C235b	0.595(18)	4818(7)	4078(6)	705(4)	51(1)
C236b	0.595(18)	7200(8)	5411(4)	871(5)	51(1)
P(22)	1	9511(1)	2399(1)	162(1)	47(1)
C241a	0.713(5)	9818(6)	1612(4)	664(3)	74(1)
C242a	0.713(5)	11302(6)	2864(5)	100(4)	74(1)
C243a	0.713(5)	8875(6)	1633(4)	-514(3)	74(1)
C244b	0.287(5)	11460(12)	2761(12)	226(9)	74(1)
C245b	0.287(5)	9392(14)	1258(7)	216(7)	74(1)
C246b	0.287(5)	9141(14)	2214(10)	-689(4)	74(1)
N(2)	1	6400(2)	2574(1)	-13(1)	31(1)

O(21)	1	6076(2)	1308(1)	380(1)	43(1)
O(22)	1	6038(2)	3570(1)	-622(1)	50(1)
C(221)	1	5711(3)	1742(2)	19(1)	31(1)
C(222)	1	4445(3)	1467(2)	-459(1)	31(1)
C(223)	1	3391(3)	708(2)	-609(1)	41(1)
C(224)	1	2337(3)	672(2)	-1080(1)	45(1)
C(225)	1	2335(3)	1352(2)	-1388(1)	43(1)
C(226)	1	3404(3)	2111(2)	-1238(1)	38(1)
C(227)	1	4438(3)	2147(2)	-769(1)	32(1)
C(228)	1	5698(3)	2857(2)	-481(1)	34(1)
C(211)	1	9667(3)	3987(2)	1026(1)	31(1)
C(212)	1	10460(3)	4727(2)	872(1)	39(1)
C(213)	1	11672(3)	5229(2)	1235(2)	46(1)
C(214)	1	12133(3)	5015(2)	1761(2)	50(1)
C(215)	1	11380(3)	4298(2)	1930(1)	49(1)
C(216)	1	10168(3)	3792(2)	1564(1)	39(1)
Ni(3)	1	-305(1)	1500(1)	3464(1)	31(1)
P(31)	1	1474(1)	1500(1)	4150(1)	45(1)
C331a	0.649(4)	1820(7)	2395(4)	4780(3)	69(1)
C332a	0.649(4)	3308(6)	1597(4)	3892(3)	69(1)
C333a	0.649(4)	1429(6)	490(4)	4406(3)	69(1)
C334b	0.351(4)	2303(12)	2599(6)	4587(5)	69(1)
C335b	0.351(4)	2864(10)	925(7)	3981(5)	69(1)
C336b	0.351(4)	926(11)	982(7)	4801(4)	69(1)
P(32)	1	-2258(1)	1477(1)	2858(1)	38(1)
C(341)	1	-3480(4)	2234(3)	3116(2)	65(1)
C(342)	1	-1977(4)	1749(3)	2148(2)	65(1)
C(343)	1	-3394(4)	402(3)	2641(2)	65(1)
N(3)	1	920(2)	1470(1)	2840(1)	34(1)
O(31)	1	236(2)	-17(1)	2355(1)	45(1)
O(32)	1	2113(2)	2931(1)	3071(1)	52(1)
C(321)	1	954(3)	727(2)	2405(1)	35(1)
C(322)	1	2020(3)	978(2)	2007(1)	34(1)
C(323)	1	2498(4)	484(2)	1520(1)	47(1)
C(324)	1	3520(4)	925(2)	1239(2)	52(1)
C(325)	1	4029(3)	1828(2)	1441(1)	47(1)
C(326)	1	3548(3)	2324(2)	1928(1)	43(1)
C(327)	1	2554(3)	1881(2)	2208(1)	35(1)
C(328)	1	1864(3)	2185(2)	2753(1)	37(1)
C(311)	1	-1539(3)	1511(2)	4064(1)	37(1)
C(312)	1	-1760(3)	2313(2)	4415(1)	45(1)
C(313)	1	-2665(4)	2334(3)	4848(2)	56(1)
C(314)	1	-3398(4)	1548(3)	4943(2)	61(1)
C(315)	1	-3211(4)	737(3)	4603(2)	55(1)
C(316)	1	-2293(3)	721(2)	4170(1)	46(1)

Table I. 3 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2} x 10^3) for $(PMe_3)_2Ni(Ph)(phthal)$

ATOM	Occ.	x	y	z	U(eq)
H13Aa	0.614	11349	6697	3577	121
H13Ba	0.614	11239	7661	3928	121
H13Ca	0.614	11772	7535	3303	121
H13Da	0.614	8544	6594	2181	121
H13Ea	0.614	9771	6089	2386	121
H13Fa	0.614	10158	7054	2265	121
H13Ga	0.614	8140	8266	2940	121
H13Ha	0.614	9786	8497	2892	121
H13Ia	0.614	9240	8669	3514	121
H13Jb	0.386	11206	6405	3409	121
H13Kb	0.386	11737	7178	3092	121
H13Lb	0.386	10824	6279	2720	121
H13Mb	0.386	10327	7943	4170	121
H13Nb	0.386	9330	8520	3881	121
H13Ob	0.386	10886	8484	3709	121
H13Pb	0.386	8141	7963	2659	121
H13Qb	0.386	8751	7212	2243	121
H13Rb	0.386	9778	8092	2578	121
H(14A)	1	6724	5259	4678	101
H(14B)	1	6841	4439	4174	101
H(14C)	1	5356	4544	4403	101
H(14D)	1	4753	6515	4380	101
H(14E)	1	3702	5601	4168	101
H(14F)	1	3892	6268	3740	101
H(14G)	1	5684	4319	2970	101
H(14H)	1	4497	4904	2849	101
H(14I)	1	4271	4228	3269	101
H(123)	1	4180	9345	3679	56
H(124)	1	2568	9557	2904	63
H(125)	1	2231	8600	1990	62
H(126)	1	3516	7403	1806	55
H(112)	1	9632	6275	4526	46
H(113)	1	11197	5323	4732	57
H(114)	1	11342	4051	4036	60
H(115)	1	9938	3751	3129	59
H(116)	1	8393	4714	2916	46
H23Aa	0.405	6976	4091	1893	77
H23Ba	0.405	6370	4978	1849	77
H23Ca	0.405	8019	4948	1840	77
H23Da	0.405	6944	5167	238	77
H23Ea	0.405	8154	5547	778	77
H23Fa	0.405	6569	5718	831	77
H23Ga	0.405	4593	3770	330	77
H23Ha	0.405	4375	4431	910	77
H23Ia	0.405	4537	3435	925	77
H23Jb	0.595	6510	3733	1796	77
H23Kb	0.595	6171	4716	1883	77

H23Lb	0.595	7774	4547	1923	77
H23Mb	0.595	4434	3459	680	77
H23Nb	0.595	4623	4227	325	77
H23Ob	0.595	4374	4450	993	77
H23Pb	0.595	7292	5434	465	77
H23Qb	0.595	8092	5681	1116	77
H23Rb	0.595	6446	5732	998	77
H24Aa	0.713	8907	1324	738	112
H24Ba	0.713	10361	1941	1033	112
H24Ca	0.713	10345	1166	480	112
H24Da	0.713	11700	3295	458	112
H24Ea	0.713	11296	3154	-230	112
H24Fa	0.713	11878	2395	40	112
H24Ga	0.713	7912	1350	-501	112
H24Ha	0.713	9490	1185	-576	112
H24Ia	0.713	8877	1946	-834	112
H24Jb	0.287	11665	3404	304	112
H24Kb	0.287	11801	2518	-139	112
H24Lb	0.287	11935	2550	545	112
H24Mb	0.287	8407	969	114	112
H24Nb	0.287	9731	1226	614	112
H24Ob	0.287	9973	963	-53	112
H24Pb	0.287	8120	2118	-810	112
H24Qb	0.287	9534	1698	-867	112
H24Rb	0.287	9584	2733	-813	112
H(223)	1	3392	246	-404	49
H(224)	1	1611	175	-1191	54
H(225)	1	1611	1306	-1701	51
H(226)	1	3416	2570	-1447	46
H(212)	1	10165	4886	518	46
H(213)	1	12177	5715	1120	56
H(214)	1	12947	5352	2003	60
H(215)	1	11680	4150	2288	59
H(216)	1	9675	3307	1684	47
H33Aa	0.649	1867	2956	4654	104
H33Ba	0.649	2721	2376	5005	104
H33Ca	0.649	1059	2340	5022	104
H33Da	0.649	3497	2143	3751	104
H33Ea	0.649	3332	1094	3576	104
H33Fa	0.649	4029	1604	4216	104
H33Ga	0.649	1270	-9	4073	104
H33Ha	0.649	662	433	4645	104
H33Ia	0.649	2331	497	4640	104
H33Jb	0.351	1566	2933	4719	104
H33Kb	0.351	2865	2917	4349	104
H33Lb	0.351	2916	2529	4926	104
H33Mb	0.351	2480	332	3755	104
H33Nb	0.351	3425	884	4341	104
H33Ob	0.351	3465	1236	3752	104
H33Pb	0.351	125	1235	4949	104
H33Qb	0.351	1724	1109	5112	104

H33Rb	0.351	655	344	4668	104
H(34A)	1	-2952	2831	3256	98
H(34B)	1	-3925	2042	3434	98
H(34C)	1	-4208	2232	2795	98
H(34D)	1	-1243	1438	1987	98
H(34E)	1	-1679	2384	2201	98
H(34F)	1	-2859	1568	1880	98
H(34G)	1	-2841	-43	2477	98
H(34H)	1	-4172	429	2348	98
H(34I)	1	-3777	245	2981	98
H(323)	1	2147	-124	1385	56
H(324)	1	3862	607	913	62
H(325)	1	4708	2111	1246	57
H(326)	1	3887	2935	2061	51
H(312)	1	-1281	2852	4357	54
H(313)	1	-2781	2882	5077	67
H(314)	1	-4012	1563	5233	73
H(315)	1	-3700	203	4664	66
H(316)	1	-2176	171	3945	55

Table I. 4 Anisotropic parameters (Å ^{2} x 10^3) for (PMe$_3$)$_2$Ni(Ph)(phthal)

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U^{11} + ... + 2 h k a* b* U^{12}]

ATOM	U11	U22	U33	U23	U13	U12
Ni(1)	23(1)	33(1)	34(1)	8(1)	4(1)	5(1)
P(11)	28(1)	43(1)	56(1)	21(1)	8(1)	5(1)
C131a	52(2)	92(3)	107(3)	51(2)	19(2)	-4(2)
C132a	52(2)	92(3)	107(3)	51(2)	19(2)	-4(2)
C133a	52(2)	92(3)	107(3)	51(2)	19(2)	-4(2)
C134b	52(2)	92(3)	107(3)	51(2)	19(2)	-4(2)
C135b	52(2)	92(3)	107(3)	51(2)	19(2)	-4(2)
C136b	52(2)	92(3)	107(3)	51(2)	19(2)	-4(2)
P(12)	29(1)	38(1)	47(1)	10(1)	9(1)	3(1)
C(141)	53(1)	72(1)	80(2)	27(1)	18(1)	-1(1)
C(142)	53(1)	72(1)	80(2)	27(1)	18(1)	-1(1)
C(143)	53(1)	72(1)	80(2)	27(1)	18(1)	-1(1)
N(1)	26(1)	39(1)	38(1)	8(1)	2(1)	6(1)
O(11)	50(1)	54(1)	40(1)	2(1)	-6(1)	18(1)
O(12)	52(1)	55(1)	44(1)	-1(1)	1(1)	12(1)
C(121)	28(1)	38(1)	41(2)	11(1)	2(1)	6(1)
C(122)	26(1)	38(1)	41(2)	16(1)	3(1)	4(1)
C(123)	37(2)	45(2)	60(2)	16(2)	4(1)	11(1)
C(124)	40(2)	48(2)	78(3)	31(2)	4(2)	14(1)
C(125)	38(2)	61(2)	62(2)	35(2)	-6(2)	3(2)
C(126)	36(2)	58(2)	43(2)	20(2)	-2(1)	0(1)
C(127)	26(1)	42(2)	41(2)	16(1)	4(1)	2(1)
C(128)	27(1)	42(2)	39(2)	12(1)	5(1)	3(1)
C(111)	26(1)	36(1)	31(1)	9(1)	6(1)	5(1)
C(112)	35(2)	50(2)	29(1)	4(1)	6(1)	8(1)
C(113)	38(2)	72(2)	40(2)	30(2)	4(1)	10(2)
C(114)	42(2)	54(2)	67(2)	33(2)	13(2)	21(2)
C(115)	52(2)	39(2)	61(2)	9(2)	18(2)	18(1)
C(116)	37(2)	44(2)	34(2)	6(1)	2(1)	10(1)
Ni(2)	26(1)	31(1)	28(1)	6(1)	1(1)	2(1)
P(21)	37(1)	40(1)	35(1)	6(1)	2(1)	12(1)
C231a	55(1)	50(2)	51(2)	8(1)	9(1)	21(1)
C232a	55(1)	50(2)	51(2)	8(1)	9(1)	21(1)
C233a	55(1)	50(2)	51(2)	8(1)	9(1)	21(1)
C234b	55(1)	50(2)	51(2)	8(1)	9(1)	21(1)
C235b	55(1)	50(2)	51(2)	8(1)	9(1)	21(1)
C236b	55(1)	50(2)	51(2)	8(1)	9(1)	21(1)
P(22)	28(1)	40(1)	65(1)	-8(1)	2(1)	5(1)
C241a	52(2)	69(2)	93(3)	-13(2)	18(2)	13(1)
C242a	52(2)	69(2)	93(3)	-13(2)	18(2)	13(1)
C243a	52(2)	69(2)	93(3)	-13(2)	18(2)	13(1)
C244b	52(2)	69(2)	93(3)	-13(2)	18(2)	13(1)
C245b	52(2)	69(2)	93(3)	-13(2)	18(2)	13(1)
C246b	52(2)	69(2)	93(3)	-13(2)	18(2)	13(1)
N(2)	27(1)	34(1)	30(1)	8(1)	1(1)	0(1)

O(21)	44(1)	41(1)	44(1)	17(1)	-2(1)	6(1)
O(22)	49(1)	49(1)	50(1)	26(1)	-5(1)	-12(1)
C(221)	28(1)	34(1)	31(1)	6(1)	7(1)	6(1)
C(222)	29(1)	31(1)	31(1)	2(1)	5(1)	3(1)
C(223)	42(2)	31(1)	48(2)	4(1)	5(1)	3(1)
C(224)	37(2)	38(2)	48(2)	-5(1)	-1(1)	-5(1)
C(225)	39(2)	45(2)	36(2)	-4(1)	-6(1)	4(1)
C(226)	38(2)	42(2)	33(1)	6(1)	-1(1)	4(1)
C(227)	28(1)	34(1)	32(1)	4(1)	6(1)	3(1)
C(228)	30(1)	40(2)	31(1)	10(1)	1(1)	0(1)
C(211)	30(1)	33(1)	30(1)	6(1)	3(1)	3(1)
C(212)	42(2)	41(2)	33(2)	12(1)	6(1)	1(1)
C(213)	41(2)	38(2)	54(2)	4(1)	12(2)	-8(1)
C(214)	36(2)	55(2)	48(2)	-7(2)	-3(1)	-3(1)
C(215)	40(2)	65(2)	39(2)	10(2)	-5(1)	8(2)
C(216)	37(2)	43(2)	38(2)	15(1)	0(1)	0(1)
Ni(3)	29(1)	31(1)	31(1)	6(1)	1(1)	5(1)
P(31)	45(1)	41(1)	47(1)	6(1)	-10(1)	14(1)
C331a	52(2)	85(2)	72(2)	22(2)	-9(2)	21(2)
C332a	52(2)	85(2)	72(2)	22(2)	-9(2)	21(2)
C333a	52(2)	85(2)	72(2)	22(2)	-9(2)	21(2)
C334b	52(2)	85(2)	72(2)	22(2)	-9(2)	21(2)
C335b	52(2)	85(2)	72(2)	22(2)	-9(2)	21(2)
C336b	52(2)	85(2)	72(2)	22(2)	-9(2)	21(2)
P(32)	27(1)	54(1)	35(1)	14(1)	3(1)	2(1)
C(341)	52(1)	92(2)	54(1)	25(1)	-1(1)	6(1)
C(342)	52(1)	92(2)	54(1)	25(1)	-1(1)	6(1)
C(343)	52(1)	92(2)	54(1)	25(1)	-1(1)	6(1)
N(3)	26(1)	32(1)	41(1)	5(1)	5(1)	3(1)
O(31)	44(1)	33(1)	53(1)	5(1)	1(1)	-3(1)
O(32)	53(1)	33(1)	66(2)	-4(1)	21(1)	-1(1)
C(321)	26(1)	34(1)	41(2)	7(1)	-5(1)	4(1)
C(322)	32(1)	36(1)	36(2)	8(1)	1(1)	8(1)
C(323)	57(2)	41(2)	42(2)	4(1)	10(2)	13(1)
C(324)	59(2)	60(2)	41(2)	11(2)	14(2)	20(2)
C(325)	42(2)	62(2)	45(2)	22(2)	12(1)	13(2)
C(326)	39(2)	42(2)	49(2)	14(1)	8(1)	6(1)
C(327)	28(1)	38(1)	38(2)	8(1)	3(1)	8(1)
C(328)	30(1)	33(1)	45(2)	4(1)	6(1)	6(1)
C(311)	36(2)	43(2)	33(1)	12(1)	2(1)	9(1)
C(312)	44(2)	48(2)	42(2)	2(1)	5(1)	11(1)
C(313)	47(2)	73(2)	42(2)	-3(2)	7(2)	15(2)
C(314)	43(2)	102(3)	38(2)	12(2)	9(2)	13(2)
C(315)	49(2)	76(2)	44(2)	29(2)	5(2)	2(2)
C(316)	52(2)	47(2)	40(2)	14(1)	5(1)	8(1)

Table I. 5 Bond lengths [Å] and angles [deg.] for $(PMe_3)_2Ni(Ph)(phthal)$

Ni(1)-C(111)	1.895(3)	N(2)-C(228)	1.387(3)
Ni(1)-N(1)	1.936(2)	O(21)-C(221)	1.221(3)
Ni(1)-P(12)	2.1879(8)	O(22)-C(228)	1.217(3)
Ni(1)-P(11)	2.1886(8)	C(221)-C(222)	1.500(4)
P(11)-C136b	1.748(8)	C(222)-C(227)	1.381(4)
P(11)-C131a	1.762(6)	C(222)-C(223)	1.390(4)
P(11)-C134b	1.798(8)	C(223)-C(224)	1.390(4)
P(11)-C133a	1.804(6)	C(224)-C(225)	1.379(4)
P(11)-C135b	1.859(9)	C(225)-C(226)	1.397(4)
P(11)-C132a	1.863(7)	C(226)-C(227)	1.374(4)
P(12)-C(142)	1.797(4)	C(227)-C(228)	1.502(4)
P(12)-C(143)	1.806(4)	C(211)-C(216)	1.392(4)
P(12)-C(141)	1.813(4)	C(211)-C(212)	1.401(4)
N(1)-C(121)	1.368(3)	C(212)-C(213)	1.388(4)
N(1)-C(128)	1.382(4)	C(213)-C(214)	1.369(5)
O(11)-C(121)	1.226(3)	C(214)-C(215)	1.374(5)
O(12)-C(128)	1.222(3)	C(215)-C(216)	1.392(4)
C(121)-C(122)	1.504(4)	Ni(3)-C(311)	1.902(3)
C(122)-C(127)	1.377(4)	Ni(3)-N(3)	1.939(2)
C(122)-C(123)	1.379(4)	Ni(3)-P(31)	2.1951(8)
C(123)-C(124)	1.395(4)	Ni(3)-P(32)	2.1955(8)
C(124)-C(125)	1.385(5)	P(31)-C335b	1.717(8)
C(125)-C(126)	1.393(5)	P(31)-C333a	1.766(5)
C(126)-C(127)	1.381(4)	P(31)-C331a	1.770(6)
C(127)-C(128)	1.493(4)	P(31)-C334b	1.820(9)
C(111)-C(112)	1.390(4)	P(31)-C332a	1.886(5)
C(111)-C(116)	1.391(4)	P(31)-C336b	1.924(8)
C(112)-C(113)	1.383(4)	P(32)-C(343)	1.795(4)
C(113)-C(114)	1.378(5)	P(32)-C(342)	1.811(3)
C(114)-C(115)	1.364(5)	P(32)-C(341)	1.812(4)
C(115)-C(116)	1.389(4)	N(3)-C(321)	1.375(3)
Ni(2)-C(211)	1.899(3)	N(3)-C(328)	1.379(3)
Ni(2)-N(2)	1.930(2)	O(31)-C(321)	1.226(3)
Ni(2)-P(22)	2.1835(8)	O(32)-C(328)	1.215(3)
Ni(2)-P(21)	2.1921(8)	C(321)-C(322)	1.498(4)
P(21)-C231a	1.781(8)	C(322)-C(327)	1.382(4)
P(21)-C236b	1.795(6)	C(322)-C(323)	1.383(4)
P(21)-C233a	1.802(9)	C(323)-C(324)	1.393(4)
P(21)-C232a	1.823(8)	C(324)-C(325)	1.378(5)
P(21)-C234b	1.827(6)	C(325)-C(326)	1.388(4)
P(21)-C235b	1.832(6)	C(326)-C(327)	1.375(4)
P(22)-C243a	1.761(5)	C(327)-C(328)	1.503(4)
P(22)-C245b	1.773(10)	C(311)-C(312)	1.394(4)
P(22)-C242a	1.777(6)	C(311)-C(316)	1.401(4)
P(22)-C244b	1.832(11)	C(312)-C(313)	1.382(4)
P(22)-C241a	1.868(6)	C(313)-C(314)	1.377(5)
P(22)-C246b	1.925(10)	C(314)-C(315)	1.384(5)
N(2)-C(221)	1.375(3)	C(315)-C(316)	1.390(4)

