Nickel(II) Complexes Containing Bidentate Diarylamido Phosphine Ligands

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A series of diamagnetic divalent nickel complexes supported by bidentate diarylamido phosphine ligands have been prepared and characterized. Deprotonation of *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H[^{i}Pr-NP]) and *N*-(2-diphenylphosphinophenyl)-2,6-dimethylaniline (H[Me-NP]) with *n*-BuLi in THF at −35 °C produced the corresponding lithium complexes, [^{i}Pr-NP]Li(THF)$_2$ and [Me-NP]Li(THF)$_2$, respectively. The chloride complex {[^{i}Pr-NP]NiCl}$_2$ is accessible from the reaction of NiCl$_2$(DME) with [^{i}Pr-NP]Li(THF)$_2$ or H[^{i}Pr-NP] in the presence of triethylamine. Addition of PMe$_3$ to {[^{i}Pr-NP]NiCl}$_2$ afforded [^{i}Pr-NP]NiCl(PMe$_3$), from which [^{i}Pr-NP]NiMe(PMe$_3$), [^{i}Pr-NP]NiPh(PMe$_3$), and [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) were prepared from the metathetical reactions with appropriate Grignard reagents. Solution NMR data of [^{i}Pr-NP]NiMe(PMe$_3$) revealed two geometric isomers at room temperature with the major species carrying PMe$_3$ cis to the phosphorus donor of the amido phosphine ligand. Interestingly, only one of the possible isomers is observed for [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiPh(PMe$_3$), in which the two phosphorus donors in the former are exclusively cis whereas those in the latter are trans. The benzyl complexes [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph) are prepared directly from the reactions of [^{i}Pr-NP]Li(THF)$_2$ and [Me-NP]Li(THF)$_2$, respectively, with Ni(COD)$_2$ in the presence of benzyl chloride. The η^3-feature of the benzyl ligand maintained in solution is elucidated by the $^1J_{\mathrm{CH}}$ value observed for the benzylic methylene group in the NMR spectroscopy. In addition to the spectroscopic data for all new molecules, X-ray structures of H[^{i}Pr-NP], [Me-NP]Li(THF)$_2$, [^{i}Pr-NP]NiCl(PMe$_3$), [^{i}Pr-NP]NiMe(PMe$_3$), [^{i}Pr-NP]NiPh(PMe$_3$), [^{i}Pr-NP]Ni(η^3-CH$_2$Ph), and [Me-NP]Ni(η^3-CH$_2$Ph) are presented.

Introduction

Divalent nickel complexes supported by monoanionic, bidentate, four-electron [L−X]$^-$ ligands are currently under extensive investigation, particularly for the development of neutral, single-component catalysts for olefin oligomerization, polymerization, and copolymerization.[1] Recent progress in this aspect highlights molecules that are reminiscent of catalysts for Shell Higher Olefin Process (SHOP).[2,3] Several classes of ligands investigated thus far include [O−P]$^-$,[4−8] [O−N]$^-$,[9−20] and [N−N]$^-$ (Chart 1).[21−27] With careful modification of the ligand design, the reactivity and stability (or functional group compatibility) of the nickel catalysts may be finely tuned. In comparison, nickel chemistry

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Chart 1. Representative Examples of Monoanionic, Bidentate, Four-Electron [L−X]− Ligands

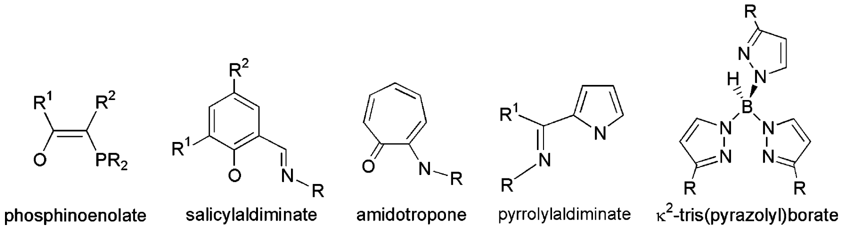
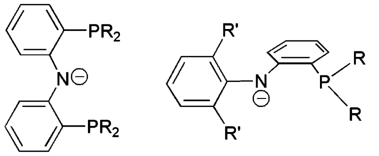


Chart 2



involving bidentate [N−P]$^-$ ligands remains relatively undeveloped.[28−32]

We have recently established a synthetic protocol for the preparation of a series of potentially rigid and robust amido phosphine ligands that are *o*-phenylene derivatives (Chart 2).[33] Nickel alkyl complexes of a tridentate bis(2-diphenylphosphinophenyl)amide ([PNP]$^-$) ligand, including those containing *β*-hydrogen atoms, have shown unusual thermal stability. One intriguing feature worthy of note regarding the nickel derivatives of [PNP]$^-$ is that analogous complexes supported by the closely related [N(SiMe$_2$CH$_2$PR$_2$)$_2$]$^-$ ligands[34] are either synthetically inaccessible or thermally unstable. In addition, the palladium complexes of [PNP]$^-$ are markedly stable at temperatures as high as 200 °C. As a result, extremely high turnover numbers and frequencies have been achieved for catalytic Heck olefination of aryl halides.[35] In a parallel pursuit, we have set out to examine group 10 metal complexes of bidentate amido phosphine ligands, with primary goals directed to catalytic reactions with olefinic substrates. Utilization of sterically demanding ligands is attempted to prevent or diminish the possibility of the formation of bis-ligand complexes that have proven to be inactive in the SHOP-type catalytic systems.[9,12,36,37] In this contribution, we aim to demonstrate the synthetic possibility of divalent nickel complexes incorporating the bidentate diarylamido phosphine ([NP]$^-$) ligands. Spectroscopic data and molecular structures of these compounds are discussed.

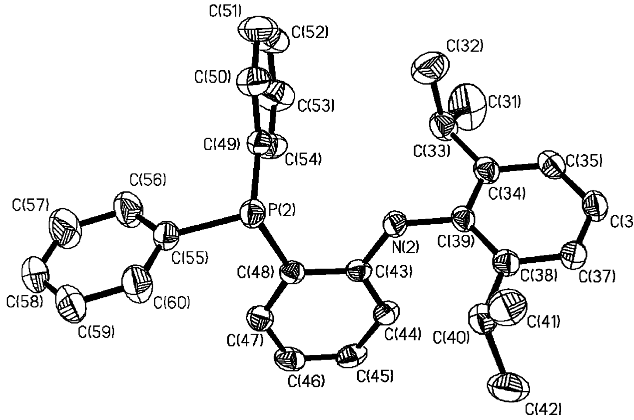


Figure 1. Molecular structure of H[^{i}Pr-NP] with thermal ellipsoids drawn at the 35% probability level. Only one of the two independent molecules found in the asymmetric unit cell is presented for clarity. Selected bond distances (Å) and angles (deg): N(2)−C(43) 1.3877(19), N(2)−C(39) 1.426(2), P(2)−C(49) 1.829(2), P(2)−C(48) 1.8297(18), P(2)−C(55) 1.8326(18), C(43)−N(2)−C(39) 124.80(14), C(49)−P(2)−C(48) 100.90(8), C(49)−P(2)−C(55) 102.69(9), C(48)−P(2)−C(55) 102.43(8).