C(111)-Ni(1)-N(1)	176.62(11)	C246b-P(22)-Ni(2)	106.2(4)
C(111)-Ni(1)-P(12)	87.75(8)	C(221)-N(2)-C(228)	109.2(2)
N(1)-Ni(1)-P(12)	92.04(7)	C(221)-N(2)-Ni(2)	126.92(17)
C(111)-Ni(1)-P(11)	88.16(8)	C(228)-N(2)-Ni(2)	123.81(17)
N(1)-Ni(1)-P(11)	91.85(7)	O(21)-C(221)-N(2)	125.2(2)
P(12)-Ni(1)-P(11)	174.80(3)	O(21)-C(221)-C(222)	126.3(2)
C136b-P(11)-C134b	106.4(4)	N(2)-C(221)-C(222)	108.5(2)
C131a-P(11)-C133a	104.9(3)	C(227)-C(222)-C(223)	121.1(3)
C136b-P(11)-C135b	102.4(5)	C(227)-C(222)-C(221)	107.2(2)
C134b-P(11)-C135b	99.8(5)	C(223)-C(222)-C(221)	131.6(2)
C131a-P(11)-C132a	102.4(3)	C(224)-C(223)-C(222)	116.8(3)
C133a-P(11)-C132a	99.1(3)	C(225)-C(224)-C(223)	121.9(3)
C136b-P(11)-Ni(1)	118.1(3)	C(224)-C(225)-C(226)	121.1(3)
C131a-P(11)-Ni(1)	122.0(2)	C(227)-C(226)-C(225)	116.9(3)
C134b-P(11)-Ni(1)	120.1(3)	C(226)-C(227)-C(222)	122.3(2)
C133a-P(11)-Ni(1)	115.6(2)	C(226)-C(227)-C(228)	131.2(2)
C135b-P(11)-Ni(1)	106.9(3)	C(222)-C(227)-C(228)	106.5(2)
C132a-P(11)-Ni(1)	109.72(19)	O(22)-C(228)-N(2)	125.3(2)
C(142)-P(12)-C(143)	104.78(18)	O(22)-C(228)-C(227)	126.2(2)
C(142)-P(12)-C(141)	101.80(17)	N(2)-C(228)-C(227)	108.5(2)
C(143)-P(12)-C(141)	101.86(18)	C(216)-C(211)-C(212)	115.8(2)
C(142)-P(12)-Ni(1)	115.80(12)	C(216)-C(211)-Ni(2)	122.8(2)
C(143)-P(12)-Ni(1)	110.32(12)	C(212)-C(211)-Ni(2)	121.4(2)
C(141)-P(12)-Ni(1)	120.37(12)	C(213)-C(212)-C(211)	121.8(3)
C(121)-N(1)-C(128)	109.3(2)	C(214)-C(213)-C(212)	120.6(3)
C(121)-N(1)-Ni(1)	128.81(19)	C(213)-C(214)-C(215)	119.4(3)
C(128)-N(1)-Ni(1)	121.83(19)	C(214)-C(215)-C(216)	119.9(3)
O(11)-C(121)-N(1)	126.1(3)	C(211)-C(216)-C(215)	122.4(3)
O(11)-C(121)-C(122)	125.4(3)	C(311)-Ni(3)-N(3)	178.73(11)
N(1)-C(121)-C(122)	108.5(2)	C(311)-Ni(3)-P(31)	87.32(9)
C(127)-C(122)-C(123)	121.9(3)	N(3)-Ni(3)-P(31)	93.62(7)
C(127)-C(122)-C(121)	106.8(2)	C(311)-Ni(3)-P(32)	85.84(8)
C(123)-C(122)-C(121)	131.3(3)	N(3)-Ni(3)-P(32)	93.20(7)
C(122)-C(123)-C(124)	116.8(3)	P(31)-Ni(3)-P(32)	173.09(3)
C(125)-C(124)-C(123)	121.3(3)	C333a-P(31)-C331a	107.5(3)
C(124)-C(125)-C(126)	121.3(3)	C335b-P(31)-C334b	106.2(5)
C(127)-C(126)-C(125)	116.8(3)	C333a-P(31)-C332a	100.4(3)
C(122)-C(127)-C(126)	121.8(3)	C331a-P(31)-C332a	99.5(3)
C(122)-C(127)-C(128)	106.8(2)	C335b-P(31)-C336b	98.8(4)
C(126)-C(127)-C(128)	131.3(3)	C334b-P(31)-C336b	97.0(5)
O(12)-C(128)-N(1)	125.3(3)	C335b-P(31)-Ni(3)	120.6(4)
O(12)-C(128)-C(127)	126.1(3)	C333a-P(31)-Ni(3)	114.73(19)
N(1)-C(128)-C(127)	108.6(2)	C331a-P(31)-Ni(3)	118.00(19)
C(112)-C(111)-C(116)	116.3(2)	C334b-P(31)-Ni(3)	115.4(3)
C(112)-C(111)-Ni(1)	123.1(2)	C332a-P(31)-Ni(3)	114.29(18)
C(116)-C(111)-Ni(1)	120.7(2)	C336b-P(31)-Ni(3)	115.1(3)
C(113)-C(112)-C(111)	121.9(3)	C(343)-P(32)-C(342)	102.19(18)
C(114)-C(113)-C(112)	120.1(3)	C(343)-P(32)-C(341)	103.61(18)
C(115)-C(114)-C(113)	119.6(3)	C(342)-P(32)-C(341)	101.62(17)
C(114)-C(115)-C(116)	120.0(3)	C(343)-P(32)-Ni(3)	114.25(12)

C(115)-C(116)-C(111)	122.2(3)	C(342)-P(32)-Ni(3)	116.07(12)
C(211)-Ni(2)-N(2)	179.38(10)	C(341)-P(32)-Ni(3)	117.05(12)
C(211)-Ni(2)-P(22)	86.89(8)	C(321)-N(3)-C(328)	109.4(2)
N(2)-Ni(2)-P(22)	92.75(7)	C(321)-N(3)-Ni(3)	124.68(18)
C(211)-Ni(2)-P(21)	86.92(8)	C(328)-N(3)-Ni(3)	125.92(18)
N(2)-Ni(2)-P(21)	93.45(7)	O(31)-C(321)-N(3)	125.7(3)
P(22)-Ni(2)-P(21)	173.81(3)	O(31)-C(321)-C(322)	125.9(3)
C231a-P(21)-C233a	104.7(5)	N(3)-C(321)-C(322)	108.5(2)
C231a-P(21)-C232a	104.7(4)	C(327)-C(322)-C(323)	120.7(3)
C233a-P(21)-C232a	104.4(4)	C(327)-C(322)-C(321)	107.2(2)
C236b-P(21)-C234b	104.4(3)	C(323)-C(322)-C(321)	132.1(3)
C236b-P(21)-C235b	99.7(3)	C(322)-C(323)-C(324)	118.1(3)
C234b-P(21)-C235b	100.1(3)	C(325)-C(324)-C(323)	120.6(3)
C231a-P(21)-Ni(2)	117.7(4)	C(324)-C(325)-C(326)	121.4(3)
C236b-P(21)-Ni(2)	118.7(3)	C(327)-C(326)-C(325)	117.7(3)
C233a-P(21)-Ni(2)	115.0(5)	C(326)-C(327)-C(322)	121.6(3)
C232a-P(21)-Ni(2)	109.1(4)	C(326)-C(327)-C(328)	132.1(3)
C234b-P(21)-Ni(2)	112.6(2)	C(322)-C(327)-C(328)	106.3(2)
C235b-P(21)-Ni(2)	118.9(3)	O(32)-C(328)-N(3)	125.6(3)
C243a-P(22)-C242a	105.9(3)	O(32)-C(328)-C(327)	125.7(3)
C245b-P(22)-C244b	102.5(6)	N(3)-C(328)-C(327)	108.6(2)
C243a-P(22)-C241a	100.7(3)	C(312)-C(311)-C(316)	116.4(3)
C242a-P(22)-C241a	101.9(3)	C(312)-C(311)-Ni(3)	121.3(2)
C245b-P(22)-C246b	98.1(5)	C(316)-C(311)-Ni(3)	122.3(2)
C244b-P(22)-C246b	96.5(6)	C(313)-C(312)-C(311)	122.1(3)
C243a-P(22)-Ni(2)	116.71(18)	C(314)-C(313)-C(312)	120.4(3)
C245b-P(22)-Ni(2)	124.2(4)	C(313)-C(314)-C(315)	119.3(3)
C242a-P(22)-Ni(2)	119.4(3)	C(314)-C(315)-C(316)	120.0(3)
C244b-P(22)-Ni(2)	122.9(6)	C(315)-C(316)-C(311)	121.8(3)
C241a-P(22)-Ni(2)	109.61(17)		

Table I. 6 Torsion angles [deg.] for (PMe$_3$)$_2$Ni(Ph)(phthal)

C(111)-Ni(1)-P(11)-C136b	146.2(5)	C(228)-N(2)-C(221)-O(21)	179.2(3)
N(1)-Ni(1)-P(11)-C136b	-30.4(5)	Ni(2)-N(2)-C(221)-O(21)	-3.0(4)
P(12)-Ni(1)-P(11)-C136b	108.0(6)	C(228)-N(2)-C(221)-C(222)	-1.0(3)
C(111)-Ni(1)-P(11)-C131a	-33.2(3)	Ni(2)-N(2)-C(221)-C(222)	176.86(17)
N(1)-Ni(1)-P(11)-C131a	150.2(3)	O(21)-C(221)-C(222)-C(227)	-179.3(3)
P(12)-Ni(1)-P(11)-C131a	-71.4(5)	N(2)-C(221)-C(222)-C(227)	0.9(3)
C(111)-Ni(1)-P(11)-C134b	13.3(5)	O(21)-C(221)-C(222)-C(223)	1.5(5)
N(1)-Ni(1)-P(11)-C134b	-163.3(5)	N(2)-C(221)-C(222)-C(223)	-178.4(3)
P(12)-Ni(1)-P(11)-C134b	-24.9(6)	C(227)-C(222)-C(223)-C(224)	-0.3(4)
C(111)-Ni(1)-P(11)-C133a	-162.6(3)	C(221)-C(222)-C(223)-C(224)	178.8(3)
N(1)-Ni(1)-P(11)-C133a	20.8(3)	C(222)-C(223)-C(224)-C(225)	0.4(4)
P(12)-Ni(1)-P(11)-C133a	159.2(5)	C(223)-C(224)-C(225)-C(226)	0.1(5)
C(111)-Ni(1)-P(11)-C135b	-99.2(4)	C(224)-C(225)-C(226)-C(227)	-0.7(4)
N(1)-Ni(1)-P(11)-C135b	84.2(4)	C(225)-C(226)-C(227)-C(222)	0.7(4)
P(12)-Ni(1)-P(11)-C135b	-137.4(5)	C(225)-C(226)-C(227)-C(228)	-178.1(3)
C(111)-Ni(1)-P(11)-C132a	86.4(2)	C(223)-C(222)-C(227)-C(226)	-0.2(4)
N(1)-Ni(1)-P(11)-C132a	-90.2(2)	C(221)-C(222)-C(227)-C(226)	-179.6(2)
P(12)-Ni(1)-P(11)-C132a	48.2(5)	C(223)-C(222)-C(227)-C(228)	178.9(2)
C(111)-Ni(1)-P(12)-C(142)	151.40(17)	C(221)-C(222)-C(227)-C(228)	-0.5(3)
N(1)-Ni(1)-P(12)-C(142)	-31.98(17)	C(221)-N(2)-C(228)-O(22)	179.3(3)
P(11)-Ni(1)-P(12)-C(142)	-170.4(4)	Ni(2)-N(2)-C(228)-O(22)	1.4(4)
C(111)-Ni(1)-P(12)-C(143)	-89.84(16)	C(221)-N(2)-C(228)-C(227)	0.7(3)
N(1)-Ni(1)-P(12)-C(143)	86.79(16)	Ni(2)-N(2)-C(228)-C(227)	-177.23(16)
P(11)-Ni(1)-P(12)-C(143)	-51.6(4)	C(226)-C(227)-C(228)-O(22)	0.3(5)
C(111)-Ni(1)-P(12)-C(141)	28.26(18)	C(222)-C(227)-C(228)-O(22)	-178.7(3)
N(1)-Ni(1)-P(12)-C(141)	155.11(17)	C(226)-C(227)-C(228)-N(2)	178.9(3)
P(11)-Ni(1)-P(12)-C(141)	66.5(4)	C(222)-C(227)-C(228)-N(2)	-0.1(3)
C(111)-Ni(1)-N(1)-C(121)	177(22)	N(2)-Ni(2)-C(211)-C(216)	-138(9)
P(12)-Ni(1)-N(1)-C(121)	91.0(2)	P(22)-Ni(2)-C(211)-C(216)	-84.3(2)
P(11)-Ni(1)-N(1)-C(121)	-92.5(2)	P(21)-Ni(2)-C(211)-C(216)	95.7(2)
C(111)-Ni(1)-N(1)-C(128)	-4.2(18)	N(2)-Ni(2)-C(211)-C(212)	40(9)
P(12)-Ni(1)-N(1)-C(128)	-90.6(2)	P(22)-Ni(2)-C(211)-C(212)	94.1(2)
P(11)-Ni(1)-N(1)-C(128)	85.9(2)	P(21)-Ni(2)-C(211)-C(212)	-85.9(2)
C(128)-N(1)-C(121)-O(11)	180.0(3)	C(216)-C(211)-C(212)-C(213)	0.3(4)
Ni(1)-N(1)-C(121)-O(11)	-1.4(4)	Ni(2)-C(211)-C(212)-C(213)	-178.2(2)
C(128)-N(1)-C(121)-C(122)	1.1(3)	C(211)-C(212)-C(213)-C(214)	-0.2(5)
Ni(1)-N(1)-C(121)-C(122)	179.70(17)	C(212)-C(213)-C(214)-C(215)	-0.2(5)
O(11)-C(121)-C(122)-C(127)	-179.4(3)	C(213)-C(214)-C(215)-C(216)	0.5(5)
N(1)-C(121)-C(122)-C(127)	-0.5(3)	C(212)-C(211)-C(216)-C(215)	0.0(4)
O(11)-C(121)-C(122)-C(123)	0.5(5)	Ni(2)-C(211)-C(216)-C(215)	178.5(2)
N(1)-C(121)-C(122)-C(123)	179.3(3)	C(214)-C(215)-C(216)-C(211)	-0.4(5)
C(127)-C(122)-C(123)-C(124)	1.4(4)	C(311)-Ni(3)-P(31)-C335b	145.0(5)
C(121)-C(122)-C(123)-C(124)	-178.5(3)	N(3)-Ni(3)-P(31)-C335b	-34.1(5)
C(122)-C(123)-C(124)-C(125)	-0.6(5)	P(32)-Ni(3)-P(31)-C335b	136.8(5)
C(123)-C(124)-C(125)-C(126)	-0.6(5)	C(311)-Ni(3)-P(31)-C333a	70.1(3)
C(124)-C(125)-C(126)-C(127)	1.0(4)	N(3)-Ni(3)-P(31)-C333a	-109.0(2)
C(123)-C(122)-C(127)-C(126)	-0.9(4)	P(32)-Ni(3)-P(31)-C333a	61.9(4)
C(121)-C(122)-C(127)-C(126)	178.9(2)	C(311)-Ni(3)-P(31)-C331a	-58.2(3)
C(123)-C(122)-C(127)-C(128)	179.9(3)	N(3)-Ni(3)-P(31)-C331a	122.6(3)

C(121)-C(122)-C(127)-C(128)	-0.3(3)	P(32)-Ni(3)-P(31)-C331a	-66.4(4)
C(125)-C(126)-C(127)-C(122)	-0.3(4)	C(311)-Ni(3)-P(31)-C334b	-85.1(4)
C(125)-C(126)-C(127)-C(128)	178.7(3)	N(3)-Ni(3)-P(31)-C334b	95.8(4)
C(121)-N(1)-C(128)-O(12)	178.9(3)	P(32)-Ni(3)-P(31)-C334b	-93.3(5)
Ni(1)-N(1)-C(128)-O(12)	0.2(4)	C(311)-Ni(3)-P(31)-C332a	-174.7(2)
C(121)-N(1)-C(128)-C(127)	-1.3(3)	N(3)-Ni(3)-P(31)-C332a	6.2(2)
Ni(1)-N(1)-C(128)-C(127)	179.99(16)	P(32)-Ni(3)-P(31)-C332a	177.1(3)
C(122)-C(127)-C(128)-O(12)	-179.2(3)	C(311)-Ni(3)-P(31)-C336b	26.7(4)
C(126)-C(127)-C(128)-O(12)	1.7(5)	N(3)-Ni(3)-P(31)-C336b	-152.4(4)
C(122)-C(127)-C(128)-N(1)	1.0(3)	P(32)-Ni(3)-P(31)-C336b	18.5(5)
C(126)-C(127)-C(128)-N(1)	-178.1(3)	C(311)-Ni(3)-P(32)-C(343)	-76.83(16)
N(1)-Ni(1)-C(111)-C(112)	177.0(16)	N(3)-Ni(3)-P(32)-C(343)	102.33(15)
P(12)-Ni(1)-C(111)-C(112)	-96.4(2)	P(31)-Ni(3)-P(32)-C(343)	-68.6(3)
P(11)-Ni(1)-C(111)-C(112)	86.8(2)	C(311)-Ni(3)-P(32)-C(342)	164.60(18)
N(1)-Ni(1)-C(111)-C(116)	-2.0(18)	N(3)-Ni(3)-P(32)-C(342)	-16.24(17)
P(12)-Ni(1)-C(111)-C(116)	84.6(2)	P(31)-Ni(3)-P(32)-C(342)	172.8(3)
P(11)-Ni(1)-C(111)-C(116)	-92.2(2)	C(311)-Ni(3)-P(32)-C(341)	44.49(16)
C(116)-C(111)-C(112)-C(113)	0.0(4)	N(3)-Ni(3)-P(32)-C(341)	-136.35(15)
Ni(1)-C(111)-C(112)-C(113)	-179.0(2)	P(31)-Ni(3)-P(32)-C(341)	52.7(3)
C(111)-C(112)-C(113)-C(114)	-0.5(4)	C(311)-Ni(3)-N(3)-C(321)	-32(5)
C(112)-C(113)-C(114)-C(115)	0.5(5)	P(31)-Ni(3)-N(3)-C(321)	105.3(2)
C(113)-C(114)-C(115)-C(116)	0.0(5)	P(32)-Ni(3)-N(3)-C(321)	-73.6(2)
C(114)-C(115)-C(116)-C(111)	-0.5(5)	C(311)-Ni(3)-N(3)-C(328)	146(5)
C(112)-C(111)-C(116)-C(115)	0.5(4)	P(31)-Ni(3)-N(3)-C(328)	-76.2(2)
Ni(1)-C(111)-C(116)-C(115)	179.5(2)	P(32)-Ni(3)-N(3)-C(328)	104.9(2)
C(211)-Ni(2)-P(21)-C231a	-45.1(6)	C(328)-N(3)-C(321)-O(31)	-179.7(3)
N(2)-Ni(2)-P(21)-C231a	135.4(6)	Ni(3)-N(3)-C(321)-O(31)	-0.9(4)
P(22)-Ni(2)-P(21)-C231a	-45.1(7)	C(328)-N(3)-C(321)-C(322)	0.6(3)
C(211)-Ni(2)-P(21)-C236b	61.2(4)	Ni(3)-N(3)-C(321)-C(322)	179.35(17)
N(2)-Ni(2)-P(21)-C236b	-118.3(4)	O(31)-C(321)-C(322)-C(327)	178.2(3)
P(22)-Ni(2)-P(21)-C236b	61.2(5)	N(3)-C(321)-C(322)-C(327)	-2.1(3)
C(211)-Ni(2)-P(21)-C233a	-169.2(5)	O(31)-C(321)-C(322)-C(323)	-2.2(5)
N(2)-Ni(2)-P(21)-C233a	11.3(5)	N(3)-C(321)-C(322)-C(323)	177.5(3)
P(22)-Ni(2)-P(21)-C233a	-169.2(6)	C(327)-C(322)-C(323)-C(324)	-0.5(4)
C(211)-Ni(2)-P(21)-C232a	73.9(5)	C(321)-C(322)-C(323)-C(324)	180.0(3)
N(2)-Ni(2)-P(21)-C232a	-105.6(5)	C(322)-C(323)-C(324)-C(325)	-0.3(5)
P(22)-Ni(2)-P(21)-C232a	74.0(6)	C(323)-C(324)-C(325)-C(326)	0.3(5)
C(211)-Ni(2)-P(21)-C234b	-61.0(4)	C(324)-C(325)-C(326)-C(327)	0.6(5)
N(2)-Ni(2)-P(21)-C234b	119.5(4)	C(325)-C(326)-C(327)-C(322)	-1.4(4)
P(22)-Ni(2)-P(21)-C234b	-61.0(5)	C(325)-C(326)-C(327)-C(328)	176.7(3)
C(211)-Ni(2)-P(21)-C235b	-177.5(3)	C(323)-C(322)-C(327)-C(326)	1.4(4)
N(2)-Ni(2)-P(21)-C235b	3.0(3)	C(321)-C(322)-C(327)-C(326)	-179.0(2)
P(22)-Ni(2)-P(21)-C235b	-177.4(5)	C(323)-C(322)-C(327)-C(328)	-177.1(3)
C(211)-Ni(2)-P(22)-C243a	-164.8(3)	C(321)-C(322)-C(327)-C(328)	2.5(3)
N(2)-Ni(2)-P(22)-C243a	14.7(3)	C(321)-N(3)-C(328)-O(32)	-177.9(3)
P(21)-Ni(2)-P(22)-C243a	-164.9(4)	Ni(3)-N(3)-C(328)-O(32)	3.4(4)
C(211)-Ni(2)-P(22)-C245b	117.0(6)	C(321)-N(3)-C(328)-C(327)	1.0(3)
N(2)-Ni(2)-P(22)-C245b	-63.5(6)	Ni(3)-N(3)-C(328)-C(327)	-177.76(17)
P(21)-Ni(2)-P(22)-C245b	116.9(7)	C(326)-C(327)-C(328)-O(32)	-1.7(5)
C(211)-Ni(2)-P(22)-C242a	-35.2(3)	C(322)-C(327)-C(328)-O(32)	176.6(3)
N(2)-Ni(2)-P(22)-C242a	144.3(3)	C(326)-C(327)-C(328)-N(3)	179.5(3)