Results and Discussion

Preparation of Lithium Derivatives of the Amido Phosphine Ligands. The ligand precursors *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H[^{i}Pr-NP]) and *N*-(2-diphenylphosphinophenyl)-2,6-dimethylaniline (H[Me-NP]) were prepared following the procedures reported previously.[38,39] During our synthetic work, colorless crystals of H[^{i}Pr-NP] suitable for X-ray diffraction analysis were obtained by slow evaporation of a methanol solution at room temperature. An X-ray crystallographic study revealed that the molecular structure of H[^{i}Pr-NP] (Table 1, Figure 1) resembles that of the dimethyl analogue.[39] The diisopropylphenyl substituent is roughly perpendicular to the *o*-phenylene backbone, and the two phenyl rings at the phosphorus donor are virtually orthogonal to each other. The isopropylmethyl groups are oriented such that they are tilted away from the diphenylphosphino moiety, consistent with the steric crowding of this compound as suggested by the NMR spectroscopic data.[38]

The preparation of [^{i}Pr-NP]Li(THF)$_2$ has been communicated recently.[38] Likewise, addition of 1 equiv of *n*-BuLi to H[Me-NP] dissolved in THF at −35 °C led to

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Table 1. Crystallographic Data for H[^{i}Pr-NP], [Me-NP]Li(THF)$_2$, [^{i}Pr-NP]NiCl(PMe$_3$), [^{i}Pr-NP]NiMe(PMe$_3$), [^{i}Pr-NP]NiPh(PMe$_3$), [^{i}Pr-NP]Ni(η^3-CH$_2$Ph), and [Me-NP]Ni(η^3-CH$_2$Ph)

	{H[^{i}Pr-NP]}$_2$	[Me-NP]Li(THF)$_2$	[^{i}Pr-NP]NiCl(PMe$_3$)	[^{i}Pr-NP]NiMe(PMe$_3$)	[^{i}Pr-NP]NiPh(PMe$_3$)	[^{i}Pr-NP]Ni(η^3-CH$_2$Ph)	[Me-NP]Ni(η^3-CH$_2$Ph)
formula	$C_{60}H_{64}N_2P_2$	$C_{34}H_{39}LiNO_2P$	$C_{33}H_{40}ClNNiP_2$	$C_{34}H_{43}NNiP_2$	$C_{39}H_{45}NNiP_2$	$C_{37}H_{37}NNiP$	$C_{33}H_{29}NNiP$
fw	875.07	531.57	606.76	568.34	648.41	585.36	529.286
D_{calc} (g cm^{-3})	1.172	1.178	1.254	1.206	1.238	1.279	1.300
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a (Å)	12.0940(6)	13.818(2)	10.2880(2)	10.3530(2)	10.611(2)	9.1100(3)	9.5852(2)
b (Å)	14.2831(7)	12.222(2)	17.8490(4)	17.7380(4)	35.051(7)	10.8780(3)	14.0420(3)
c (Å)	28.7245(14)	17.973(3)	18.1290(5)	18.2700(3)	9.6820(19)	16.7810(7)	20.0909(5)
α (deg)	90	90	90	90	90	82.9480(10)	90
β (deg)	91.6930(10)	98.969	105.0920(10)	105.8010(10)	105.03(3)	88.1140(10)	90
γ (deg)	90	90	90	90	90	67.064(2)	90
V (Å^3)	4959.7(4)	2998.2(9)	3214.22(13)	3228.35(11)	3477.8(12)	1519.71(9)	2704.14(11)
Z	4	4	4	4	4	2	4
T (K)	150(2)	150(2)	293(2)	293(2)	293(2)	293(2)	298
diffractometer	SMART CCD	SMART CCD	Kappa CCD	Kappa CCD	Kappa CCD	Kappa CCD	Kappa CCD
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
$2\theta_{\max}$ (deg)	55.06	55.20	50.14	50.06	50.06	50.08	50.06
total no. of reflns	30 848	18 431	23 876	19 020	10 435	11 575	17 634
no. of indep reflns	11 328	6837	5680	5700	5037	5291	4758
R_{int}	0.0375	0.0750	0.0664	0.0538	0.0699	0.0890	0.059
absorp coeff (mm^{-1})	0.128	0.122	0.808	0.722	0.677	0.717	0.80
no. of data/restraints/ params	11328/0/599	6837/0/354	5680/0/343	5700/0/344	5037/0/388	5291/0/361	4758/0/325
goodness of fit	1.036	0.803	1.062	1.239	1.087	1.124	0.913
final R indices [$I > 2\sigma(I)$]	R1 = 0.0471	R1 = 0.0592	R1 = 0.0503	R1 = 0.0675	R1 = 0.0661	R1 = 0.0669	R1 = 0.0405
	wR2 = 0.0871	wR2 = 0.1300	wR2 = 0.1381	wR2 = 0.1539	wR2 = 0.1573	wR2 = 0.1677	wR2 = 0.1076
R indices (all data)	R1 = 0.0828	R1 = 0.1397	R1 = 0.0958	R1 = 0.1066	R1 = 0.1407	R1 = 0.1213	R1 = 0.0610
	wR2 = 0.0957	wR2 = 0.1524	wR2 = 0.1794	wR2 = 0.1967	wR2 = 0.2203	wR2 = 0.2206	wR2 = 0.1307

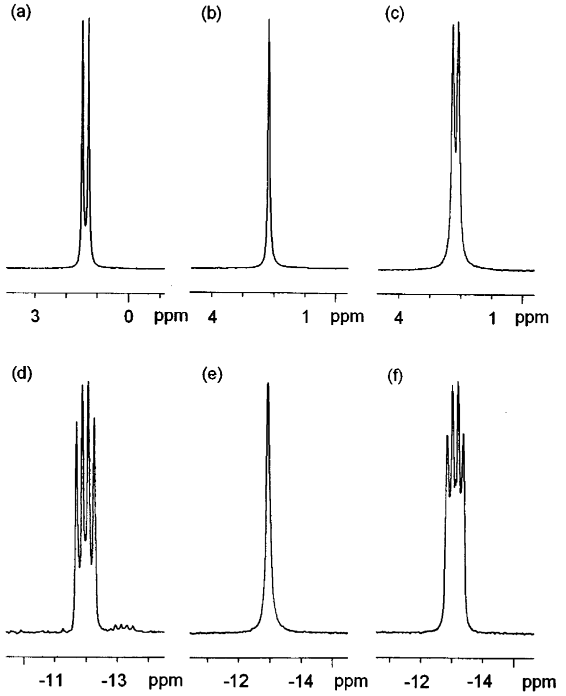


Figure 2. $^{7}\text{Li}\{^{1}\text{H}\}$ NMR (194 MHz) spectra of (a) [^{i}Pr-NP]-Li(THF)$_2$ (C_6D_6, 25 °C), (b) [Me-NP]Li(THF)$_2$ (toluene-d_8, 25 °C), (c) [Me-NP]Li(THF)$_2$ (toluene-d_8, −20 °C), and $^{31}\text{P}\{^{1}\text{H}\}$ NMR (202 MHz) spectra of (d) [^{i}Pr-NP]Li(THF)$_2$ (C_6D_6, 25 °C), (e) [Me-NP]Li(THF)$_2$ (toluene-d_8, 25 °C), (f) [Me-NP]Li(THF)$_2$ (toluene-d_8, −20 °C).

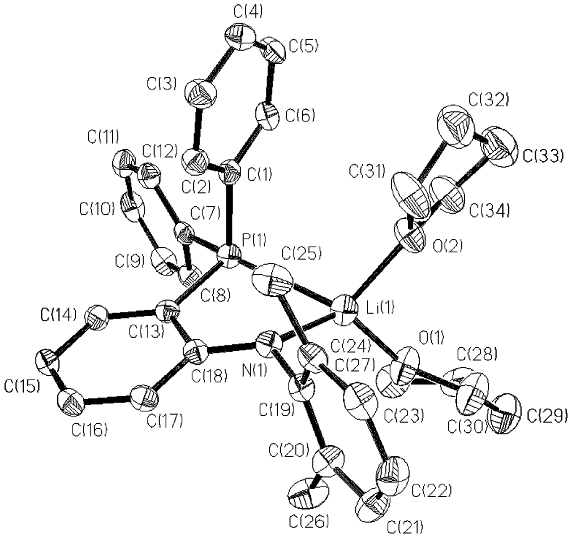
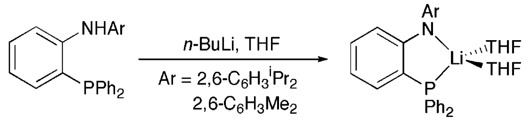