P(21)-Ni(2)-P(22)-C242a	-35.3(5)	C(322)-C(327)-C(328)-N(3)	-2.3(3)
C(211)-Ni(2)-P(22)-C244b	-21.7(7)	N(3)-Ni(3)-C(311)-C(312)	-134(5)
N(2)-Ni(2)-P(22)-C244b	157.8(7)	P(31)-Ni(3)-C(311)-C(312)	87.9(2)
P(21)-Ni(2)-P(22)-C244b	-21.7(8)	P(32)-Ni(3)-C(311)-C(312)	-93.1(2)
C(211)-Ni(2)-P(22)-C241a	81.7(2)	N(3)-Ni(3)-C(311)-C(316)	44(5)
N(2)-Ni(2)-P(22)-C241a	-98.9(2)	P(31)-Ni(3)-C(311)-C(316)	-93.3(2)
P(21)-Ni(2)-P(22)-C241a	81.6(4)	P(32)-Ni(3)-C(311)-C(316)	85.7(2)
C(211)-Ni(2)-P(22)-C246b	-130.9(5)	C(316)-C(311)-C(312)-C(313)	0.3(4)
N(2)-Ni(2)-P(22)-C246b	48.6(5)	Ni(3)-C(311)-C(312)-C(313)	179.2(2)
P(21)-Ni(2)-P(22)-C246b	-131.0(5)	C(311)-C(312)-C(313)-C(314)	-0.5(5)
C(211)-Ni(2)-N(2)-C(221)	126(9)	C(312)-C(313)-C(314)-C(315)	0.4(5)
P(22)-Ni(2)-N(2)-C(221)	72.0(2)	C(313)-C(314)-C(315)-C(316)	-0.1(5)
P(21)-Ni(2)-N(2)-C(221)	-108.0(2)	C(314)-C(315)-C(316)-C(311)	-0.1(5)
C(211)-Ni(2)-N(2)-C(228)	-57(9)	C(312)-C(311)-C(316)-C(315)	0.0(4)
P(22)-Ni(2)-N(2)-C(228)	-110.5(2)	Ni(3)-C(311)-C(316)-C(315)	-178.9(2)
P(21)-Ni(2)-N(2)-C(228)	69.5(2)		

Table I. 7 Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

Plane 1.

6.6100 (0.0077) x + 7.9099 (0.0155) y - 12.8597 (0.0234) z = 5.5161 (0.0139)

*	-0.0015	(0.0018)	C111
*	-0.0016	(0.0020)	C112
*	0.0032	(0.0021)	C113
*	-0.0017	(0.0022)	C114
*	-0.0014	(0.0022)	C115
*	0.0030	(0.0020)	C116
	0.0186	(0.0038)	Ni1

Rms deviation of fitted atoms = 0.0022

Plane 2.

6.7478 (0.0081) x + 8.3782 (0.0164) y - 10.8359 (0.0282) z = 6.6473 (0.0148)

Angle to previous plane (with approximate esd) = 6.01 (0.19)

*	-0.0073	(0.0016)	N1
*	0.0047	(0.0016)	C121
*	-0.0005	(0.0016)	C122
*	-0.0036	(0.0016)	C127
*	0.0066	(0.0016)	C128
	-0.0034	(0.0043)	O11
	0.0201	(0.0042)	O12
	-0.0007	(0.0039)	Ni1

Rms deviation of fitted atoms = 0.0052

Plane 3.

6.6125 (0.0080) x + 8.5484 (0.0151) y - 11.1879 (0.0246) z = 6.6178 (0.0134)

Angle to previous plane (with approximate esd) = 1.30 (0.19)

*	0.0015	(0.0019)	C127
*	0.0053	(0.0020)	C126
*	-0.0061	(0.0022)	C125
*	0.0001	(0.0022)	C124
*	0.0067	(0.0021)	C123
*	-0.0076	(0.0019)	C122

Rms deviation of fitted atoms = 0.0053

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Plane 3.

 0.2766 (0.0065) x + 5.8380 (0.0111) y + 18.8006 (0.0076) z = 10.4632(0.0020)

 Angle to previous plane (with approximate esd) = 89.07 ( 0.07 )

 *   0.0040 (0.0010)  C111
 *  -0.0038 (0.0009)  P11
 *  -0.0038 (0.0009)  P12
 *   0.0036 (0.0009)  N1
     0.0600 (0.0010)  Ni1

 Rms deviation of fitted atoms =   0.0038

Plane 4.

 6.7952 (0.0081) x - 9.3426 (0.0160) y - 9.7106 (0.0276) z = 1.8465 (0.0138)

 Angle to previous plane (with approximate esd) = 52.47 ( 0.09 )

 *   0.0012 (0.0020)  C211
 *  -0.0020 (0.0020)  C212
 *   0.0003 (0.0022)  C213
 *   0.0021 (0.0023)  C214
 *  -0.0028 (0.0023)  C215
 *   0.0012 (0.0021)  C216
     0.0486 (0.0041)  Ni2

 Rms deviation of fitted atoms =   0.0018

Plane 5.

 6.7859 (0.0079) x - 6.2942 (0.0196) y - 14.1392 (0.0244) z = 2.7460 (0.0069)

 Angle to previous plane (with approximate esd) = 14.46 ( 0.18 )

 *  -0.0052 (0.0016)  N2
 *   0.0056 (0.0015)  C221
 *  -0.0039 (0.0016)  C222
 *   0.0011 (0.0016)  C227
 *   0.0025 (0.0016)  C228
     0.0168 (0.0041)  O21
    -0.0160 (0.0043)  O22
    -0.0846 (0.0039)  Ni2

 Rms deviation of fitted atoms =   0.0040
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Plane 6.

 6.6440 (0.0078) x - 6.4571 (0.0165) y - 14.2782 (0.0213) z = 2.6626 (0.0046)

 Angle to previous plane (with approximate esd) =  1.28 ( 0.19 )

 *  -0.0028 (0.0019)  C227
 *   0.0045 (0.0020)  C226
 *  -0.0023 (0.0021)  C225
 *  -0.0016 (0.0021)  C224
 *   0.0033 (0.0020)  C223
 *  -0.0011 (0.0019)  C222

 Rms deviation of fitted atoms =   0.0028

Plane 7.

 1.6480 (0.0057) x + 10.4063 (0.0052) y - 19.3378 (0.0089) z = 3.7543 (0.0061)

 Angle to previous plane (with approximate esd) = 71.02 ( 0.07 )

 *   0.0042 (0.0009)  C211
 *  -0.0039 (0.0009)  P21
 *  -0.0040 (0.0009)  P22
 *   0.0037 (0.0008)  N2
    -0.0043 (0.0009)  Ni2

 Rms deviation of fitted atoms =   0.0040

Plane 8.

 6.7450 (0.0082) x - 4.5018 (0.0198) y + 14.4428 (0.0227) z = 4.1512 (0.0127)

 Angle to previous plane (with approximate esd) = 61.60 ( 0.08 )

 *   0.0004 (0.0020)  C311
 *  -0.0016 (0.0022)  C312
 *   0.0018 (0.0024)  C313
 *  -0.0007 (0.0024)  C314
 *  -0.0005 (0.0023)  C315
 *   0.0007 (0.0022)  C316
    -0.0296 (0.0042)  Ni3

 Rms deviation of fitted atoms =   0.0011
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Plane 9.

 6.8420 (0.0080) x - 7.2885 (0.0192) y + 13.1621 (0.0238) z = 3.2970 (0.0063)

 Angle to previous plane (with approximate esd) = 11.77 ( 0.18 )

 *  -0.0011 (0.0016)  N3
 *  -0.0079 (0.0016)  C321
 *   0.0139 (0.0017)  C322
 *  -0.0144 (0.0017)  C327
 *   0.0095 (0.0016)  C328
    -0.0237 (0.0040)  O31
     0.0544 (0.0044)  O32
    -0.0401 (0.0040)  Ni3

 Rms deviation of fitted atoms =   0.0105

Plane 10.

 6.7728 (0.0078) x - 6.9014 (0.0170) y + 13.6027 (0.0230) z = 3.4274 (0.0043)

 Angle to previous plane (with approximate esd) =  2.01 ( 0.19 )

 *   0.0076 (0.0020)  C327
 *  -0.0052 (0.0021)  C326
 *  -0.0006 (0.0022)  C325
 *   0.0039 (0.0023)  C324
 *  -0.0015 (0.0022)  C323
 *  -0.0042 (0.0020)  C322

 Rms deviation of fitted atoms =   0.0045

Plane 11.

 0.0479 (0.0062) x + 14.9395 (0.0014) y - 0.3979 (0.0177) z = 2.0851 (0.0061)

 Angle to previous plane (with approximate esd) = 76.99 ( 0.08 )

 *   0.0033 (0.0010)  C311
 *  -0.0030 (0.0009)  P31
 *  -0.0030 (0.0009)  P32
 *   0.0028 (0.0009)  N3
     7.3562 (0.0050)  Ni1