Figure 3. Molecular structure of [Me-NP]Li(THF)$_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Li(1)−O(2) 1.921(5), Li(1)−O(1) 1.942(5), Li(1)−N(1) 1.990(5), Li(1)−P(1) 2.620(5), O(2)−Li(1)−O(1) 99.8(2), O(2)−Li(1)−N(1) 118.8(3), O(1)−Li(1)−N(1) 127.8(3), O(2)−Li(1)−P(1) 110.2(2), O(1)−Li(1)−P(1) 123.1(2), N(1)−Li(1)−P(1) 76.63(17).

the isolation of the solvated lithium amide [Me-NP]Li-(THF)$_2$, in quantitative yield (eq 1). The solution structures of both [^{i}Pr-NP]Li(THF)$_2$ and [Me-NP]Li(THF)$_2$ were characterized by multinuclear NMR spectroscopy, which is indicative of the chelating feature of these amido phosphine ligands with respect to the lithium center. For instance, the *o*-alkyl groups in both lithium complexes are shifted relatively downfield in the ^{1}H NMR spectroscopy as compared to those of the corresponding ligand precursors. The phosphorus atoms in both molecules show downfield changes upon coordination to lithium. The $^{31}\text{P}\{^{1}\text{H}\}$ and $^{7}\text{Li}\{^{1}\text{H}\}$ NMR spectra (Figure 2) are mutually consistent with the coordination of the phosphorus donor to the quadrupolar lithium-7 center ($I = 3/2$, natural abundance 92.6%). A somewhat lower temperature, however, is required for the observation of $^{1}J_{\text{LiP}}$ in [Me-NP]Li(THF)$_2$ than in [^{i}Pr-NP]Li-(THF)$_2$. The coupling constants $^{1}J_{\text{LiP}}$ of 38 and 34 Hz for [^{i}Pr-NP]Li(THF)$_2$ and [Me-NP]Li(THF)$_2$, respectively, are well comparable to those found for the lithium phosphide derivatives such as [Li(tmeda)]$_2$[1,2-C_6H_4-(PPh)$_2$] (35 Hz)[40] and [Li(tmeda)]$_2$[1,2-C_6H_4(PSiMe$_3$)$_2$] (38 Hz).[40]



(1)

[^{i}Pr-NP]Li(THF)$_2$
[Me-NP]Li(THF)$_2$

A single-crystal diffraction study revealed the solid-state structure of [Me-NP]Li(THF)$_2$. Yellow crystals of [Me-NP]Li(THF)$_2$ were grown from a concentrated diethyl ether solution at −35 °C. As illustrated in Figure 3, this compound is a four-coordinate species with the lithium center surrounded by two THF molecules and the nitrogen and phosphorus donors of the amido phosphine ligand. The geometry at lithium is distorted tetrahedral with angles ranging from 76.63(17)° to 127.8(3)°, the most acute being associated with the chelating amido phosphine ligand. The lithium atom is deviated from the N−phenylene−P plane by 0.5954 Å. A distorted tetrahedral geometry is observed for the phosphorus donor, the bond angles involving which are found in the range between 95.64(14)° and 147.71(14)°. Nevertheless, the Li(1)−P(1) bond distance of 2.620(5) Å is similar to those found in [Me$_2$Al(CH$_2$PMe$_2$)$_2$][Li-(tmeda)] (2.606(5) Å),[41,42] LiC(SiMe$_2$CH$_2$PPh$_2$)$_3$ (2.652 Å average),[43] and [(tmeda)LiCH$_2$PPh$_2$]$_2$ (2.686(5) Å),[44] but slightly shorter than those of the tridentate analogue [PNP]Li(THF)$_2$ (2.8015 Å average).[33] The dimethylphenyl ring is approximately perpendicular to the N−phenylene−P plane. The remaining parameters are unexceptional.

Synthesis and Characterization of Nickel η^1-Alkyl and -aryl Complexes. Addition of [^{i}Pr-NP]Li-(THF)$_2$ to NiCl$_2$(DME) suspended in THF at −35 °C resulted in slow dissolution of NiCl$_2$(DME) to give a homogeneous, deep red solution, from which diamagnetic {[^{i}Pr-NP]NiCl}$_2$ was isolated as a red solid in 81% yield (eq 2). Alternatively, the chloride complex can be prepared from the reaction of H[^{i}Pr-NP] with NiCl$_2$-(DME) in the presence of triethylamine in THF at room

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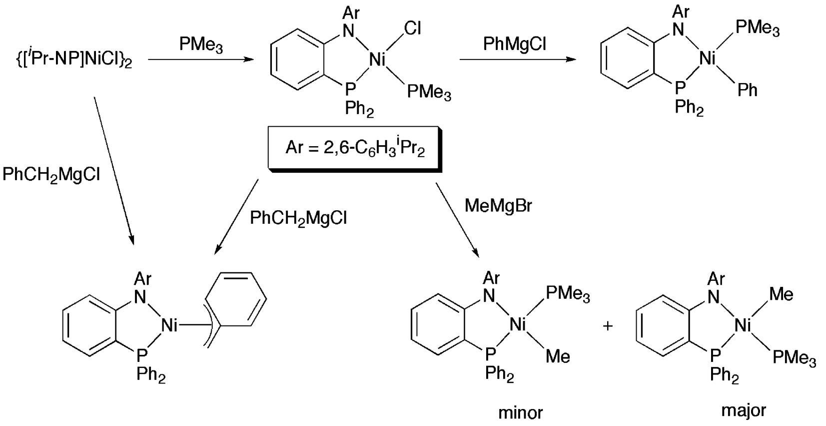
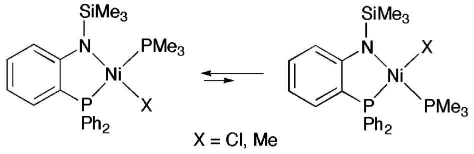
Scheme 1





(3)

temperature. Attempts to grow crystals suitable for X-ray diffraction analysis were not successful. We tentatively formulate this compound as a chloride-bridged dimer, presumably in the solid state, on the basis of its facile association with Lewis bases (vide infra). The phosphorus donor of $\{[{}^{i}\text{Pr-NP}]\text{NiCl}\}_2$ in C_6D_6 appears as a broad singlet resonance at 32.45 ppm ($\Delta\nu_{1/2} = 80$ Hz) in the $^{31}P\{^{1}H\}$ NMR spectroscopy, a value that is shifted significantly downfield from those of $H[{}^{i}\text{Pr-NP}]$ at −20.11 ppm and $[{}^{i}\text{Pr-NP}]\text{Li(THF)}_2$ at −11.99 ppm.[38] Similar to those found in $H[{}^{i}\text{Pr-NP}]$ and $[{}^{i}\text{Pr-NP}]\text{Li(THF)}_2$, the isopropylmethyl groups in $\{[{}^{i}\text{Pr-NP}]\text{NiCl}\}_2$ are diastereotopic, as evidenced by ^{1}H and ^{13}C NMR spectroscopy, implying restricted rotation about the N−Ar bond.[38,45] Analogous reactions involving the $[\text{Me-NP}]^-$ ligand have so far been inconclusive. We suspect that concomitant formation of $[\text{Me-NP}]_2\text{Ni}$ and the desired chloride complex becomes possible due to the smaller size of the $[\text{Me-NP}]^-$ ligand.