 Rms deviation of fitted atoms =   0.0030
```

APPENDIX II

Table II. 1 Crystal data and structure refinement for (DPPE)Ni(Ph)(phthal)

Empirical formula	C40 H33 N Ni O2 P2	
Formula weight	680.324	
Temperature	293(2)K	
Wavelength	1.54178 A	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 36.6410(2) Å	alpha = 90°
	b = 9.9030(1) Å	beta = 118.92(1)°
	c = 21.4137(1) Å	gamma = 90°
Volume	6800.98(5) $Å^3$	
Z	8	
Density (calculated)	1.3289 Mg/m^3	
Absorption coefficient	1.990 mm^{-1}	
Crystal size	0.19 x 0.12 x 0.12 mm	
Theta range for data collection	2.76 to 72.85 °	
Reflections collected	39967	
Independent reflections	6633 [R(int) = 0.0487]	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.036	
Final R indices [I >2σ(I)]	R1 = 0.0434, wR2 = 0.1210	
R indices (all data)	R1 = 0.0502, wR2 = 0.1254	
Largest diff. peak and hole	0.547 and -0.254 $e.Å^3$	

$R = \Sigma (|| F_0 | - | F_c ||) / \Sigma (| F_0 |)$

$wR2 = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / \Sigma (F_0{}^2)^2 \}^{½}$

$S = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.})\}^{½}$

Table II. 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for (DPPE)Ni(Ph)(phthal)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Ni	1260(1)	4931(1)	289(1)	37(1)
N	1332(1)	6203(2)	-325(1)	40(1)
C(1)	1715(1)	6777(2)	-116(1)	44(1)
O(1)	2036(1)	6521(2)	435(1)	63(1)
C(2)	1668(1)	7758(2)	-681(1)	45(1)
C(3)	1954(1)	8588(2)	-733(1)	60(1)
C(4)	1811(1)	9387(3)	-1338(2)	70(1)
C(5)	1401(1)	9342(3)	-1863(1)	68(1)
C(6)	1114(1)	8498(2)	-1810(1)	57(1)
C(7)	1256(1)	7716(2)	-1204(1)	43(1)
C(8)	1042(1)	6719(2)	-964(1)	43(1)
O(2)	671(1)	6427(2)	-1281(1)	65(1)
C(9)	1391(1)	1902(2)	958(1)	55(1)
C(10)	1611(1)	1871(2)	510(1)	57(1)
C(11)	1110(1)	6385(2)	714(1)	42(1)
C(12)	1379(1)	7347(2)	1171(1)	53(1)
C(13)	1232(1)	8472(2)	1368(1)	64(1)
C(14)	817(1)	8658(3)	1113(2)	77(1)
C(15)	541(1)	7705(3)	663(2)	81(1)
C(16)	688(1)	6573(3)	471(1)	63(1)
P(2)	1333(1)	3683(1)	1150(1)	41(1)
C(21)	947(1)	3672(2)	1452(1)	48(1)
C(22)	996(1)	4474(3)	2011(1)	59(1)
C(23)	685(1)	4537(3)	2207(2)	74(1)
C(24)	324(1)	3814(4)	1832(2)	86(1)
C(25)	272(1)	3032(4)	1274(2)	88(1)
C(26)	579(1)	2947(3)	1070(1)	70(1)
C(31)	1837(1)	3970(2)	1933(1)	43(1)
C(32)	2137(1)	4741(2)	1876(1)	50(1)
C(33)	2532(1)	4852(3)	2452(1)	60(1)
C(34)	2634(1)	4212(3)	3086(1)	60(1)
C(35)	2340(1)	3446(2)	3148(1)	58(1)
C(36)	1944(1)	3323(2)	2579(1)	51(1)
P(1)	1334(1)	3086(1)	-217(1)	46(1)
C(41)	838(1)	2266(2)	-776(1)	54(1)
C(42)	480(1)	3044(3)	-1105(2)	73(1)
C(43)	99(1)	2438(4)	-1524(2)	102(1)
C(44)	67(1)	1072(4)	-1612(2)	97(1)
C(45)	419(1)	282(3)	-1289(2)	89(1)
C(46)	801(1)	878(3)	-883(2)	75(1)
C(51)	1607(1)	3130(2)	-732(1)	52(1)
C(52)	2010(1)	3643(3)	-413(2)	74(1)
C(53)	2222(1)	3746(3)	-795(2)	90(1)
C(54)	2038(1)	3347(3)	-1493(2)	92(1)

C(55)	1641(1)	2873(3)	-1815(2)	87(1)
C(56)	1422(1)	2759(3)	-1443(1)	67(1)

Table II. 3 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for (DPPE)Ni(Ph)(phthal)

Atom	x	y	z	U(eq)
H(3)	2232	8612	-378	72
H(4)	1996	9963	-1389	84
H(5)	1314	9889	-2264	82
H(6)	837	8463	-2168	68
H(9A)	1554	1412	1400	66
H(9B)	1120	1478	701	66
H(10A)	1598	973	319	68
H(10B)	1901	2128	795	68
H(12)	1665	7240	1351	63
H(13)	1420	9105	1677	77
H(14)	720	9420	1241	92
H(15)	256	7819	489	97
H(16)	499	5929	173	76
H(22)	1238	4978	2261	70
H(23)	722	5069	2591	89
H(24)	115	3860	1959	103
H(25)	26	2544	1023	105
H(26)	539	2413	685	84
H(32)	2072	5180	1450	60
H(33)	2732	5367	2412	72
H(34)	2901	4297	3471	71
H(35)	2410	3010	3576	70
H(36)	1747	2805	2624	61
H(42)	497	3976	-1045	87
H(43)	-140	2969	-1748	122
H(44)	-192	675	-1890	116
H(45)	398	-651	-1345	106
H(46)	1039	343	-676	89
H(52)	2137	3919	61	88
H(53)	2492	4089	-577	108
H(54)	2185	3400	-1745	110
H(55)	1515	2622	-2293	104
H(56)	1150	2433	-1670	81

Table II. 4 Anisotropic parameters (A^2 x 10^3) for (DPPE)Ni(Ph)(phthal)

Atom	U11	U22	U33	U23	U13	U12
Ni	39(1)	35(1)	38(1)	2(1)	20(1)	-2(1)
N	41(1)	42(1)	39(1)	3(1)	22(1)	-4(1)
C(1)	44(1)	45(1)	45(1)	1(1)	24(1)	-4(1)
O(1)	46(1)	79(1)	54(1)	11(1)	16(1)	-7(1)
C(2)	54(1)	38(1)	51(1)	0(1)	33(1)	-3(1)
C(3)	64(1)	53(1)	75(2)	-1(1)	43(1)	-12(1)
C(4)	102(2)	48(1)	94(2)	5(1)	73(2)	-10(1)
C(5)	108(2)	48(1)	67(1)	13(1)	56(2)	2(1)
C(6)	74(2)	50(1)	48(1)	8(1)	31(1)	5(1)
C(7)	54(1)	39(1)	45(1)	2(1)	31(1)	0(1)
C(8)	45(1)	44(1)	43(1)	0(1)	25(1)	-2(1)
O(2)	44(1)	86(1)	55(1)	10(1)	17(1)	-11(1)
C(9)	70(1)	40(1)	56(1)	7(1)	31(1)	-4(1)
C(10)	66(1)	44(1)	62(1)	5(1)	31(1)	7(1)
C(11)	51(1)	39(1)	43(1)	6(1)	28(1)	3(1)
C(12)	61(1)	42(1)	63(1)	0(1)	36(1)	-3(1)
C(13)	88(2)	41(1)	72(2)	-6(1)	45(1)	-5(1)
C(14)	98(2)	61(2)	81(2)	-4(1)	51(2)	22(1)
C(15)	61(2)	95(2)	82(2)	-5(2)	31(2)	29(1)
C(16)	53(1)	73(2)	61(1)	-11(1)	24(1)	6(1)
P(2)	42(1)	41(1)	42(1)	6(1)	22(1)	-3(1)
C(21)	39(1)	59(1)	45(1)	15(1)	20(1)	-2(1)
C(22)	51(1)	72(2)	58(1)	7(1)	30(1)	1(1)
C(23)	64(2)	103(2)	69(2)	16(2)	42(1)	16(1)
C(24)	54(2)	136(3)	80(2)	36(2)	42(2)	15(2)
C(25)	43(1)	133(3)	81(2)	22(2)	26(1)	-18(1)
C(26)	50(1)	97(2)	58(1)	4(1)	22(1)	-18(1)
C(31)	41(1)	43(1)	47(1)	7(1)	22(1)	4(1)
C(32)	44(1)	54(1)	54(1)	9(1)	26(1)	1(1)
C(33)	43(1)	65(2)	69(2)	5(1)	26(1)	-4(1)
C(34)	41(1)	62(1)	61(1)	1(1)	14(1)	9(1)
C(35)	61(1)	56(1)	49(1)	12(1)	20(1)	11(1)
C(36)	50(1)	51(1)	50(1)	13(1)	24(1)	2(1)
P(1)	54(1)	39(1)	50(1)	-1(1)	30(1)	0(1)
C(41)	62(1)	48(1)	60(1)	-9(1)	36(1)	-6(1)
C(42)	63(2)	60(2)	83(2)	-11(1)	26(1)	-2(1)
C(43)	59(2)	102(3)	120(3)	-19(2)	25(2)	-2(2)
C(44)	81(2)	103(3)	111(3)	-41(2)	50(2)	-37(2)
C(45)	91(2)	69(2)	117(3)	-31(2)	59(2)	-27(2)
C(46)	75(2)	55(2)	99(2)	-17(1)	46(2)	-11(1)
C(51)	67(1)	40(1)	62(1)	1(1)	41(1)	4(1)
C(52)	74(2)	80(2)	83(2)	-6(1)	50(2)	-5(1)
C(53)	93(2)	87(2)	124(3)	2(2)	79(2)	-8(2)
C(54)	142(3)	60(2)	129(3)	6(2)	110(3)	0(2)
C(55)	155(3)	55(2)	81(2)	-1(1)	82(2)	-4(2)
C(56)	95(2)	54(1)	67(1)	-3(1)	50(2)	-8(1)

Table II. 5 Bond lengths [Å] and angles [°] for (DPPE)Ni(Ph)(phthal)

Ni-C(11)	1.9210(19)	C(21)-C(22)	1.375(3)
Ni-N	1.9272(15)	C(21)-C(26)	1.392(3)
Ni-P(2)	2.1261(5)	C(22)-C(23)	1.393(3)
Ni-P(1)	2.2062(6)	C(23)-C(24)	1.372(4)
N-C(8)	1.363(2)	C(24)-C(25)	1.357(5)
N-C(1)	1.372(2)	C(25)-C(26)	1.394(3)
C(1)-O(1)	1.225(2)	C(31)-C(32)	1.392(3)
C(1)-C(2)	1.496(3)	C(31)-C(36)	1.397(3)
C(2)-C(3)	1.378(3)	C(32)-C(33)	1.378(3)
C(2)-C(7)	1.379(3)	C(33)-C(34)	1.376(3)
C(3)-C(4)	1.386(4)	C(34)-C(35)	1.375(3)
C(4)-C(5)	1.375(4)	C(35)-C(36)	1.378(3)
C(5)-C(6)	1.391(3)	P(1)-C(51)	1.815(2)
C(6)-C(7)	1.379(3)	P(1)-C(41)	1.815(2)
C(7)-C(8)	1.497(3)	C(41)-C(42)	1.383(3)
C(8)-O(2)	1.225(2)	C(41)-C(46)	1.389(3)
C(9)-C(10)	1.523(3)	C(42)-C(43)	1.381(4)
C(9)-P(2)	1.846(2)	C(43)-C(44)	1.363(5)
C(10)-P(1)	1.836(2)	C(44)-C(45)	1.375(5)
C(11)-C(12)	1.382(3)	C(45)-C(46)	1.374(4)
C(11)-C(16)	1.384(3)	C(51)-C(56)	1.382(3)
C(12)-C(13)	1.388(3)	C(51)-C(52)	1.387(3)
C(13)-C(14)	1.357(4)	C(52)-C(53)	1.377(4)
C(14)-C(15)	1.378(4)	C(53)-C(54)	1.367(5)
C(15)-C(16)	1.390(4)	C(54)-C(55)	1.357(5)
P(2)-C(21)	1.818(2)	C(55)-C(56)	1.385(4)
P(2)-C(31)	1.818(2)		

□

C(11)-Ni-N	89.91(7)	C(9)-P(2)-Ni	110.03(7)
C(11)-Ni-P(2)	88.25(5)	C(22)-C(21)-C(26)	119.3(2)
N-Ni-P(2)	165.81(5)	C(22)-C(21)-P(2)	120.77(16)
C(11)-Ni-P(1)	169.88(6)	C(26)-C(21)-P(2)	119.59(18)
N-Ni-P(1)	96.72(5)	C(21)-C(22)-C(23)	120.5(2)
P(2)-Ni-P(1)	87.15(2)	C(24)-C(23)-C(22)	119.9(3)
C(8)-N-C(1)	110.37(15)	C(25)-C(24)-C(23)	119.9(2)
C(8)-N-Ni	129.35(12)	C(24)-C(25)-C(26)	121.3(3)
C(1)-N-Ni	120.19(12)	C(21)-C(26)-C(25)	119.0(3)
O(1)-C(1)-N	125.73(18)	C(32)-C(31)-C(36)	118.88(19)
O(1)-C(1)-C(2)	126.36(18)	C(32)-C(31)-P(2)	119.84(15)
N-C(1)-C(2)	107.91(16)	C(36)-C(31)-P(2)	120.99(15)
C(3)-C(2)-C(7)	121.9(2)	C(33)-C(32)-C(31)	119.7(2)
C(3)-C(2)-C(1)	131.3(2)	C(34)-C(33)-C(32)	121.0(2)
C(7)-C(2)-C(1)	106.77(16)	C(35)-C(34)-C(33)	119.8(2)
C(2)-C(3)-C(4)	117.2(2)	C(34)-C(35)-C(36)	120.1(2)
C(5)-C(4)-C(3)	121.1(2)	C(35)-C(36)-C(31)	120.5(2)
C(4)-C(5)-C(6)	121.5(2)	C(51)-P(1)-C(41)	106.32(10)
C(7)-C(6)-C(5)	117.2(2)	C(51)-P(1)-C(10)	106.83(10)
C(6)-C(7)-C(2)	121.00(19)	C(41)-P(1)-C(10)	103.46(11)

C(6)-C(7)-C(8)	132.1(2)	C(51)-P(1)-Ni	120.88(7)
C(2)-C(7)-C(8)	106.88(16)	C(41)-P(1)-Ni	111.93(7)
O(2)-C(8)-N	125.69(18)	C(10)-P(1)-Ni	105.98(8)
O(2)-C(8)-C(7)	126.25(18)	C(42)-C(41)-C(46)	118.3(2)
N-C(8)-C(7)	108.06(16)	C(42)-C(41)-P(1)	119.11(18)
C(10)-C(9)-P(2)	108.18(14)	C(46)-C(41)-P(1)	122.6(2)
C(9)-C(10)-P(1)	106.09(15)	C(43)-C(42)-C(41)	120.1(3)
C(12)-C(11)-C(16)	117.4(2)	C(44)-C(43)-C(42)	120.9(3)
C(12)-C(11)-Ni	125.57(15)	C(43)-C(44)-C(45)	119.9(3)
C(16)-C(11)-Ni	116.57(16)	C(46)-C(45)-C(44)	119.6(3)
C(11)-C(12)-C(13)	121.2(2)	C(45)-C(46)-C(41)	121.2(3)
C(14)-C(13)-C(12)	120.7(2)	C(56)-C(51)-C(52)	118.7(2)
C(13)-C(14)-C(15)	119.3(2)	C(56)-C(51)-P(1)	122.69(19)
C(14)-C(15)-C(16)	120.1(2)	C(52)-C(51)-P(1)	118.50(18)
C(11)-C(16)-C(15)	121.3(2)	C(53)-C(52)-C(51)	120.3(3)
C(21)-P(2)-C(31)	106.88(9)	C(54)-C(53)-C(52)	120.4(3)
C(21)-P(2)-C(9)	105.47(10)	C(55)-C(54)-C(53)	119.8(3)
C(31)-P(2)-C(9)	100.34(10)	C(54)-C(55)-C(56)	120.9(3)
C(21)-P(2)-Ni	121.24(7)	C(51)-C(56)-C(55)	119.9(3)
C(31)-P(2)-Ni	110.76(6)		

Table II. 6 Torsion angles [°] for (DPPE)Ni(Ph)(phthal)

C(11)-Ni-N-C(8)	-85.05(18)	C(9)-P(2)-C(21)-C(26)	-46.9(2)
P(2)-Ni-N-C(8)	-167.56(15)	Ni-P(2)-C(21)-C(26)	78.8(2)
P(1)-Ni-N-C(8)	87.28(16)	C(26)-C(21)-C(22)-C(23)	1.5(4)
C(11)-Ni-N-C(1)	91.22(15)	P(2)-C(21)-C(22)-C(23)	175.3(2)
P(2)-Ni-N-C(1)	8.7(3)	C(21)-C(22)-C(23)-C(24)	-1.2(4)
P(1)-Ni-N-C(1)	-96.45(14)	C(22)-C(23)-C(24)-C(25)	0.5(4)
C(8)-N-C(1)-O(1)	179.9(2)	C(23)-C(24)-C(25)-C(26)	-0.1(5)
Ni-N-C(1)-O(1)	3.0(3)	C(22)-C(21)-C(26)-C(25)	-1.2(4)
C(8)-N-C(1)-C(2)	-0.5(2)	P(2)-C(21)-C(26)-C(25)	-175.0(2)
Ni-N-C(1)-C(2)	-177.39(12)	C(24)-C(25)-C(26)-C(21)	0.5(5)
O(1)-C(1)-C(2)-C(3)	-0.2(4)	C(21)-P(2)-C(31)-C(32)	-144.25(17)
N-C(1)-C(2)-C(3)	-179.8(2)	C(9)-P(2)-C(31)-C(32)	105.95(18)
O(1)-C(1)-C(2)-C(7)	179.5(2)	Ni-P(2)-C(31)-C(32)	-10.25(19)
N-C(1)-C(2)-C(7)	-0.1(2)	C(21)-P(2)-C(31)-C(36)	41.9(2)
C(7)-C(2)-C(3)-C(4)	-0.1(3)	C(9)-P(2)-C(31)-C(36)	-67.86(19)
C(1)-C(2)-C(3)-C(4)	179.6(2)	Ni-P(2)-C(31)-C(36)	175.95(15)
C(2)-C(3)-C(4)-C(5)	-0.3(4)	C(36)-C(31)-C(32)-C(33)	0.1(3)
C(3)-C(4)-C(5)-C(6)	0.1(4)	P(2)-C(31)-C(32)-C(33)	-173.88(18)
C(4)-C(5)-C(6)-C(7)	0.6(4)	C(31)-C(32)-C(33)-C(34)	-0.1(4)
C(5)-C(6)-C(7)-C(2)	-1.1(3)	C(32)-C(33)-C(34)-C(35)	0.2(4)
C(5)-C(6)-C(7)-C(8)	179.5(2)	C(33)-C(34)-C(35)-C(36)	-0.2(4)
C(3)-C(2)-C(7)-C(6)	0.8(3)	C(34)-C(35)-C(36)-C(31)	0.2(4)
C(1)-C(2)-C(7)-C(6)	-178.96(18)	C(32)-C(31)-C(36)-C(35)	-0.1(3)
C(3)-C(2)-C(7)-C(8)	-179.65(19)	P(2)-C(31)-C(36)-C(35)	173.77(18)
C(1)-C(2)-C(7)-C(8)	0.6(2)	C(9)-C(10)-P(1)-C(51)	177.13(15)
C(1)-N-C(8)-O(2)	-178.3(2)	C(9)-C(10)-P(1)-C(41)	-70.89(17)
Ni-N-C(8)-O(2)	-1.8(3)	C(9)-C(10)-P(1)-Ni	47.01(16)
C(1)-N-C(8)-C(7)	0.8(2)	C(11)-Ni-P(1)-C(51)	153.1(3)
Ni-N-C(8)-C(7)	177.39(12)	N-Ni-P(1)-C(51)	22.48(10)
C(6)-C(7)-C(8)-O(2)	-2.3(4)	P(2)-Ni-P(1)-C(51)	-143.82(9)
C(2)-C(7)-C(8)-O(2)	178.3(2)	C(11)-Ni-P(1)-C(41)	26.7(3)
C(6)-C(7)-C(8)-N	178.6(2)	N-Ni-P(1)-C(41)	-103.94(9)
C(2)-C(7)-C(8)-N	-0.9(2)	P(2)-Ni-P(1)-C(41)	89.76(8)
P(2)-C(9)-C(10)-P(1)	-48.91(18)	C(11)-Ni-P(1)-C(10)	-85.5(3)
N-Ni-C(11)-C(12)	-71.90(18)	N-Ni-P(1)-C(10)	143.95(9)
P(2)-Ni-C(11)-C(12)	94.03(17)	P(2)-Ni-P(1)-C(10)	-22.35(8)
P(1)-Ni-C(11)-C(12)	157.0(2)	C(51)-P(1)-C(41)-C(42)	-104.2(2)
N-Ni-C(11)-C(16)	99.76(17)	C(10)-P(1)-C(41)-C(42)	143.5(2)
P(2)-Ni-C(11)-C(16)	-94.32(17)	Ni-P(1)-C(41)-C(42)	29.8(2)
P(1)-Ni-C(11)-C(16)	-31.3(4)	C(51)-P(1)-C(41)-C(46)	76.5(2)
C(16)-C(11)-C(12)-C(13)	-1.3(3)	C(10)-P(1)-C(41)-C(46)	-35.9(2)
Ni-C(11)-C(12)-C(13)	170.34(17)	Ni-P(1)-C(41)-C(46)	-149.54(19)
C(11)-C(12)-C(13)-C(14)	-0.1(4)	C(46)-C(41)-C(42)-C(43)	0.4(4)
C(12)-C(13)-C(14)-C(15)	1.0(4)	P(1)-C(41)-C(42)-C(43)	-178.9(3)
C(13)-C(14)-C(15)-C(16)	-0.5(5)	C(41)-C(42)-C(43)-C(44)	0.8(5)
C(12)-C(11)-C(16)-C(15)	1.8(4)	C(42)-C(43)-C(44)-C(45)	-0.8(6)
Ni-C(11)-C(16)-C(15)	-170.6(2)	C(43)-C(44)-C(45)-C(46)	-0.5(6)
C(14)-C(15)-C(16)-C(11)	-0.9(4)	C(44)-C(45)-C(46)-C(41)	1.7(5)

C(10)-C(9)-P(2)-C(21)	164.12(15)	C(42)-C(41)-C(46)-C(45)	-1.7(4)
C(10)-C(9)-P(2)-C(31)	-84.98(16)	P(1)-C(41)-C(46)-C(45)	177.6(2)
C(10)-C(9)-P(2)-Ni	31.77(17)	C(41)-P(1)-C(51)-C(56)	8.0(2)
C(11)-Ni-P(2)-C(21)	45.41(10)	C(10)-P(1)-C(51)-C(56)	118.0(2)
N-Ni-P(2)-C(21)	128.1(2)	Ni-P(1)-C(51)-C(56)	-120.95(19)
P(1)-Ni-P(2)-C(21)	-125.57(9)	C(41)-P(1)-C(51)-C(52)	-176.4(2)
C(11)-Ni-P(2)-C(31)	-80.97(9)	C(10)-P(1)-C(51)-C(52)	-66.4(2)
N-Ni-P(2)-C(31)	1.7(2)	Ni-P(1)-C(51)-C(52)	54.6(2)
P(1)-Ni-P(2)-C(31)	108.05(7)	C(56)-C(51)-C(52)-C(53)	-1.6(4)
C(11)-Ni-P(2)-C(9)	168.99(10)	P(1)-C(51)-C(52)-C(53)	-177.3(2)
N-Ni-P(2)-C(9)	-108.3(2)	C(51)-C(52)-C(53)-C(54)	0.1(5)
P(1)-Ni-P(2)-C(9)	-1.98(8)	C(52)-C(53)-C(54)-C(55)	1.4(5)
C(31)-P(2)-C(21)-C(22)	33.2(2)	C(53)-C(54)-C(55)-C(56)	-1.5(5)
C(9)-P(2)-C(21)-C(22)	139.37(19)	C(52)-C(51)-C(56)-C(55)	1.5(4)
Ni-P(2)-C(21)-C(22)	-94.93(18)	P(1)-C(51)-C(56)-C(55)	177.1(2)
C(31)-P(2)-C(21)-C(26)	-153.12(19)	C(54)-C(55)-C(56)-C(51)	0.0(4)

Table II. 7 Planes in (DPPE)Ni(Ph)(phthal)

Plane 1.

0.1969 (0.0007)	N
-0.1781 (0.0006)	P1
0.1965 (0.0007)	P2
-0.2154 (0.0007)	C11
-0.0471 (0.0007)	Ni

Rms deviation of fitted atoms = 0.1972

Plane 2.

Angle to previous plane (with approximate esd) = 86.88 (0.05)

-0.0017 (0.0014)	C2
0.0052 (0.0014)	C7
-0.0047 (0.0016)	C6
0.0008 (0.0018)	C5
0.0027 (0.0018)	C4
-0.0023 (0.0017)	C3

Rms deviation of fitted atoms = 0.0033

Plane 3.

Angle to previous plane (with approximate esd) = 0.61 (0.15)

-0.0037 (0.0012)	N
0.0009 (0.0012)	C1
0.0022 (0.0012)	C2
-0.0043 (0.0012)	C7
0.0049 (0.0011)	C8
-0.0032 (0.0032)	O1
0.0328 (0.0032)	O2
0.0690 (0.0029)	Ni

Rms deviation of fitted atoms = 0.0035

Plane 4.

Angle to previous plane (with approximate esd) = 79.21 (0.07)

0.0094 (0.0015)	C11
-0.0027 (0.0016)	C12
-0.0053 (0.0018)	C13
0.0066 (0.0020)	C14
0.0002 (0.0021)	C15
-0.0082 (0.0019)	C16

Rms deviation of fitted atoms = 0.0062

APPENDIX III

Table III. 1 Crystal data and structure refinement for (DPPE)Ni(3-MePh)(phthal)

Empirical formula	C41 H35 N Ni O2 P2	
Formula weight	694.350	
Temperature	293(2)K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 2_1 /n	
Unit cell dimensions	a = 12.42740(10) Å	alpha = 90 °
	b = 14.78980(10) Å	beta = 92.1670(10) °
	c = 19.52040(10) Å	gamma = 90 °
Volume	3585.26(4) Å^3	
Z	4	
Density (calculated)	1.2864 Mg/m^3	
Absorption coefficient	1.898 mm^{-1}	
Crystal size	0.14 x 0.10 x 0.27 mm	
Theta range for data collection	3.75 to 72.83 °	
Index ranges	$-14 \leq h \leq 15$, $-17 \leq k \leq 18$, $-23 \leq l \leq 23$	
Reflections collected	35478	
Independent reflections	7081 [R(int) = 0.0407]	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	0.943	
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1575	
R indices (all data)	R1 = 0.1106, wR2 = 0.1768	
Largest diff. peak and hole	0.537 and -0.295 e.Å^{-3}	

$R = \Sigma (|| F_0 | - | F_c ||) / \Sigma (| F_0 |)$

$wR2 = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / \Sigma (F_0{}^2)^2 \}^{1/2}$

$S = \{ \Sigma [w (F_0{}^2 - F_c{}^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.}) \}^{1/2}$

Table III. 2 Atomic coordinates (x 10^{-4}) and equivalent isotropic displacement parameters (Å^2 x 10^{-3}) for (DPPE)Ni(3-Me-Ph)(phthal)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	Occ.	x	y	z	U(eq)
Ni	1	5344(1)	3049(1)	2227(1)	54(1)
P(1)	1	5089(1)	3750(1)	1283(1)	57(1)
P(2)	1	6550(1)	4106(1)	2501(1)	56(1)
N	1	5270(2)	2543(2)	3135(1)	52(1)
O(1)	1	6686(3)	1559(2)	3151(2)	96(1)
O(2)	1	3811(3)	3358(2)	3496(2)	98(1)
C(1)	1	5940(3)	1912(3)	3426(2)	62(1)
C(2)	1	5590(3)	1737(3)	4144(2)	63(1)
C(3)	1	5992(4)	1153(3)	4640(2)	100(2)
C(4)	1	5455(5)	1157(4)	5263(3)	119(2)
C(5)	1	4605(5)	1692(4)	5363(2)	111(2)
C(6)	1	4208(4)	2279(3)	4854(2)	91(1)
C(7)	1	4727(3)	2278(3)	4244(2)	64(1)
C(8)	1	4512(3)	2803(3)	3592(2)	62(1)
C(9)	1	6134(3)	4627(3)	1190(2)	67(1)
C(10)	1	6331(3)	5044(2)	1894(2)	65(1)
C11a	0.675(9)	4572(5)	2067(4)	1804(4)	52(2)
C12a	0.675(9)	3455(5)	2020(4)	1750(4)	70(2)
C13a	0.675(9)	2956(5)	1271(5)	1448(4)	83(3)
C14a	0.675(9)	3574(6)	569(4)	1200(4)	87(4)
C15a	0.675(9)	4691(6)	616(4)	1253(3)	96(3)
C16a	0.675(9)	5190(5)	1365(5)	1555(4)	79(2)
C17a	0.675(9)	1754(7)	1225(7)	1348(6)	170(5)
C11Bb	0.325(9)	4189(10)	2187(8)	1884(9)	52(5)
C12Bb	0.325(9)	4635(9)	1437(9)	1573(8)	61(4)
C13Bb	0.325(9)	3969(12)	774(8)	1283(8)	92(8)
C14Bb	0.325(9)	2857(11)	861(9)	1305(8)	89(7)
C15Bb	0.325(9)	2411(8)	1610(10)	1617(9)	109(7)
C16Bb	0.325(9)	3077(10)	2274(9)	1906(9)	93(6)
C17Bb	0.325(9)	4504(15)	12(12)	915(10)	142(8)
C(21)	1	4983(4)	3189(3)	457(2)	67(1)
C(22)	1	4038(4)	3095(3)	90(2)	98(2)
C(23)	1	4001(6)	2667(5)	-538(3)	136(2)
C(24)	1	4881(7)	2315(5)	-793(3)	136(2)
C(25)	1	5850(6)	2375(4)	-422(3)	134(2)
C(26)	1	5885(4)	2829(3)	197(2)	98(2)
C(31)	1	3903(3)	4450(3)	1358(2)	64(1)
C(32)	1	3564(4)	5037(3)	839(2)	92(1)
C(33)	1	2701(5)	5604(4)	940(3)	115(2)
C(34)	1	2196(4)	5603(4)	1541(4)	115(2)
C(35)	1	2526(4)	5026(4)	2051(3)	94(1)
C(36)	1	3375(3)	4444(3)	1963(2)	72(1)
C(41)	1	7933(3)	3766(3)	2367(2)	63(1)
C(42)	1	8742(4)	4394(4)	2354(2)	92(1)

C(43)	1	9790(4)	4132(5)	2271(3)	114(2)
C(44)	1	10051(5)	3267(6)	2211(3)	120(2)
C(45)	1	9256(5)	2628(4)	2228(3)	113(2)
C(46)	1	8199(4)	2877(3)	2297(2)	86(1)
C51a	0.50	6605(5)	4616(4)	3363(2)	50(7)
C52a	0.50	7536(4)	4631(5)	3781(3)	93(3)
C53a	0.50	7516(5)	5005(6)	4433(3)	130(5)
C54a	0.50	6564(7)	5364(6)	4668(3)	128(10)
C55a	0.50	5633(5)	5349(5)	4251(3)	83(3)
C56a	0.50	5654(4)	4975(4)	3598(3)	63(2)
C51Bb	0.50	6572(7)	4587(6)	3341(4)	74(9)
C52Bb	0.50	7210(6)	4183(5)	3855(5)	90(4)
C53Bb	0.50	7204(6)	4514(6)	4521(4)	103(4)
C54Bb	0.50	6558(8)	5249(7)	4674(4)	139(10)
C55Bb	0.50	5920(7)	5653(6)	4160(6)	145(7)
C56Bb	0.50	5927(7)	5322(6)	3494(5)	126(5)

Table III. 3 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^{-3}) for (DPPE)Ni(3-Me-Ph)(phthal)

Atom	Occ.	x	y	z	U(eq)
H(3)	1	6579	781	4569	120
H(4)	1	5698	776	5616	143
H(5)	1	4273	1673	5781	133
H(6)	1	3620	2652	4924	109
H(9A)	1	6791	4359	1030	80
H(9B)	1	5889	5083	863	80
H(10A)	1	5713	5401	2019	78
H(10B)	1	6958	5434	1895	78
H12a	0.675(9)	3042	2490	1917	84
H14a	0.675(9)	3239	68	997	104
H15a	0.675(9)	5104	146	1086	116
H16a	0.675(9)	5938	1396	1590	94
H17Aa	0.675(9)	1424	1367	1771	255
H17Ba	0.675(9)	1548	626	1205	255
H17Ca	0.675(9)	1522	1651	1002	255
H12Bb	0.325(9)	5379	1379	1558	74
H14Bb	0.325(9)	2411	417	1111	107
H15Bb	0.325(9)	1667	1668	1631	131
H16Bb	0.325(9)	2779	2775	2115	111
H17Db	0.325(9)	4842	244	517	213
H17Eb	0.325(9)	3974	-431	777	213
H17Fb	0.325(9)	5039	-263	1216	213
H(22)	1	3407	3323	265	117
H(23)	1	3349	2624	-786	163
H(24)	1	4848	2030	-1219	163
H(25)	1	6469	2113	-587	161
H(26)	1	6540	2889	440	118
H(32)	1	3914	5049	427	110
H(33)	1	2465	5991	590	139
H(34)	1	1624	5995	1606	138
H(35)	1	2175	5025	2463	113
H(36)	1	3589	4048	2312	86
H(42)	1	8580	5004	2403	110
H(43)	1	10326	4570	2256	137
H(44)	1	10764	3097	2159	144
H(45)	1	9431	2019	2192	135
H(46)	1	7664	2438	2296	103
H52a	0.50	8173	4390	3624	112
H53a	0.50	8138	5015	4713	156
H54a	0.50	6550	5615	5105	154
H55a	0.50	4996	5590	4408	100
H56a	0.50	5031	4965	3319	76
H52Bb	0.50	7642	3691	3752	107
H53Bb	0.50	7631	4243	4865	124
H54Bb	0.50	6554	5470	5119	166
H55Bb	0.50	5488	6145	4262	174

H56Bb	0.50	5499	5593	3150	151

Table III. 4 Anisotropic parameters ($Å^2 \times 10^{-3}$) for (DPPE)Ni(3-Me-Ph)(phthal)

Atom	U11	U22	U33	U23	U13	U12
Ni	66(1)	55(1)	41(1)	6(1)	-9(1)	-7(1)
P(1)	67(1)	64(1)	41(1)	9(1)	-8(1)	-10(1)
P(2)	60(1)	62(1)	44(1)	2(1)	-5(1)	-8(1)
N	62(2)	50(2)	44(2)	4(1)	-5(1)	0(1)
O(1)	99(2)	103(2)	86(2)	29(2)	21(2)	37(2)
O(2)	102(2)	110(2)	82(2)	24(2)	10(2)	40(2)
C(1)	70(3)	61(2)	54(2)	6(2)	-8(2)	-3(2)
C(2)	73(3)	64(2)	49(2)	11(2)	-12(2)	-9(2)
C(3)	111(4)	111(4)	76(3)	36(3)	-18(3)	6(3)
C(4)	150(6)	136(5)	71(4)	50(3)	-12(4)	-4(4)
C(5)	150(6)	138(5)	45(2)	16(3)	-2(3)	-22(4)
C(6)	116(4)	103(3)	55(3)	0(2)	6(3)	-13(3)
C(7)	78(3)	68(3)	43(2)	-1(2)	-8(2)	-14(2)
C(8)	74(3)	61(2)	49(2)	4(2)	-5(2)	-3(2)
C(9)	75(3)	79(3)	47(2)	13(2)	-4(2)	-18(2)
C(10)	68(2)	69(2)	57(2)	11(2)	-8(2)	-16(2)
C11a	61(5)	51(5)	43(4)	13(3)	2(4)	-9(4)
C12a	72(6)	68(5)	69(5)	0(4)	-6(4)	-4(5)
C13a	81(7)	78(6)	88(6)	-9(5)	-14(5)	-34(5)
C14a	118(9)	83(7)	56(5)	2(4)	-22(5)	-27(6)
C15a	151(9)	64(6)	72(5)	-8(4)	-18(6)	1(6)
C16a	90(7)	68(5)	78(5)	0(4)	-12(5)	-2(5)
C17a	104(8)	167(10)	236(13)	-63(9)	-35(7)	-41(7)
C11Bb	45(10)	73(10)	36(7)	1(6)	-3(7)	17(8)
C12Bb	59(10)	53(10)	71(9)	12(7)	-17(8)	-9(8)
C13Bb	160(2)	49(10)	63(10)	-21(8)	-27(13)	5(14)
C14Bb	102(18)	81(15)	80(11)	3(11)	-33(12)	-53(13)
C15Bb	87(17)	109(16)	131(17)	-23(13)	6(12)	-10(12)
C16Bb	79(12)	72(11)	130(16)	-33(10)	30(11)	-17(9)
C(21)	85(3)	73(3)	42(2)	12(2)	-6(2)	-12(2)
C(22)	104(4)	112(4)	75(3)	-17(3)	-28(3)	-4(3)
C(23)	154(6)	151(6)	98(5)	-34(4)	-56(4)	-13(5)
C(24)	204(8)	139(5)	63(4)	-26(3)	-17(4)	-26(6)
C(25)	169(6)	143(5)	93(4)	-39(4)	24(4)	-7(5)
C(26)	99(4)	124(4)	71(3)	-28(3)	-5(3)	-10(3)
C(31)	68(3)	66(2)	58(2)	8(2)	-12(2)	-12(2)
C(32)	103(4)	101(4)	71(3)	31(3)	-4(2)	6(3)
C(33)	106(4)	115(4)	125(5)	54(4)	0(4)	28(3)
C(34)	86(4)	103(4)	155(6)	18(4)	-5(4)	25(3)
C(35)	66(3)	123(4)	95(4)	-5(3)	8(3)	2(3)
C(36)	66(3)	86(3)	63(3)	11(2)	-10(2)	-11(2)
C(41)	65(3)	84(3)	40(2)	0(2)	-3(2)	-11(2)
C(42)	68(3)	114(4)	92(3)	-16(3)	-3(2)	-18(3)
C(43)	62(4)	164(6)	117(5)	-24(4)	-2(3)	-15(4)
C(44)	83(4)	202(8)	75(4)	-2(4)	15(3)	29(5)
C(45)	115(5)	119(5)	106(4)	17(4)	29(4)	40(4)

C(46)	81(3)	94(4)	82(3)	9(3)	17(2)	10(3)
C51a	68(10)	47(7)	35(6)	-2(3)	-8(3)	-5(3)
C52a	96(7)	144(10)	38(4)	-19(5)	-8(4)	-7(7)
C53a	128(10)	222(15)	39(5)	-16(7)	-18(6)	-45(11)
C54a	200(2)	164(14)	15(4)	-18(5)	-9(6)	38(10)
C55a	116(8)	74(6)	64(6)	-15(5)	44(6)	-4(6)
C56a	67(5)	60(5)	63(5)	-11(4)	13(4)	-9(4)

Table III. 5 Bond lengths [Å] and angles [°] for (DPPE)Ni(3-Me-Ph)(phthal)

Ni-C11a	1.911(4)	N-C(1)	1.360(4)
Ni-N	1.930(3)	N-C(8)	1.376(5)
Ni-C11Bb	2.014(9)	O(1)-C(1)	1.207(4)
Ni-P(1)	2.1266(10)	O(2)-C(8)	1.207(4)
Ni-P(2)	2.2173(10)	C(1)-C(2)	1.506(5)
P(1)-C(31)	1.812(4)	C(2)-C(7)	1.358(5)
P(1)-C(21)	1.815(4)	C(2)-C(3)	1.377(5)
P(1)-C(9)	1.849(3)	C(3)-C(4)	1.409(7)
P(2)-C51Bb	1.786(7)	C(4)-C(5)	1.340(7)
P(2)-C(41)	1.819(4)	C(5)-C(6)	1.394(6)
P(2)-C(10)	1.839(4)	C(6)-C(7)	1.377(5)
P(2)-C51a	1.843(5)	C(7)-C(8)	1.505(5)
C(9)-C(10)	1.517(4)	C13Bb-C17Bb	1.505(16)
C11a-C12a	1.3900	C14Bb-C15Bb	1.3900
C11a-C16a	1.3900	C15Bb-C16Bb	1.3900
C12a-C13a	1.3900	C(21)-C(26)	1.357(6)
C13a-C14a	1.3900	C(21)-C(22)	1.359(5)
C13a-C17a	1.501(10)	C(22)-C(23)	1.379(7)
C14a-C15a	1.3900	C(23)-C(24)	1.325(8)
C15a-C16a	1.3900	C(24)-C(25)	1.386(8)
C11Bb-C12Bb	1.3900	C(25)-C(26)	1.381(6)
C11Bb-C16Bb	1.3900	C(31)-C(36)	1.372(5)
C12Bb-C13Bb	1.3900	C(31)-C(32)	1.388(5)
C13Bb-C14Bb	1.3900	C(32)-C(33)	1.381(6)
C(33)-C(34)	1.351(7)	C52a-C53a	1.3900
C(34)-C(35)	1.363(7)	C53a-C54a	1.3900
C(35)-C(36)	1.377(6)	C54a-C55a	1.3900
C(41)-C(46)	1.364(5)	C55a-C56a	1.3900
C(41)-C(42)	1.369(5)	C51Bb-C52Bb	1.3900
C(42)-C(43)	1.375(6)	C51Bb-C56Bb	1.3900
C(43)-C(44)	1.326(8)	C52Bb-C53Bb	1.3900
C(44)-C(45)	1.370(7)	C53Bb-C54Bb	1.3900
C(45)-C(46)	1.376(6)	C54Bb-C55Bb	1.3900
C51a-C52a	1.3900	C55Bb-C56Bb	1.3900
C51a-C56a	1.3900		

C11a-Ni-N	93.6(3)	C(31)-P(1)-Ni	107.67(13)
N-Ni-C11Bb	90.1(5)	C(21)-P(1)-Ni	123.40(12)
C11a-Ni-P(1)	86.6(3)	C(9)-P(1)-Ni	110.22(11)
N-Ni-P(1)	166.90(9)	C51Bb-P(2)-C(41)	105.1(3)
C11Bb-Ni-P(1)	86.6(5)	C51Bb-P(2)-C(10)	106.7(3)
C11a-Ni-P(2)	164.5(2)	C(41)-P(2)-C(10)	103.45(17)
N-Ni-P(2)	96.08(8)	C(41)-P(2)-C51a	104.0(2)
C11Bb-Ni-P(2)	173.1(5)	C(10)-P(2)-C51a	106.2(2)
P(1)-Ni-P(2)	86.70(4)	C51Bb-P(2)-Ni	119.3(3)
C(31)-P(1)-C(21)	107.49(18)	C(41)-P(2)-Ni	113.85(14)
C(31)-P(1)-C(9)	100.58(18)	C(10)-P(2)-Ni	107.08(11)
C(21)-P(1)-C(9)	105.12(17)	C51a-P(2)-Ni	120.7(2)

C(1)-N-C(8)	110.1(3)	C(7)-C(6)-C(5)	116.8(5)
C(1)-N-Ni	126.9(3)	C(2)-C(7)-C(6)	121.5(4)
C(8)-N-Ni	123.0(2)	C(2)-C(7)-C(8)	107.4(3)
O(1)-C(1)-N	125.4(4)	C(6)-C(7)-C(8)	131.1(4)
O(1)-C(1)-C(2)	126.3(4)	O(2)-C(8)-N	126.7(3)
N-C(1)-C(2)	108.2(3)	O(2)-C(8)-C(7)	125.8(4)
C(7)-C(2)-C(3)	122.4(4)	N-C(8)-C(7)	107.5(3)
C(7)-C(2)-C(1)	106.8(3)	C(10)-C(9)-P(1)	106.6(2)
C(3)-C(2)-C(1)	130.8(4)	C(9)-C(10)-P(2)	107.0(2)
C(2)-C(3)-C(4)	115.7(5)	C12a-C11a-C16a	120.0
C(5)-C(4)-C(3)	121.9(5)	C12a-C11a-Ni	123.6(3)
C(4)-C(5)-C(6)	121.6(5)	C16a-C11a-Ni	116.4(3)
C13a-C12a-C11a	120.0	C14Bb-C13Bb-C17Bb	122.8(11)
C12a-C13a-C14a	120.0	C12Bb-C13Bb-C17Bb	117.1(12)
C12a-C13a-C17a	121.2(6)	C15Bb-C14Bb-C13Bb	120.0
C14a-C13a-C17a	118.7(6)	C16Bb-C15Bb-C14Bb	120.0
C13a-C14a-C15a	120.0	C15Bb-C16Bb-C11Bb	120.0
C16a-C15a-C14a	120.0	C(26)-C(21)-C(22)	118.2(4)
C15a-C16a-C11a	120.0	C(26)-C(21)-P(1)	118.6(3)
C12Bb-C11Bb-C16Bb	120.0	C(22)-C(21)-P(1)	123.2(4)
C12Bb-C11Bb-Ni	111.1(7)	C(21)-C(22)-C(23)	121.0(5)
C16Bb-C11Bb-Ni	128.9(7)	C(24)-C(23)-C(22)	121.0(6)
C13Bb-C12Bb-C11Bb	120.0	C(23)-C(24)-C(25)	119.4(6)
C14Bb-C13Bb-C12Bb	120.0	C(26)-C(25)-C(24)	119.2(6)
C(21)-C(26)-C(25)	121.2(5)	C(41)-C(42)-C(43)	120.7(5)
C(36)-C(31)-C(32)	119.4(4)	C(44)-C(43)-C(42)	121.2(6)
C(36)-C(31)-P(1)	118.9(3)	C(43)-C(44)-C(45)	119.0(6)
C(32)-C(31)-P(1)	121.6(3)	C(44)-C(45)-C(46)	120.6(6)
C(33)-C(32)-C(31)	119.4(4)	C(41)-C(46)-C(45)	120.3(5)
C(34)-C(33)-C(32)	120.8(5)	C52a-C51a-C56a	120.0
C(33)-C(34)-C(35)	119.9(5)	C52a-C51a-P(2)	122.9(3)
C(34)-C(35)-C(36)	120.7(5)	C56a-C51a-P(2)	117.1(3)
C(31)-C(36)-C(35)	119.8(4)	C51a-C52a-C53a	120.0
C(46)-C(41)-C(42)	118.1(4)	C54a-C53a-C52a	120.0
C(46)-C(41)-P(2)	121.0(3)	C53a-C54a-C55a	120.0
C(42)-C(41)-P(2)	120.9(4)	C54a-C55a-C56a	120.0
C55a-C56a-C51a	120.0	C52Bb-C53Bb-C54Bb	120.0
C52Bb-C51Bb-C56Bb	120.0	C55Bb-C54Bb-C53Bb	120.0
C52Bb-C51Bb-P(2)	118.6(6)	C56Bb-C55Bb-C54Bb	120.0
C56Bb-C51Bb-P(2)	121.3(6)	C55Bb-C56Bb-C51Bb	120.0
C53Bb-C52Bb-C51Bb	120.0		

Table III. 6 Torsion angles [°] for (DPPE)Ni(3-Me-Ph)(phthal)

C11a-Ni-P(1)-C(31)	95.5(2)	C11a-Ni-P(2)-C51Bb	-159.7(10)
N-Ni-P(1)-C(31)	4.3(4)	N-Ni-P(2)-C51Bb	-31.3(4)
C11Bb-Ni-P(1)-C(31)	80.0(4)	C11Bb-Ni-P(2)-C51Bb	123(3)
P(2)-Ni-P(1)-C(31)	-98.45(13)	P(1)-Ni-P(2)-C51Bb	135.9(4)
C11a-Ni-P(1)-C(21)	-30.5(3)	C11a-Ni-P(2)-C(41)	-34.6(9)
N-Ni-P(1)-C(21)	-121.7(4)	N-Ni-P(2)-C(41)	93.83(15)
C11Bb-Ni-P(1)-C(21)	-46.0(4)	C11Bb-Ni-P(2)-C(41)	-112(3)
P(2)-Ni-P(1)-C(21)	135.54(18)	P(1)-Ni-P(2)-C(41)	99.01(13)
C11a-Ni-P(1)-C(9)	-155.7(3)	C11a-Ni-P(2)-C(10)	79.1(9)
N-Ni-P(1)-C(9)	113.1(4)	N-Ni-P(2)-C(10)	152.47(16)
C11Bb-Ni-P(1)-C(9)	-171.2(4)	C11Bb-Ni-P(2)-C(10)	2(3)
P(2)-Ni-P(1)-C(9)	10.38(14)	P(1)-Ni-P(2)-C(10)	14.68(14)
C11a-Ni-P(2)-C51a	-159.4(9)	C(8)-N-C(1)-O(1)	-179.8(4)
N-Ni-P(2)-C51a	-31.0(3)	Ni-N-C(1)-O(1)	-1.0(6)
C11Bb-Ni-P(2)-C51a	123(3)	C(8)-N-C(1)-C(2)	0.1(4)
P(1)-Ni-P(2)-C51a	136.2(2)	Ni-N-C(1)-C(2)	178.9(2)
C11a-Ni-N-C(1)	83.6(3)	O(1)-C(1)-C(2)-C(7)	179.6(4)
C11Bb-Ni-N-C(1)	98.6(4)	N-C(1)-C(2)-C(7)	-0.2(4)
P(1)-Ni-N-C(1)	174.0(3)	O(1)-C(1)-C(2)-C(3)	-1.3(7)
P(2)-Ni-N-C(1)	-84.4(3)	N-C(1)-C(2)-C(3)	178.9(4)
C11a-Ni-N-C(8)	-97.8(3)	C(7)-C(2)-C(3)-C(4)	-0.5(7)
C11Bb-Ni-N-C(8)	-82.7(4)	C(1)-C(2)-C(3)-C(4)	-179.4(4)
P(1)-Ni-N-C(8)	-7.4(6)	C(2)-C(3)-C(4)-C(5)	0.3(8)
P(2)-Ni-N-C(8)	94.3(3)	C(3)-C(4)-C(5)-C(6)	-0.2(10)
C(4)-C(5)-C(6)-C(7)	0.3(8)	C(6)-C(7)-C(8)-O(2)	1.3(7)
C(3)-C(2)-C(7)-C(6)	0.6(6)	C(2)-C(7)-C(8)-N	-0.2(4)
C(1)-C(2)-C(7)-C(6)	179.7(4)	C(6)-C(7)-C(8)-N	-179.7(4)
C(3)-C(2)-C(7)-C(8)	-179.0(4)	C(31)-P(1)-C(9)-C(10)	74.4(3)
C(1)-C(2)-C(7)-C(8)	0.2(4)	C(21)-P(1)-C(9)-C(10)	-174.1(3)
C(5)-C(6)-C(7)-C(2)	-0.4(6)	Ni-P(1)-C(9)-C(10)	-39.1(3)
C(5)-C(6)-C(7)-C(8)	179.0(4)	P(1)-C(9)-C(10)-P(2)	50.0(3)
C(1)-N-C(8)-O(2)	179.1(4)	C51Bb-P(2)-C(10)-C(9)	-171.2(4)
Ni-N-C(8)-O(2)	0.2(6)	C(41)-P(2)-C(10)-C(9)	78.2(3)
C(1)-N-C(8)-C(7)	0.1(4)	C51a-P(2)-C(10)-C(9)	-172.6(3)
Ni-N-C(8)-C(7)	-178.8(2)	Ni-P(2)-C(10)-C(9)	-42.4(3)
C(2)-C(7)-C(8)-O(2)	-179.2(4)	N-Ni-C11a-C12a	85.4(5)
C11Bb-Ni-C11a-C12a	8(2)	C17a-C13a-C14a-C15a	176.6(8)
P(1)-Ni-C11a-C12a	-81.5(5)	C13a-C14a-C15a-C16a	0.0
P(2)-Ni-C11a-C12a	-145.9(6)	C14a-C15a-C16a-C11a	0.0
N-Ni-C11a-C16a	-93.2(3)	C12a-C11a-C16a-C15a	0.0
C11Bb-Ni-C11a-C16a	-171(3)	Ni-C11a-C16a-C15a	178.6(6)
P(1)-Ni-C11a-C16a	99.9(3)	C11a-Ni-C11Bb-C12Bb	5(2)
P(2)-Ni-C11a-C16a	35.5(11)	N-Ni-C11Bb-C12Bb	-97.8(8)
C16a-C11a-C12a-C13a	0.0	P(1)-Ni-C11Bb-C12Bb	94.9(8)
Ni-C11a-C12a-C13a	-178.5(6)	P(2)-Ni-C11Bb-C12Bb	108(3)
C11a-C12a-C13a-C14a	0.0	C11a-Ni-C11Bb-C16Bb	-172(3)
C11a-C12a-C13a-C17a	-176.5(8)	N-Ni-C11Bb-C16Bb	84.4(9)
C12a-C13a-C14a-C15a	0.0	P(1)-Ni-C11Bb-C16Bb	-82.9(9)

P(2)-Ni-C11Bb-C16Bb	-70(4)	C(9)-P(1)-C(21)-C(26)	55.6(4)
C16Bb-C11Bb-C12Bb-C13Bb	0.0	Ni-P(1)-C(21)-C(26)	-71.8(4)
Ni-C11Bb-C12Bb-C13Bb	-178.0(11)	C(31)-P(1)-C(21)-C(22)	-19.3(4)
C11Bb-C12Bb-C13Bb-C14Bb	0.0	C(9)-P(1)-C(21)-C(22)	-125.8(4)
C11Bb-C12Bb-C13Bb-C17Bb	176.2(15)	Ni-P(1)-C(21)-C(22)	106.8(4)
C12Bb-C13Bb-C14Bb-C15Bb	0.0	C(26)-C(21)-C(22)-C(23)	-1.7(7)
C17Bb-C13Bb-C14Bb-C15Bb	-176.0(16)	P(1)-C(21)-C(22)-C(23)	179.7(4)
C13Bb-C14Bb-C15Bb-C16Bb	0.0	C(21)-C(22)-C(23)-C(24)	1.7(10)
C14Bb-C15Bb-C16Bb-C11Bb	0.0	C(22)-C(23)-C(24)-C(25)	0.4(11)
C12Bb-C11Bb-C16Bb-C15Bb	0.0	C(23)-C(24)-C(25)-C(26)	-2.3(11)
Ni-C11Bb-C16Bb-C15Bb	177.6(14)	C(22)-C(21)-C(26)-C(25)	-0.3(7)
C(31)-P(1)-C(21)-C(26)	162.1(4)	P(1)-C(21)-C(26)-C(25)	178.4(4)
C(24)-C(25)-C(26)-C(21)	2.3(9)	C(32)-C(31)-C(36)-C(35)	-0.9(6)
C(21)-P(1)-C(31)-C(36)	135.5(3)	P(1)-C(31)-C(36)-C(35)	174.6(3)
C(9)-P(1)-C(31)-C(36)	-114.8(3)	C(34)-C(35)-C(36)-C(31)	0.8(7)
Ni-P(1)-C(31)-C(36)	0.5(3)	C51Bb-P(2)-C(41)-C(46)	114.7(4)
C(21)-P(1)-C(31)-C(32)	-49.2(4)	C(10)-P(2)-C(41)-C(46)	-133.5(3)
C(9)-P(1)-C(31)-C(32)	60.5(4)	C51a-P(2)-C(41)-C(46)	115.7(4)
Ni-P(1)-C(31)-C(32)	175.9(3)	Ni-P(2)-C(41)-C(46)	-17.6(4)
C(36)-C(31)-C(32)-C(33)	0.0(7)	C51Bb-P(2)-C(41)-C(42)	-63.2(4)
P(1)-C(31)-C(32)-C(33)	-175.3(4)	C(10)-P(2)-C(41)-C(42)	48.6(3)
C(31)-C(32)-C(33)-C(34)	1.0(8)	C51a-P(2)-C(41)-C(42)	-62.2(4)
C(32)-C(33)-C(34)-C(35)	-1.1(9)	Ni-P(2)-C(41)-C(42)	164.5(3)
C(33)-C(34)-C(35)-C(36)	0.3(8)	C(46)-C(41)-C(42)-C(43)	0.3(6)
P(2)-C(41)-C(42)-C(43)	178.3(4)	C(41)-P(2)-C51a-C56a	177.6(4)
C(41)-C(42)-C(43)-C(44)	-1.1(8)	C(10)-P(2)-C51a-C56a	68.8(4)
C(42)-C(43)-C(44)-C(45)	0.6(9)	Ni-P(2)-C51a-C56a	-53.2(4)
C(43)-C(44)-C(45)-C(46)	0.8(9)	C56a-C51a-C52a-C53a	0.0
C(42)-C(41)-C(46)-C(45)	1.0(6)	P(2)-C51a-C52a-C53a	-178.3(5)
P(2)-C(41)-C(46)-C(45)	-176.9(3)	C51a-C52a-C53a-C54a	0.0
C(44)-C(45)-C(46)-C(41)	-1.6(8)	C52a-C53a-C54a-C55a	0.0
C51Bb-P(2)-C51a-C52a	137(19)	C53a-C54a-C55a-C56a	0.0
C(41)-P(2)-C51a-C52a	-4.1(4)	C54a-C55a-C56a-C51a	0.0
C(10)-P(2)-C51a-C52a	-112.9(4)	C52a-C51a-C56a-C55a	0.0
Ni-P(2)-C51a-C52a	125.2(4)	P(2)-C51a-C56a-C55a	178.4(5)
C51Bb-P(2)-C51a-C56a	-42(19)	C(41)-P(2)-C51Bb-C52Bb	-39.3(5)
C(10)-P(2)-C51Bb-C52Bb	-148.7(4)	C56Bb-C51Bb-C52Bb-C53Bb	0.0
C51a-P(2)-C51Bb-C52Bb	-79(19)	P(2)-C51Bb-C52Bb-C53Bb	-176.8(6)
Ni-P(2)-C51Bb-C52Bb	89.9(4)	C51Bb-C52Bb-C53Bb-C54Bb	0.0
C(41)-P(2)-C51Bb-C56Bb	144.0(4)	C52Bb-C53Bb-C54Bb-C55Bb	0.0
C(10)-P(2)-C51Bb-C56Bb	34.6(5)	C53Bb-C54Bb-C55Bb-C56Bb	0.0
C51a-P(2)-C51Bb-C56Bb	105(19)	C54Bb-C55Bb-C56Bb-C51Bb	0.0
Ni-P(2)-C51Bb-C56Bb	-86.8(5)	C52Bb-C51Bb-C56Bb-C55Bb	0.0
P(2)-C51Bb-C56Bb-C55Bb	176.7(6)		

Table III. 7 Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

Plane 1.

*	0.002 (0.003)	C2
*	-0.001 (0.003)	C3
*	0.001 (0.004)	C4
*	0.000 (0.004)	C5
*	0.001 (0.003)	C6
*	-0.002 (0.003)	C7

Rms deviation of fitted atoms = 0.001

Plane 2.

Angle to previous plane (with approximate esd) = 0.69 (0.28)

*	0.000 (0.002)	N
*	0.001 (0.002)	C1
*	-0.001 (0.002)	C2
*	0.001 (0.002)	C7
*	-0.001 (0.002)	C8
	0.033 (0.005)	Ni
	0.005 (0.006)	O1
	0.014 (0.006)	O2

Rms deviation of fitted atoms = 0.001

Plane 3.

Angle to previous plane (with approximate esd) = 87.19 (0.25)

*	0.000 (0.000)	C11_a
*	0.000 (0.000)	C12_a
*	0.000 (0.000)	C13_a
*	0.000 (0.000)	C14_a
*	0.000 (0.000)	C15_a
*	0.000 (0.000)	C16_a
	0.041 (0.017)	Ni
	-0.079 (0.018)	C17_a

Rms deviation of fitted atoms = 0.000

```
Plane 3.

 Angle to previous plane (with approximate esd) = 87.42 ( 0.27 )

 *   0.251 (0.002)  C11_a
 *  -0.236 (0.002)  P1
 *   0.210 (0.002)  P2
 *  -0.225 (0.002)  N
    -0.001 (0.002)  Ni

 Rms deviation of fitted atoms =   0.231

Plane 4.

 Angle to previous plane (with approximate esd) = 89.93 ( 0.11 )

 *   0.000 (0.002)  N
 *   0.001 (0.002)  C1
 *  -0.001 (0.002)  C2
 *   0.001 (0.002)  C7
 *  -0.001 (0.002)  C8
     0.033 (0.005)  Ni
     0.005 (0.006)  O1
     0.014 (0.006)  O2

 Rms deviation of fitted atoms =   0.001

Plane 5.

 Angle to previous plane (with approximate esd) = 86.14 ( 0.54 )

 *   0.000 (0.000)  C11B_b
 *   0.000 (0.000)  C12B_b
 *   0.000 (0.000)  C13B_b
 *   0.000 (0.000)  C14B_b
 *   0.000 (0.000)  C15B_b
 *   0.000 (0.000)  C16B_b
    -0.065 (0.037)  Ni
    -0.089 (0.036)  C17B_b

 Rms deviation of fitted atoms =   0.000
```

APPENDIX IV

Table IV. 1 Crystal data and structure refinement for $(PCy_3)_2Ni$ (H)(phthal)

Empirical formula	C44 H71 N Ni O2 P2	
Formula weight	766.668	
Temperature	293(2)K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.776(3) Å	alpha = 113.70(3) deg.
	b = 18.666(4) Å	beta = 104.37(3) deg.
	c = 19.985(4) Å	gamma = 100.54(3) deg.
Volume	4320.7(16) Å^3	
Z	4	
Density (calculated)	1.1786 Mg/m^3	
Absorption coefficient	1.602 mm^{-1}	
Crystal size	0.42 x 0.09 x 0.14 mm	
Theta range for data collection	2.59 to 69.92 deg.	
Reflections collected	63716	
Independent reflections	16376 [R(int) = 0.077]	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0823, wR2 = 0.1737	
R indices (all data)	R1 = 0.1239, wR2 = 0.1915	
Largest diff. peak and hole	0.304 and -0.318 e.Å^{-3}	

$R = \Sigma (|| F_0 | - | F_c ||) / \Sigma (| F_0 |)$

$wR2 = \{ \Sigma [w (F_0^2 - F_c^2)^2] / \Sigma (F_0^2)^2 \}^{½}$

$S = \{ \Sigma [w (F_0^2 - F_c^2)^2] / (\text{Nbr of reflect.} - \text{Nbr of param.}) \}^{½}$

Table IV. 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(PCy_3)_2Ni(H)(phthal)$

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

ATOM	x	y	z	U(eq)
Ni(1)	4521(1)	1301(1)	2516(1)	64(1)
N(1)	4266(3)	282(2)	2575(2)	67(1)
C(1)	4859(4)	-244(3)	2439(3)	71(1)
O(1)	5636(3)	-136(2)	2253(2)	89(1)
C(2)	4424(4)	-944(3)	2568(3)	69(1)
C(3)	4743(5)	-1610(4)	2531(3)	90(2)
C(4)	4131(7)	-2160(4)	2682(4)	117(2)
C(5)	3239(6)	-2058(5)	2837(5)	123(3)
C(6)	2924(5)	-1380(4)	2881(4)	101(2)
C(7)	3543(4)	-834(3)	2744(3)	76(1)
C(8)	3455(4)	-41(3)	2767(3)	72(1)
O(2)	2789(3)	277(3)	2930(2)	95(1)
P(1)	3155(1)	1010(1)	1512(1)	65(1)
C(11)	6609(3)	1584(3)	4057(3)	71(1)
C(12)	7779(4)	1970(4)	4570(4)	91(2)
C(13)	8153(5)	1408(4)	4884(4)	103(2)
C(14)	7504(6)	1218(5)	5326(4)	122(2)
C(15)	6339(5)	845(4)	4834(4)	109(2)
C(16)	5951(4)	1396(3)	4522(3)	80(2)
C(17)	5802(3)	3015(3)	4131(3)	66(1)
C(18)	4799(4)	2846(3)	4316(3)	80(2)
C(19)	4533(5)	3633(4)	4679(4)	97(2)
C(20)	5435(5)	4278(4)	5413(4)	99(2)
C(21)	6454(5)	4443(4)	5257(3)	90(2)
C(22)	6734(4)	3658(3)	4879(3)	79(2)
C(23)	7079(3)	2447(3)	3187(3)	67(1)
C(24)	6862(4)	3031(3)	2847(3)	79(2)
C(25)	7754(4)	3309(4)	2592(4)	88(2)
C(26)	7958(5)	2576(4)	2023(4)	100(2)
C(27)	8188(4)	1993(4)	2357(4)	96(2)
C(28)	7294(4)	1722(3)	2608(3)	80(2)
P(2)	6010(1)	2069(1)	3488(1)	64(1)
C(29)	3609(4)	1291(4)	819(3)	78(2)
C(30)	4551(4)	1006(4)	695(4)	88(2)
C(31)	5040(5)	1396(5)	261(4)	114(2)
C(32)	4268(6)	1256(5)	-467(5)	127(3)
C(33)	3352(6)	1543(5)	-334(4)	129(3)
C(34)	2816(5)	1154(5)	81(4)	104(2)
C(35)	2276(3)	-69(3)	986(3)	68(1)
C(36)	2821(4)	-664(3)	570(3)	76(2)
C(37)	2180(4)	-1555(4)	259(3)	87(2)
C(38)	1076(4)	-1755(4)	-286(4)	93(2)
C(39)	516(4)	-1181(4)	112(4)	93(2)
C(40)	1152(4)	-280(3)	417(3)	83(2)
C(41)	2263(3)	1626(3)	1763(3)	65(1)

C(42)	2780(4)	2540(3)	2105(3)	81(2)
C(43)	2022(5)	3029(4)	2310(4)	89(2)
C(44)	1566(5)	2840(4)	2855(4)	92(2)
C(45)	1042(5)	1932(4)	2523(4)	96(2)
C(46)	1796(4)	1441(4)	2318(3)	83(2)
Ni(2)	1933(1)	3696(1)	7567(1)	64(1)
N(51)	1611(3)	2604(2)	7474(2)	65(1)
C(51)	2338(4)	2210(3)	7609(3)	68(1)
O(51)	3295(3)	2509(2)	7804(2)	90(1)
C(52)	1765(4)	1382(3)	7477(3)	70(1)
C(53)	2122(5)	763(4)	7529(4)	101(2)
C(54)	1376(7)	66(5)	7390(5)	127(3)
C(55)	312(6)	4(4)	7221(5)	126(3)
C(56)	-29(5)	630(4)	7160(4)	102(2)
C(57)	708(4)	1319(3)	7288(3)	73(1)
C(58)	613(4)	2082(3)	7269(3)	70(1)
O(52)	-212(3)	2237(2)	7090(2)	95(1)
P(3)	2497(1)	3539(1)	6606(1)	64(1)
C(61)	1699(3)	3883(3)	5984(3)	67(1)
C(62)	505(4)	3543(3)	5790(3)	78(2)
C(63)	-88(4)	4001(4)	5447(4)	88(2)
C(64)	137(5)	3932(4)	4725(4)	97(2)
C(65)	1301(5)	4259(4)	4891(3)	88(2)
C(66)	1922(4)	3827(4)	5255(3)	80(2)
C(67)	2532(4)	2490(3)	6003(3)	75(1)
C(68)	1425(4)	1868(3)	5528(3)	84(2)
C(69)	1493(6)	1002(4)	5177(4)	114(2)
C(70)	2193(7)	900(4)	4686(5)	131(3)
C(71)	3264(6)	1513(4)	5151(4)	111(2)
C(72)	3223(5)	2399(4)	5499(4)	90(2)
C(73)	3864(3)	4222(3)	6934(3)	68(1)
C(74)	3976(4)	5131(3)	7296(3)	82(2)
C(75)	5120(4)	5670(4)	7583(4)	101(2)
C(76)	5852(4)	5478(4)	8142(4)	105(2)
C(77)	5764(4)	4577(4)	7780(4)	99(2)
C(78)	4617(4)	4038(4)	7504(3)	83(2)
P(4)	1525(1)	4377(1)	8573(1)	65(1)
C(79)	2604(4)	5348(3)	9284(3)	75(1)
C(80)	2467(5)	5904(4)	10027(3)	104(2)
C(81)	3345(5)	6746(4)	10462(4)	127(3)
C(82)	4428(5)	6660(5)	10622(4)	121(2)
C(83)	4556(4)	6100(4)	9894(4)	110(2)
C(84)	3700(4)	5256(4)	9443(3)	89(2)
C(85)	1171(4)	3784(3)	9079(3)	67(1)
C(86)	570(4)	4087(4)	9634(3)	82(2)
C(87)	234(4)	3449(4)	9892(3)	89(2)
C(88)	1179(4)	3271(4)	10285(3)	89(2)
C(89)	1808(4)	2998(4)	9762(4)	91(2)
C(90)	2128(4)	3612(3)	9485(3)	74(1)
C(91)	376(4)	4728(3)	8324(3)	66(1)
C(92)	550(4)	5310(3)	7982(3)	80(2)

C(93)	-415(4)	5577(4)	7764(4)	88(2)
C(94)	-1398(4)	4843(4)	7225(4)	95(2)
C(95)	-1580(4)	4268(4)	7569(4)	102(2)
C(96)	-623(4)	3977(3)	7758(3)	83(2)

Table IV. 3 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $(PCy_3)_2Ni(H)(phthal)$

ATOM	x	y	z	U(eq)
H(1)	4600(3)	2020(2)	2450(2)	52(11)
H(3)	5338	-1687	2410	109
H(4)	4332	-2611	2678	140
H(5)	2833	-2453	2914	148
H(6)	2326	-1303	2997	121
H(11)	6553	1040	3660	85
H(12A)	8190	2064	4266	109
H(12B)	7892	2500	5004	109
H(13A)	8100	898	4452	123
H(13B)	8889	1675	5226	123
H(14A)	7619	1721	5790	146
H(14B)	7732	835	5493	146
H(15A)	6214	313	4400	130
H(15B)	5942	757	5148	130
H(16A)	6007	1908	4954	96
H(16B)	5213	1125	4185	96
H(17)	5665	3298	3814	79
H(18A)	4216	2447	3838	96
H(18B)	4900	2614	4673	96
H(19A)	4382	3844	4307	116
H(19B)	3905	3515	4804	116
H(20A)	5533	4093	5807	119
H(20B)	5263	4787	5616	119
H(21A)	7026	4830	5746	108
H(21B)	6384	4696	4915	108
H(22A)	6890	3437	5243	94
H(22B)	7357	3784	4751	94
H(23)	7722	2755	3655	80
H(24A)	6204	2753	2401	95
H(24B)	6783	3512	3238	95
H(25A)	7568	3644	2346	106
H(25B)	8393	3646	3048	106
H(26A)	8555	2772	1897	120
H(26B)	7345	2276	1542	120
H(27A)	8265	1513	1964	116
H(27B)	8846	2271	2803	116
H(28A)	7469	1377	2844	96
H(28B)	6656	1392	2148	96
H(29)	3917	1893	1115	94
H(30A)	4320	410	393	106
H(30B)	5076	1166	1197	106
H(31A)	5365	1985	601	137
H(31B)	5592	1169	143	137
H(32A)	4009	671	-835	153
H(32B)	4611	1547	-695	153
H(33A)	2837	1404	-834	154
H(33B)	3599	2139	-21	154

H(34A)	2276	1397	202	124
H(34B)	2476	567	-262	124
H(35)	2172	-206	1393	81
H(36A)	2916	-577	140	91
H(36B)	3515	-547	934	91
H(37A)	2529	-1915	-19	105
H(37B)	2141	-1656	693	105
H(38A)	674	-2321	-457	111
H(38B)	1113	-1706	-745	111
H(39A)	423	-1263	544	112
H(39B)	-179	-1309	-257	112
H(40A)	795	79	685	100
H(40B)	1199	-187	-20	100
H(41)	1675	1449	1277	78
H(42A)	3031	2650	1732	97
H(42B)	3388	2727	2573	97
H(43A)	2398	3615	2557	106
H(43B)	1454	2889	1834	106
H(44A)	2127	3041	3354	111
H(44B)	1053	3126	2947	111
H(45A)	431	1743	2057	115
H(45B)	797	1830	2902	115
H(46A)	2364	1581	2793	100
H(46B)	1417	856	2073	100
H(2)	2180(3)	4540(3)	7650(3)	82(14)
H(53)	2835	809	7653	121
H(54)	1588	-373	7410	153
H(55)	-172	-463	7149	151
H(56)	-741	587	7035	122
H(61)	1878	4477	6321	80
H(62A)	247	2960	5417	94
H(62B)	375	3602	6262	94
H(63A)	-842	3766	5312	106
H(63B)	132	4577	5832	106
H(64A)	-135	3358	4328	117
H(64B)	-230	4237	4519	117
H(65A)	1560	4848	5245	106
H(65B)	1411	4176	4408	106
H(66A)	2672	4080	5396	96
H(66B)	1728	3251	4875	96
H(67)	2845	2315	6383	91
H(68A)	1011	1918	5863	100
H(68B)	1077	1981	5113	100
H(69A)	788	613	4853	136
H(69B)	1773	872	5595	136
H(70A)	2247	347	4498	158
H(70B)	1876	971	4235	158
H(71A)	3684	1454	4820	133
H(71B)	3606	1406	5571	133
H(72A)	3932	2784	5816	108
H(72B)	2933	2526	5081	108

H(73)	4070	4085	6473	82
H(74A)	3729	5274	7732	98
H(74B)	3536	5241	6911	98
H(75A)	5340	5579	7139	121
H(75B)	5168	6247	7845	121
H(76A)	6575	5807	8291	126
H(76B)	5679	5626	8612	126
H(77A)	6216	4469	8160	118
H(77B)	6000	4438	7338	118
H(78A)	4568	3461	7249	99
H(78B)	4406	4139	7954	99
H(79)	2610	5674	9003	90
H(80A)	2493	5646	10363	125
H(80B)	1782	5985	9899	125
H(81A)	3260	7032	10150	153
H(81B)	3274	7079	10954	153
H(82A)	4951	7200	10857	145
H(82B)	4550	6445	10992	145
H(83A)	5243	6024	10029	132
H(83B)	4540	6359	9558	132
H(84A)	3780	4938	8950	107
H(84B)	3782	4958	9744	107
H(85)	694	3242	8659	80
H(86A)	1020	4605	10089	99
H(86B)	-49	4180	9370	99
H(87A)	-128	3650	10253	107
H(87B)	-255	2942	9440	107
H(88A)	941	2843	10419	107
H(88B)	1631	3765	10766	107
H(89A)	2436	2931	10047	109
H(89B)	1386	2467	9312	109
H(90A)	2487	3400	9124	89
H(90B)	2619	4124	9929	89
H(91)	251	5024	8808	80
H(92A)	719	5040	7518	96
H(92B)	1150	5796	8359	96
H(93A)	-527	5913	8236	106
H(93B)	-284	5911	7509	106
H(94A)	-2005	5034	7136	115
H(94B)	-1326	4548	6724	115
H(95A)	-2197	3792	7201	122
H(95B)	-1720	4548	8044	122
H(96A)	-513	3658	7279	99
H(96B)	-756	3625	7995	99

Table IV. 4 Anisotropic parameters ($Å^2 \times 10^3$) for $(PCy_3)_2Ni(H)(phthal)$

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

ATOM	U11	U22	U33	U23	U13	U12
Ni(1)	50(1)	81(1)	72(1)	39(1)	24(1)	31(1)
N(1)	63(2)	77(3)	71(3)	38(2)	27(2)	31(2)
C(1)	63(3)	82(4)	66(3)	29(3)	22(3)	32(3)
O(1)	71(2)	103(3)	106(3)	49(2)	45(2)	41(2)
C(2)	68(3)	68(3)	68(3)	28(3)	21(3)	29(3)
C(3)	89(4)	86(4)	101(5)	42(4)	33(3)	45(4)
C(4)	143(7)	99(5)	145(7)	73(5)	61(6)	68(5)
C(5)	141(7)	109(6)	167(7)	88(6)	80(6)	54(5)
C(6)	103(5)	116(5)	120(5)	74(5)	58(4)	51(4)
C(7)	74(3)	81(4)	79(4)	41(3)	30(3)	29(3)
C(8)	69(3)	87(4)	73(3)	43(3)	28(3)	36(3)
O(2)	87(3)	123(3)	125(3)	76(3)	65(2)	63(2)
P(1)	50(1)	81(1)	71(1)	37(1)	26(1)	33(1)
C(11)	53(3)	90(4)	76(3)	45(3)	19(2)	30(3)
C(12)	57(3)	115(5)	106(4)	63(4)	15(3)	31(3)
C(13)	80(4)	118(5)	119(5)	73(5)	12(4)	42(4)
C(14)	117(6)	137(6)	125(6)	90(5)	13(5)	41(5)
C(15)	99(5)	125(6)	119(5)	83(5)	23(4)	31(4)
C(16)	72(3)	88(4)	81(4)	46(3)	22(3)	20(3)
C(17)	56(3)	76(3)	71(3)	36(3)	24(2)	28(2)
C(18)	69(3)	90(4)	102(4)	47(3)	49(3)	40(3)
C(19)	84(4)	112(5)	119(5)	55(4)	59(4)	51(4)
C(20)	126(5)	98(5)	101(5)	49(4)	61(4)	62(4)
C(21)	94(4)	83(4)	86(4)	30(3)	31(3)	37(3)
C(22)	67(3)	92(4)	80(4)	40(3)	24(3)	34(3)
C(23)	52(3)	80(3)	74(3)	37(3)	25(2)	32(2)
C(24)	70(3)	86(4)	99(4)	47(3)	45(3)	38(3)
C(25)	83(4)	99(4)	105(4)	56(4)	51(3)	34(3)
C(26)	88(4)	123(5)	107(5)	53(4)	62(4)	37(4)
C(27)	75(4)	111(5)	118(5)	47(4)	60(4)	41(4)
C(28)	70(3)	90(4)	100(4)	49(3)	45(3)	40(3)
P(2)	49(1)	83(1)	71(1)	40(1)	25(1)	30(1)
C(29)	69(3)	117(5)	81(4)	58(3)	41(3)	50(3)
C(30)	72(3)	112(5)	100(4)	52(4)	48(3)	43(3)
C(31)	106(5)	144(6)	136(6)	77(5)	81(5)	57(5)
C(32)	158(7)	172(8)	123(6)	91(6)	95(6)	92(6)
C(33)	152(7)	198(8)	106(5)	99(6)	73(5)	104(6)
C(34)	99(4)	153(6)	97(5)	77(5)	47(4)	66(4)
C(35)	50(2)	75(3)	76(3)	33(3)	19(2)	25(2)
C(36)	58(3)	87(4)	79(3)	31(3)	24(3)	38(3)
C(37)	80(4)	88(4)	90(4)	34(3)	32(3)	36(3)
C(38)	80(4)	88(4)	92(4)	29(3)	30(3)	20(3)
C(39)	54(3)	93(4)	102(4)	29(4)	14(3)	17(3)
C(40)	59(3)	96(4)	85(4)	35(3)	16(3)	34(3)
C(41)	53(3)	71(3)	72(3)	29(3)	22(2)	31(2)

C(42)	71(3)	90(4)	96(4)	41(3)	43(3)	41(3)
C(43)	96(4)	95(4)	106(5)	55(4)	55(4)	52(4)
C(44)	101(4)	111(5)	95(4)	52(4)	51(4)	68(4)
C(45)	89(4)	120(5)	124(5)	66(4)	70(4)	68(4)
C(46)	77(3)	100(4)	107(4)	58(4)	55(3)	50(3)
Ni(2)	53(1)	74(1)	71(1)	34(1)	26(1)	29(1)
N(51)	56(2)	70(3)	77(3)	36(2)	26(2)	32(2)
C(51)	62(3)	83(4)	69(3)	39(3)	26(2)	33(3)
O(51)	54(2)	108(3)	118(3)	61(3)	29(2)	35(2)
C(52)	73(3)	75(4)	73(3)	38(3)	31(3)	35(3)
C(53)	101(5)	99(5)	131(6)	67(5)	47(4)	54(4)
C(54)	138(7)	103(6)	169(8)	75(6)	59(6)	64(5)
C(55)	118(6)	91(5)	186(8)	80(5)	56(6)	35(5)
C(56)	82(4)	77(4)	138(6)	45(4)	37(4)	25(3)
C(57)	63(3)	71(4)	81(4)	32(3)	25(3)	23(3)
C(58)	61(3)	77(4)	70(3)	29(3)	25(3)	30(3)
O(52)	60(2)	94(3)	118(3)	39(2)	21(2)	36(2)
P(3)	50(1)	72(1)	74(1)	32(1)	25(1)	26(1)
C(61)	50(2)	80(3)	76(3)	38(3)	27(2)	28(2)
C(62)	52(3)	91(4)	92(4)	42(3)	25(3)	25(3)
C(63)	54(3)	107(5)	103(4)	51(4)	20(3)	33(3)
C(64)	84(4)	100(5)	93(4)	42(4)	10(3)	35(4)
C(65)	96(4)	106(5)	82(4)	52(4)	41(3)	44(4)
C(66)	77(3)	102(4)	84(4)	51(3)	43(3)	42(3)
C(67)	68(3)	81(4)	88(4)	38(3)	38(3)	37(3)
C(68)	80(4)	70(4)	78(4)	18(3)	25(3)	17(3)
C(69)	121(6)	88(5)	118(6)	36(4)	49(5)	27(4)
C(70)	183(8)	81(5)	136(7)	33(5)	92(7)	52(5)
C(71)	136(6)	89(5)	128(6)	41(4)	78(5)	63(5)
C(72)	93(4)	90(4)	106(4)	44(4)	60(4)	44(3)
C(73)	52(3)	81(4)	82(3)	42(3)	28(2)	30(2)
C(74)	49(3)	81(4)	106(4)	38(3)	21(3)	21(3)
C(75)	59(3)	100(5)	124(5)	46(4)	22(3)	12(3)
C(76)	57(3)	130(6)	107(5)	49(5)	17(3)	14(4)
C(77)	52(3)	138(6)	111(5)	64(5)	24(3)	37(4)
C(78)	57(3)	97(4)	103(4)	52(4)	25(3)	36(3)
P(4)	54(1)	77(1)	71(1)	36(1)	25(1)	33(1)
C(79)	59(3)	79(4)	85(4)	34(3)	24(3)	29(3)
C(80)	83(4)	118(5)	86(4)	19(4)	24(3)	50(4)
C(81)	105(5)	98(5)	116(6)	10(4)	3(4)	43(4)
C(82)	88(5)	109(6)	113(6)	32(5)	-4(4)	20(4)
C(83)	63(4)	122(6)	132(6)	59(5)	19(4)	22(4)
C(84)	57(3)	98(4)	98(4)	35(4)	22(3)	28(3)
C(85)	60(3)	87(4)	73(3)	45(3)	32(2)	40(3)
C(86)	72(3)	113(5)	90(4)	56(4)	44(3)	51(3)
C(87)	82(4)	122(5)	95(4)	62(4)	49(3)	50(4)
C(88)	83(4)	124(5)	90(4)	65(4)	40(3)	47(4)
C(89)	86(4)	117(5)	105(5)	69(4)	42(3)	60(4)
C(90)	67(3)	94(4)	82(4)	47(3)	35(3)	46(3)
C(91)	61(3)	73(3)	74(3)	33(3)	29(2)	37(3)
C(92)	67(3)	91(4)	95(4)	51(3)	28(3)	38(3)

C(93)	82(4)	102(5)	99(4)	57(4)	27(3)	51(4)
C(94)	74(4)	111(5)	97(4)	45(4)	15(3)	51(4)
C(95)	60(3)	107(5)	140(6)	66(5)	17(3)	36(3)
C(96)	59(3)	93(4)	103(4)	50(4)	23(3)	38(3)

Table IV. 5 Bond lengths [Å] and angles [deg.] for $(PCy_3)_2Ni(H)(phthal)$

Ni(1)-N(1)	1.925(4)	Ni(2)-N(51)	1.927(4)
Ni(1)-P(1)	2.1765(17)	Ni(2)-P(4)	2.1779(16)
Ni(1)-P(2)	2.178(2)	Ni(2)-P(3)	2.1798(16)
Ni(1)-H(1)	1.39(4)	Ni(2)-H(2)	1.48(4)
N(1)-C(1)	1.377(6)	N(51)-C(51)	1.382(5)
N(1)-C(8)	1.384(6)	N(51)-C(58)	1.385(6)
C(1)-O(1)	1.226(5)	C(51)-O(51)	1.225(5)
C(1)-C(2)	1.481(7)	C(51)-C(52)	1.484(7)
C(2)-C(7)	1.373(7)	C(52)-C(53)	1.368(7)
C(2)-C(3)	1.373(7)	C(52)-C(57)	1.380(6)
C(3)-C(4)	1.384(8)	C(53)-C(54)	1.380(9)
C(4)-C(5)	1.366(9)	C(54)-C(55)	1.392(9)
C(5)-C(6)	1.388(8)	C(55)-C(56)	1.373(8)
C(6)-C(7)	1.364(7)	C(56)-C(57)	1.371(7)
C(7)-C(8)	1.490(7)	C(57)-C(58)	1.469(7)
C(8)-O(2)	1.222(5)	C(58)-O(52)	1.227(5)
P(1)-C(35)	1.845(5)	P(3)-C(61)	1.839(5)
P(1)-C(41)	1.854(4)	P(3)-C(73)	1.854(5)
P(1)-C(29)	1.866(5)	P(3)-C(67)	1.859(5)
C(11)-C(12)	1.527(6)	C(61)-C(66)	1.528(6)
C(11)-C(16)	1.539(6)	C(61)-C(62)	1.537(6)
C(11)-P(2)	1.851(5)	C(62)-C(63)	1.522(7)
C(12)-C(13)	1.525(7)	C(63)-C(64)	1.512(8)
C(13)-C(14)	1.494(8)	C(64)-C(65)	1.505(7)
C(14)-C(15)	1.511(8)	C(65)-C(66)	1.527(7)
C(15)-C(16)	1.510(7)	C(67)-C(68)	1.523(7)
C(17)-C(18)	1.526(6)	C(67)-C(72)	1.532(6)
C(17)-C(22)	1.537(7)	C(68)-C(69)	1.514(7)
C(17)-P(2)	1.843(5)	C(69)-C(70)	1.523(8)
C(18)-C(19)	1.514(7)	C(70)-C(71)	1.482(9)
C(19)-C(20)	1.508(8)	C(71)-C(72)	1.533(7)
C(20)-C(21)	1.517(7)	C(73)-C(74)	1.514(7)
C(21)-C(22)	1.525(7)	C(73)-C(78)	1.533(6)
C(23)-C(28)	1.522(6)	C(74)-C(75)	1.527(7)
C(23)-C(24)	1.536(6)	C(75)-C(76)	1.513(8)
C(23)-P(2)	1.851(5)	C(76)-C(77)	1.506(8)
C(24)-C(25)	1.526(6)	C(77)-C(78)	1.533(7)
C(25)-C(26)	1.514(7)	P(4)-C(79)	1.846(5)
C(26)-C(27)	1.529(8)	P(4)-C(85)	1.850(5)
C(27)-C(28)	1.519(7)	P(4)-C(91)	1.852(4)
C(29)-C(34)	1.492(7)	C(79)-C(80)	1.514(7)
C(29)-C(30)	1.527(6)	C(79)-C(84)	1.521(6)
C(30)-C(31)	1.533(8)	C(80)-C(81)	1.541(9)
C(31)-C(32)	1.463(9)	C(81)-C(82)	1.498(8)
C(32)-C(33)	1.500(8)	C(82)-C(83)	1.488(9)
C(33)-C(34)	1.535(8)	C(83)-C(84)	1.529(8)
C(35)-C(36)	1.535(6)	C(85)-C(90)	1.527(6)
C(35)-C(40)	1.546(6)	C(85)-C(86)	1.537(6)
C(36)-C(37)	1.514(7)	C(86)-C(87)	1.519(7)

C(37)-C(38)	1.511(7)	C(87)-C(88)	1.510(7)
C(38)-C(39)	1.516(7)	C(88)-C(89)	1.512(7)
C(39)-C(40)	1.529(7)	C(89)-C(90)	1.503(7)
C(41)-C(42)	1.505(7)	C(91)-C(92)	1.513(7)
C(41)-C(46)	1.530(6)	C(91)-C(96)	1.545(7)
C(42)-C(43)	1.533(6)	C(92)-C(93)	1.528(6)
C(43)-C(44)	1.508(7)	C(93)-C(94)	1.510(8)
C(44)-C(45)	1.498(8)	C(94)-C(95)	1.507(8)
C(45)-C(46)	1.531(6)	C(95)-C(96)	1.534(6)

N(1)-Ni(1)-P(1)	101.85(13)	N(51)-Ni(2)-P(4)	102.15(12)
N(1)-Ni(1)-P(2)	102.18(13)	N(51)-Ni(2)-P(3)	102.29(12)
P(1)-Ni(1)-P(2)	155.97(7)	P(4)-Ni(2)-P(3)	155.55(7)
N(1)-Ni(1)-H(1)	174.7(17)	N(51)-Ni(2)-H(2)	179.1(17)
P(1)-Ni(1)-H(1)	73.7(17)	P(4)-Ni(2)-H(2)	77.0(17)
P(2)-Ni(1)-H(1)	82.3(17)	P(3)-Ni(2)-H(2)	78.5(17)
C(1)-N(1)-C(8)	108.4(4)	C(51)-N(51)-C(58)	108.3(4)
C(1)-N(1)-Ni(1)	126.1(4)	C(51)-N(51)-Ni(2)	125.9(3)
C(8)-N(1)-Ni(1)	125.5(3)	C(58)-N(51)-Ni(2)	125.9(3)
O(1)-C(1)-N(1)	124.7(5)	O(51)-C(51)-N(51)	124.6(5)
O(1)-C(1)-C(2)	125.8(5)	O(51)-C(51)-C(52)	126.7(5)
N(1)-C(1)-C(2)	109.4(4)	N(51)-C(51)-C(52)	108.8(4)
C(7)-C(2)-C(3)	121.6(6)	C(53)-C(52)-C(57)	122.0(6)
C(7)-C(2)-C(1)	106.5(5)	C(53)-C(52)-C(51)	131.3(5)
C(3)-C(2)-C(1)	132.0(5)	C(57)-C(52)-C(51)	106.7(4)
C(2)-C(3)-C(4)	116.4(6)	C(52)-C(53)-C(54)	117.0(6)
C(5)-C(4)-C(3)	121.7(6)	C(53)-C(54)-C(55)	121.4(7)
C(4)-C(5)-C(6)	121.7(7)	C(56)-C(55)-C(54)	120.5(7)
C(7)-C(6)-C(5)	116.2(6)	C(57)-C(56)-C(55)	118.2(6)
C(6)-C(7)-C(2)	122.4(6)	C(56)-C(57)-C(52)	120.8(5)
C(6)-C(7)-C(8)	130.2(5)	C(56)-C(57)-C(58)	131.9(5)
C(2)-C(7)-C(8)	107.4(5)	C(52)-C(57)-C(58)	107.3(5)
O(2)-C(8)-N(1)	125.3(5)	O(52)-C(58)-N(51)	124.7(5)
O(2)-C(8)-C(7)	126.4(5)	O(52)-C(58)-C(57)	126.3(5)
N(1)-C(8)-C(7)	108.3(4)	N(51)-C(58)-C(57)	109.0(4)
C(35)-P(1)-C(41)	104.1(2)	C(61)-P(3)-C(73)	103.7(2)
C(35)-P(1)-C(29)	109.7(3)	C(61)-P(3)-C(67)	110.4(2)
C(41)-P(1)-C(29)	104.1(2)	C(73)-P(3)-C(67)	104.1(2)
C(35)-P(1)-Ni(1)	115.35(17)	C(61)-P(3)-Ni(2)	108.32(15)
C(41)-P(1)-Ni(1)	113.62(17)	C(73)-P(3)-Ni(2)	113.04(18)
C(29)-P(1)-Ni(1)	109.34(17)	C(67)-P(3)-Ni(2)	116.49(18)
C(12)-C(11)-C(16)	110.1(4)	C(66)-C(61)-C(62)	110.5(4)
C(12)-C(11)-P(2)	119.2(4)	C(66)-C(61)-P(3)	119.1(3)
C(16)-C(11)-P(2)	112.6(3)	C(62)-C(61)-P(3)	113.3(3)
C(13)-C(12)-C(11)	110.8(5)	C(63)-C(62)-C(61)	110.8(4)
C(14)-C(13)-C(12)	111.0(5)	C(64)-C(63)-C(62)	109.8(5)
C(13)-C(14)-C(15)	111.7(6)	C(65)-C(64)-C(63)	112.3(5)
C(16)-C(15)-C(14)	111.7(5)	C(64)-C(65)-C(66)	111.2(5)
C(15)-C(16)-C(11)	110.4(5)	C(65)-C(66)-C(61)	111.1(4)
C(18)-C(17)-C(22)	110.4(4)	C(68)-C(67)-C(72)	111.0(5)

C(18)-C(17)-P(2)	113.2(4)	C(68)-C(67)-P(3)	111.9(3)
C(22)-C(17)-P(2)	118.1(3)	C(72)-C(67)-P(3)	118.4(4)
C(19)-C(18)-C(17)	110.8(4)	C(69)-C(68)-C(67)	109.8(5)
C(20)-C(19)-C(18)	111.0(5)	C(68)-C(69)-C(70)	112.2(6)
C(19)-C(20)-C(21)	111.3(5)	C(71)-C(70)-C(69)	110.8(6)
C(20)-C(21)-C(22)	112.4(5)	C(70)-C(71)-C(72)	111.7(6)
C(21)-C(22)-C(17)	109.7(4)	C(67)-C(72)-C(71)	109.5(5)
C(28)-C(23)-C(24)	110.2(4)	C(74)-C(73)-C(78)	110.6(4)
C(28)-C(23)-P(2)	110.2(3)	C(74)-C(73)-P(3)	113.6(3)
C(24)-C(23)-P(2)	113.7(3)	C(78)-C(73)-P(3)	109.5(3)
C(25)-C(24)-C(23)	111.6(4)	C(73)-C(74)-C(75)	111.8(4)
C(26)-C(25)-C(24)	111.2(5)	C(76)-C(75)-C(74)	111.3(5)
C(25)-C(26)-C(27)	112.0(5)	C(77)-C(76)-C(75)	111.6(5)
C(28)-C(27)-C(26)	110.1(4)	C(76)-C(77)-C(78)	110.5(5)
C(27)-C(28)-C(23)	112.7(5)	C(73)-C(78)-C(77)	111.4(5)
C(17)-P(2)-C(11)	110.8(2)	C(79)-P(4)-C(85)	109.5(2)
C(17)-P(2)-C(23)	104.2(2)	C(79)-P(4)-C(91)	103.4(2)
C(11)-P(2)-C(23)	103.6(2)	C(85)-P(4)-C(91)	104.7(2)
C(17)-P(2)-Ni(1)	107.65(15)	C(79)-P(4)-Ni(2)	110.80(17)
C(11)-P(2)-Ni(1)	116.56(18)	C(85)-P(4)-Ni(2)	114.35(16)
C(23)-P(2)-Ni(1)	113.43(17)	C(91)-P(4)-Ni(2)	113.36(17)
C(34)-C(29)-C(30)	113.1(5)	C(80)-C(79)-C(84)	111.8(5)
C(34)-C(29)-P(1)	119.7(4)	C(80)-C(79)-P(4)	118.5(4)
C(30)-C(29)-P(1)	111.7(4)	C(84)-C(79)-P(4)	114.2(4)
C(29)-C(30)-C(31)	110.1(5)	C(79)-C(80)-C(81)	110.4(5)
C(32)-C(31)-C(30)	113.0(6)	C(82)-C(81)-C(80)	112.2(6)
C(31)-C(32)-C(33)	111.8(6)	C(83)-C(82)-C(81)	111.7(6)
C(32)-C(33)-C(34)	112.3(6)	C(82)-C(83)-C(84)	113.0(6)
C(29)-C(34)-C(33)	110.5(5)	C(79)-C(84)-C(83)	110.9(5)
C(36)-C(35)-C(40)	109.4(4)	C(90)-C(85)-C(86)	109.8(4)
C(36)-C(35)-P(1)	111.5(3)	C(90)-C(85)-P(4)	111.4(3)
C(40)-C(35)-P(1)	118.8(4)	C(86)-C(85)-P(4)	119.2(3)
C(37)-C(36)-C(35)	111.5(4)	C(87)-C(86)-C(85)	110.0(4)
C(38)-C(37)-C(36)	111.1(5)	C(88)-C(87)-C(86)	110.9(5)
C(37)-C(38)-C(39)	111.4(5)	C(87)-C(88)-C(89)	111.6(5)
C(38)-C(39)-C(40)	110.7(5)	C(90)-C(89)-C(88)	111.6(5)
C(39)-C(40)-C(35)	110.5(4)	C(89)-C(90)-C(85)	111.5(4)
C(42)-C(41)-C(46)	110.2(4)	C(92)-C(91)-C(96)	110.0(4)
C(42)-C(41)-P(1)	113.7(3)	C(92)-C(91)-P(4)	113.5(3)
C(46)-C(41)-P(1)	110.2(3)	C(96)-C(91)-P(4)	110.2(3)
C(41)-C(42)-C(43)	112.2(4)	C(91)-C(92)-C(93)	112.7(4)
C(44)-C(43)-C(42)	110.9(5)	C(94)-C(93)-C(92)	111.7(5)
C(45)-C(44)-C(43)	111.5(5)	C(95)-C(94)-C(93)	111.0(5)
C(44)-C(45)-C(46)	111.8(5)	C(94)-C(95)-C(96)	111.8(5)
C(41)-C(46)-C(45)	111.3(4)	C(95)-C(96)-C(91)	110.1(4)

Table IV. 6 Torsion angles [deg.] for $(PCy_3)_2$Ni(H)(phthal)

P(1)-Ni(1)-N(1)-C(1)	113.0(4)	P(4)-Ni(2)-N(51)-C(51)	-112.1(4)
P(2)-Ni(1)-N(1)-C(1)	-66.8(4)	P(3)-Ni(2)-N(51)-C(51)	67.9(4)
P(1)-Ni(1)-N(1)-C(8)	-67.5(4)	P(4)-Ni(2)-N(51)-C(58)	67.0(4)
P(2)-Ni(1)-N(1)-C(8)	112.8(4)	P(3)-Ni(2)-N(51)-C(58)	-113.0(4)
C(8)-N(1)-C(1)-O(1)	179.8(5)	C(58)-N(51)-C(51)-O(51)	-179.7(5)
Ni(1)-N(1)-C(1)-O(1)	-0.6(7)	Ni(2)-N(51)-C(51)-O(51)	-0.5(7)
C(8)-N(1)-C(1)-C(2)	-1.4(5)	C(58)-N(51)-C(51)-C(52)	0.4(5)
Ni(1)-N(1)-C(1)-C(2)	178.2(3)	Ni(2)-N(51)-C(51)-C(52)	179.7(3)
O(1)-C(1)-C(2)-C(7)	-178.4(5)	O(51)-C(51)-C(52)-C(53)	-0.3(10)
N(1)-C(1)-C(2)-C(7)	2.8(6)	N(51)-C(51)-C(52)-C(53)	179.6(6)
O(1)-C(1)-C(2)-C(3)	0.8(9)	O(51)-C(51)-C(52)-C(57)	178.3(5)
N(1)-C(1)-C(2)-C(3)	-178.0(6)	N(51)-C(51)-C(52)-C(57)	-1.8(6)
C(7)-C(2)-C(3)-C(4)	-0.2(9)	C(57)-C(52)-C(53)-C(54)	-0.5(10)
C(1)-C(2)-C(3)-C(4)	-179.3(6)	C(51)-C(52)-C(53)-C(54)	178.0(6)
C(2)-C(3)-C(4)-C(5)	2.0(11)	C(52)-C(53)-C(54)-C(55)	-1.4(12)
C(3)-C(4)-C(5)-C(6)	-2.6(13)	C(53)-C(54)-C(55)-C(56)	2.4(13)
C(4)-C(5)-C(6)-C(7)	1.4(11)	C(54)-C(55)-C(56)-C(57)	-1.5(12)
C(5)-C(6)-C(7)-C(2)	0.4(10)	C(55)-C(56)-C(57)-C(52)	-0.3(10)
C(5)-C(6)-C(7)-C(8)	-178.0(6)	C(55)-C(56)-C(57)-C(58)	179.9(6)
C(3)-C(2)-C(7)-C(6)	-0.9(9)	C(53)-C(52)-C(57)-C(56)	1.3(9)
C(1)-C(2)-C(7)-C(6)	178.4(5)	C(51)-C(52)-C(57)-C(56)	-177.5(5)
C(3)-C(2)-C(7)-C(8)	177.7(5)	C(53)-C(52)-C(57)-C(58)	-178.9(5)
C(1)-C(2)-C(7)-C(8)	-3.0(6)	C(51)-C(52)-C(57)-C(58)	2.3(6)
C(1)-N(1)-C(8)-O(2)	179.3(5)	C(51)-N(51)-C(58)-O(52)	-177.9(5)
Ni(1)-N(1)-C(8)-O(2)	-0.3(8)	Ni(2)-N(51)-C(58)-O(52)	2.9(7)
C(1)-N(1)-C(8)-C(7)	-0.4(5)	C(51)-N(51)-C(58)-C(57)	1.0(5)
Ni(1)-N(1)-C(8)-C(7)	180.0(3)	Ni(2)-N(51)-C(58)-C(57)	-178.2(3)
C(6)-C(7)-C(8)-O(2)	1.1(10)	C(56)-C(57)-C(58)-O(52)	-3.5(10)
C(2)-C(7)-C(8)-O(2)	-177.5(5)	C(52)-C(57)-C(58)-O(52)	176.7(5)
C(6)-C(7)-C(8)-N(1)	-179.2(6)	C(56)-C(57)-C(58)-N(51)	177.6(6)
C(2)-C(7)-C(8)-N(1)	2.2(6)	C(52)-C(57)-C(58)-N(51)	-2.2(6)
N(1)-Ni(1)-P(1)-C(35)	-5.2(2)	N(51)-Ni(2)-P(3)-C(61)	124.6(2)
P(2)-Ni(1)-P(1)-C(35)	174.2(2)	P(4)-Ni(2)-P(3)-C(61)	-55.5(2)
N(1)-Ni(1)-P(1)-C(41)	114.9(2)	N(51)-Ni(2)-P(3)-C(73)	-121.1(2)
P(2)-Ni(1)-P(1)-C(41)	-65.7(2)	P(4)-Ni(2)-P(3)-C(73)	58.8(2)
N(1)-Ni(1)-P(1)-C(29)	-129.4(2)	N(51)-Ni(2)-P(3)-C(67)	-0.5(2)
P(2)-Ni(1)-P(1)-C(29)	50.1(2)	P(4)-Ni(2)-P(3)-C(67)	179.4(2)
C(16)-C(11)-C(12)-C(13)	56.6(6)	C(73)-P(3)-C(61)-C(66)	60.5(5)
P(2)-C(11)-C(12)-C(13)	-171.1(4)	C(67)-P(3)-C(61)-C(66)	-50.5(5)
C(11)-C(12)-C(13)-C(14)	-56.6(7)	Ni(2)-P(3)-C(61)-C(66)	-179.2(4)
C(12)-C(13)-C(14)-C(15)	55.7(8)	C(73)-P(3)-C(61)-C(62)	-166.9(4)
C(13)-C(14)-C(15)-C(16)	-56.0(8)	C(67)-P(3)-C(61)-C(62)	82.0(4)
C(14)-C(15)-C(16)-C(11)	55.9(7)	Ni(2)-P(3)-C(61)-C(62)	-46.6(4)
C(12)-C(11)-C(16)-C(15)	-56.4(6)	C(66)-C(61)-C(62)-C(63)	-57.0(6)
P(2)-C(11)-C(16)-C(15)	168.1(4)	P(3)-C(61)-C(62)-C(63)	166.4(4)
C(22)-C(17)-C(18)-C(19)	58.3(6)	C(61)-C(62)-C(63)-C(64)	57.5(6)
P(2)-C(17)-C(18)-C(19)	-166.7(4)	C(62)-C(63)-C(64)-C(65)	-57.4(7)
C(17)-C(18)-C(19)-C(20)	-57.6(7)	C(63)-C(64)-C(65)-C(66)	56.0(7)
C(18)-C(19)-C(20)-C(21)	55.4(7)	C(64)-C(65)-C(66)-C(61)	-54.4(7)

C(19)-C(20)-C(21)-C(22)	-54.8(7)	C(62)-C(61)-C(66)-C(65)	55.0(6)
C(20)-C(21)-C(22)-C(17)	54.9(6)	P(3)-C(61)-C(66)-C(65)	-171.3(4)
C(18)-C(17)-C(22)-C(21)	-56.2(6)	C(61)-P(3)-C(67)-C(68)	-56.2(4)
P(2)-C(17)-C(22)-C(21)	171.2(4)	C(73)-P(3)-C(67)-C(68)	-166.9(4)
C(28)-C(23)-C(24)-C(25)	-54.4(6)	Ni(2)-P(3)-C(67)-C(68)	67.9(4)
P(2)-C(23)-C(24)-C(25)	-178.7(4)	C(61)-P(3)-C(67)-C(72)	74.7(5)
C(23)-C(24)-C(25)-C(26)	55.0(7)	C(73)-P(3)-C(67)-C(72)	-36.0(5)
C(24)-C(25)-C(26)-C(27)	-55.5(7)	Ni(2)-P(3)-C(67)-C(72)	-161.2(4)
C(25)-C(26)-C(27)-C(28)	55.2(7)	C(72)-C(67)-C(68)-C(69)	56.6(6)
C(26)-C(27)-C(28)-C(23)	-55.7(7)	P(3)-C(67)-C(68)-C(69)	-168.7(4)
C(24)-C(23)-C(28)-C(27)	55.4(6)	C(67)-C(68)-C(69)-C(70)	-55.7(8)
P(2)-C(23)-C(28)-C(27)	-178.2(4)	C(68)-C(69)-C(70)-C(71)	55.9(9)
C(18)-C(17)-P(2)-C(11)	-81.2(4)	C(69)-C(70)-C(71)-C(72)	-56.3(8)
C(22)-C(17)-P(2)-C(11)	50.1(4)	C(68)-C(67)-C(72)-C(71)	-57.0(7)
C(18)-C(17)-P(2)-C(23)	168.0(4)	P(3)-C(67)-C(72)-C(71)	171.6(4)
C(22)-C(17)-P(2)-C(23)	-60.7(4)	C(70)-C(71)-C(72)-C(67)	57.2(8)
C(18)-C(17)-P(2)-Ni(1)	47.3(4)	C(61)-P(3)-C(73)-C(74)	52.3(4)
C(22)-C(17)-P(2)-Ni(1)	178.6(3)	C(67)-P(3)-C(73)-C(74)	167.9(4)
C(12)-C(11)-P(2)-C(17)	-75.1(5)	Ni(2)-P(3)-C(73)-C(74)	-64.7(4)
C(16)-C(11)-P(2)-C(17)	56.0(4)	C(61)-P(3)-C(73)-C(78)	176.6(4)
C(12)-C(11)-P(2)-C(23)	36.1(5)	C(67)-P(3)-C(73)-C(78)	-67.8(4)
C(16)-C(11)-P(2)-C(23)	167.2(4)	Ni(2)-P(3)-C(73)-C(78)	59.5(4)
C(12)-C(11)-P(2)-Ni(1)	161.4(4)	C(78)-C(73)-C(74)-C(75)	54.4(6)
C(16)-C(11)-P(2)-Ni(1)	-67.5(4)	P(3)-C(73)-C(74)-C(75)	178.0(4)
C(28)-C(23)-P(2)-C(17)	-176.5(3)	C(73)-C(74)-C(75)-C(76)	-54.8(7)
C(24)-C(23)-P(2)-C(17)	-52.2(4)	C(74)-C(75)-C(76)-C(77)	55.9(7)
C(28)-C(23)-P(2)-C(11)	67.5(4)	C(75)-C(76)-C(77)-C(78)	-56.4(7)
C(24)-C(23)-P(2)-C(11)	-168.2(4)	C(74)-C(73)-C(78)-C(77)	-55.2(6)
C(28)-C(23)-P(2)-Ni(1)	-59.7(4)	P(3)-C(73)-C(78)-C(77)	178.9(4)
C(24)-C(23)-P(2)-Ni(1)	64.6(4)	C(76)-C(77)-C(78)-C(73)	56.1(7)
N(1)-Ni(1)-P(2)-C(17)	-124.0(2)	N(51)-Ni(2)-P(4)-C(79)	130.9(2)
P(1)-Ni(1)-P(2)-C(17)	56.6(2)	P(3)-Ni(2)-P(4)-C(79)	-49.0(2)
N(1)-Ni(1)-P(2)-C(11)	1.1(2)	N(51)-Ni(2)-P(4)-C(85)	6.6(2)
P(1)-Ni(1)-P(2)-C(11)	-178.3(2)	P(3)-Ni(2)-P(4)-C(85)	-173.29(19)
N(1)-Ni(1)-P(2)-C(23)	121.3(2)	N(51)-Ni(2)-P(4)-C(91)	-113.3(2)
P(1)-Ni(1)-P(2)-C(23)	-58.2(2)	P(3)-Ni(2)-P(4)-C(91)	66.8(2)
C(35)-P(1)-C(29)-C(34)	52.9(5)	C(85)-P(4)-C(79)-C(80)	-52.6(5)
C(41)-P(1)-C(29)-C(34)	-58.0(5)	C(91)-P(4)-C(79)-C(80)	58.5(5)
Ni(1)-P(1)-C(29)-C(34)	-179.7(4)	Ni(2)-P(4)-C(79)-C(80)	-179.7(4)
C(35)-P(1)-C(29)-C(30)	-82.7(4)	C(85)-P(4)-C(79)-C(84)	82.4(4)
C(41)-P(1)-C(29)-C(30)	166.4(4)	C(91)-P(4)-C(79)-C(84)	-166.4(4)
Ni(1)-P(1)-C(29)-C(30)	44.7(5)	Ni(2)-P(4)-C(79)-C(84)	-44.6(5)
C(34)-C(29)-C(30)-C(31)	52.9(7)	C(84)-C(79)-C(80)-C(81)	54.6(7)
P(1)-C(29)-C(30)-C(31)	-168.5(5)	P(4)-C(79)-C(80)-C(81)	-169.3(4)
C(29)-C(30)-C(31)-C(32)	-53.3(8)	C(79)-C(80)-C(81)-C(82)	-54.8(8)
C(30)-C(31)-C(32)-C(33)	54.9(9)	C(80)-C(81)-C(82)-C(83)	54.3(9)
C(31)-C(32)-C(33)-C(34)	-54.8(9)	C(81)-C(82)-C(83)-C(84)	-53.8(9)
C(30)-C(29)-C(34)-C(33)	-53.3(7)	C(80)-C(79)-C(84)-C(83)	-53.9(7)
P(1)-C(29)-C(34)-C(33)	171.7(5)	P(4)-C(79)-C(84)-C(83)	168.0(4)
C(32)-C(33)-C(34)-C(29)	53.6(9)	C(82)-C(83)-C(84)-C(79)	53.4(8)
C(41)-P(1)-C(35)-C(36)	167.2(4)	C(79)-P(4)-C(85)-C(90)	-57.0(4)

C(29)-P(1)-C(35)-C(36)	56.3(4)	C(91)-P(4)-C(85)-C(90)	-167.3(4)
Ni(1)-P(1)-C(35)-C(36)	-67.6(4)	Ni(2)-P(4)-C(85)-C(90)	68.0(4)
C(41)-P(1)-C(35)-C(40)	38.6(4)	C(79)-P(4)-C(85)-C(86)	72.5(4)
C(29)-P(1)-C(35)-C(40)	-72.2(4)	C(91)-P(4)-C(85)-C(86)	-37.8(5)
Ni(1)-P(1)-C(35)-C(40)	163.8(3)	Ni(2)-P(4)-C(85)-C(86)	-162.5(3)
C(40)-C(35)-C(36)-C(37)	-56.6(6)	C(90)-C(85)-C(86)-C(87)	-57.6(6)
P(1)-C(35)-C(36)-C(37)	170.1(4)	P(4)-C(85)-C(86)-C(87)	172.2(4)
C(35)-C(36)-C(37)-C(38)	56.6(6)	C(85)-C(86)-C(87)-C(88)	57.6(6)
C(36)-C(37)-C(38)-C(39)	-56.4(7)	C(86)-C(87)-C(88)-C(89)	-56.1(7)
C(37)-C(38)-C(39)-C(40)	56.9(7)	C(87)-C(88)-C(89)-C(90)	54.6(7)
C(38)-C(39)-C(40)-C(35)	-57.3(6)	C(88)-C(89)-C(90)-C(85)	-55.2(6)
C(36)-C(35)-C(40)-C(39)	56.7(6)	C(86)-C(85)-C(90)-C(89)	56.7(6)
P(1)-C(35)-C(40)-C(39)	-173.7(4)	P(4)-C(85)-C(90)-C(89)	-169.0(4)
C(35)-P(1)-C(41)-C(42)	-172.1(4)	C(79)-P(4)-C(91)-C(92)	59.0(4)
C(29)-P(1)-C(41)-C(42)	-57.2(4)	C(85)-P(4)-C(91)-C(92)	173.6(4)
Ni(1)-P(1)-C(41)-C(42)	61.6(4)	Ni(2)-P(4)-C(91)-C(92)	-61.1(4)
C(35)-P(1)-C(41)-C(46)	63.5(4)	C(79)-P(4)-C(91)-C(96)	-177.1(4)
C(29)-P(1)-C(41)-C(46)	178.4(4)	C(85)-P(4)-C(91)-C(96)	-62.5(4)
Ni(1)-P(1)-C(41)-C(46)	-62.8(4)	Ni(2)-P(4)-C(91)-C(96)	62.8(4)
C(46)-C(41)-C(42)-C(43)	-55.2(6)	C(96)-C(91)-C(92)-C(93)	54.8(6)
P(1)-C(41)-C(42)-C(43)	-179.6(4)	P(4)-C(91)-C(92)-C(93)	178.8(4)
C(41)-C(42)-C(43)-C(44)	55.7(7)	C(91)-C(92)-C(93)-C(94)	-54.4(7)
C(42)-C(43)-C(44)-C(45)	-55.1(7)	C(92)-C(93)-C(94)-C(95)	54.1(7)
C(43)-C(44)-C(45)-C(46)	55.5(7)	C(93)-C(94)-C(95)-C(96)	-56.4(7)
C(42)-C(41)-C(46)-C(45)	54.6(6)	C(94)-C(95)-C(96)-C(91)	57.3(7)
P(1)-C(41)-C(46)-C(45)	-179.1(4)	C(92)-C(91)-C(96)-C(95)	-55.6(6)
C(44)-C(45)-C(46)-C(41)	-55.2(7)	P(4)-C(91)-C(96)-C(95)	178.5(4)

Table IV. 7 Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

Plane 1.

$$10.9278\ (0.0069)\ x - 3.2549\ (0.1426)\ y - 14.0579\ (0.0792)\ z = 0.9685\ (0.0088)$$

*	-0.0393	(0.0179)	H1
*	0.0237	(0.0103)	P1
*	0.0217	(0.0094)	P2
*	-0.0177	(0.0083)	N1
*	0.0116	(0.0065)	Ni1

Rms deviation of fitted atoms = 0.0246

Plane 2.

$$3.3548\ (0.0363)\ x + 0.2390\ (0.0434)\ y + 14.8082\ (0.0349)\ z = 5.2478\ (0.0120)$$

Angle to previous plane (with approximate esd) = 66.59 (0.32)

*	0.0028	(0.0030)	N1
*	-0.0122	(0.0030)	C1
*	0.0172	(0.0032)	C2
*	-0.0156	(0.0033)	C7
*	0.0079	(0.0031)	C8
	-0.0234	(0.0079)	O1
	0.0336	(0.0081)	O2
	0.0256	(0.0073)	Ni1

Rms deviation of fitted atoms = 0.0123

Plane 3.

$$2.9071\ (0.0400)\ x + 0.7100\ (0.0438)\ y + 14.8974\ (0.0255)\ z = 5.0360\ (0.0191)$$

Angle to previous plane (with approximate esd) = 2.20 (0.36)

*	0.0093	(0.0044)	C2
*	-0.0014	(0.0049)	C3
*	0.0070	(0.0054)	C4
*	-0.0148	(0.0061)	C5
*	0.0076	(0.0041)	C6
*	-0.0077	(0.0030)	C1
	0.0877	(0.0093)	C8

Rms deviation of fitted atoms = 0.0089

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Plane 4.

 10.9072 (0.0067) x - 3.8502 (0.1748) y + 7.0263 (0.0731) z = 6.0038 (0.0063)

 Angle to previous plane (with approximate esd) = 41.04 ( 0.39 )

 *   0.0035 (0.0213)  H2
 *  -0.0018 (0.0120)  P3
 *  -0.0018 (0.0122)  P4
 *   0.0018 (0.0106)  N51
 *  -0.0016 (0.0078)  Ni2

 Rms deviation of fitted atoms =   0.0022

Plane 5.

 - 3.4947 (0.0357) x - 0.2794 (0.0434) y + 18.3235 (0.0209) z = 13.0566 (0.0092)

 Angle to previous plane (with approximate esd) = 67.07 ( 0.29 )

 *   0.0017 (0.0030)  N51
 *   0.0065 (0.0030)  C51
 *  -0.0123 (0.0032)  C52
 *   0.0134 (0.0033)  C57
 *  -0.0093 (0.0031)  C58
     0.0215 (0.0079)  O51
    -0.0530 (0.0079)  O52
     0.0300 (0.0073)  Ni2

 Rms deviation of fitted atoms =   0.0096

Plane 6.

 - 3.0888 (0.0414) x - 0.3989 (0.0459) y + 18.3097 (0.0188) z = 13.1056 (0.0126)

 Angle to previous plane (with approximate esd) =  1.74 ( 0.24 )

 *  -0.0164 (0.0044)  C52
 *  -0.0055 (0.0054)  C53
 *  -0.0016 (0.0058)  C54
 *   0.0196 (0.0063)  C55
 *  -0.0117 (0.0043)  C56
 *   0.0156 (0.0031)  C51
    -0.0683 (0.0094)  C58

 Rms deviation of fitted atoms =   0.0133
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