$$[{}^{i}\text{Pr-NP}]\text{Li(THF)}_2 \xrightarrow{\text{NiCl}_2\text{(DME)}} \{[{}^{i}\text{Pr-NP}]\text{NiCl}\}_2 \xleftarrow{\text{NiCl}_2\text{(DME), NEt}_3} \text{H}[{}^{i}\text{Pr-NP}] \quad (2)$$

Treatment of $\{[{}^{i}\text{Pr-NP}]\text{NiCl}\}_2$ with PMe_3 in THF at room temperature produced high yield of diamagnetic $[{}^{i}\text{Pr-NP}]\text{NiCl(PMe}_3)$ as an emerald solid (Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectroscopy at room temperature exhibits two doublet resonances with equal intensity at 47.29 and −16.98 ppm for $[{}^{i}\text{Pr-NP}]^-$ and PMe_3, respectively. The coupling constant of 88 Hz is consistent with a cis relationship between the two phosphorus donors. This phenomenon is notably different from that found in the closely related system involving a trimethylsilyl-substituted amide as shown in eq 3, in which two isomers are present in solution with the trans form being predominant.[46] Addition of Lewis bases such as pyridine or $PMePh_2$ to $\{[{}^{i}\text{Pr-NP}]\text{NiCl}\}_2$ resulted in a yellowish green or emerald solution, whose $^{31}P\{^{1}H\}$ NMR spectrum at room temperature revealed a broad signal for the amido phosphine ligand, likely due to the formation of the two possible geometric isomers. A fast equilibrium between dissociation and association of the external base in these presumed isomeric mixtures might also be involved.

The preparation of nickel hydrocarbyl complexes containing the bidentate $[\text{NP}]^-$ ligands is of particular interest in view of the parallel comparison with the tridentate $[\text{PNP}]^-$ analogues[33] and the potential applications for organic synthesis and homogeneous catalysis. Attempts to prepare well-defined alkyl or aryl complexes from the reactions of $\{[{}^{i}\text{Pr-NP}]\text{NiCl}\}_2$ with a variety of Grignard reagents were not successful. Diamagnetic, ruby $[{}^{i}\text{Pr-NP}]\text{NiMe(PMe}_3)$, however, was isolated in high yield from the reaction of $[{}^{i}\text{Pr-NP}]\text{NiCl(PMe}_3)$ with MeMgCl in THF at −35 °C. In contrast to $[{}^{i}\text{Pr-NP}]\text{NiCl(PMe}_3)$, $[{}^{i}\text{Pr-NP}]\text{NiMe(PMe}_3)$ exists as a mixture of two geometric isomers with a relative ratio of ca. 9:1, as indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy. The coupling constant of 30 Hz observed for the major isomer found in the THF aliquot indicates that the two phosphorus donors are mutually cis to each other, whereas that of 302 Hz for the minor corresponds to a trans relationship. The major component exhibits a doublet resonance centered at 35.60 ppm for the phosphorus donor of the amido phosphine ligand, whereas the minor component appears at 38.95 ppm. The nickel-bound methyl hydrogen atoms in both isomers appear as a doublet of doublets resonance at −0.12 and −0.42 ppm for major and minor components, respectively, as a consequence of internuclear interaction with two chemically inequivalent phosphorus donors.

Single crystals of $[{}^{i}\text{Pr-NP}]\text{NiCl(PMe}_3)$ suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated THF solution at −35 °C, while those of $[{}^{i}\text{Pr-NP}]\text{NiMe(PMe}_3)$ were obtained by slow evaporation of a concentrated benzene solution at room temperature. As depicted in Figure 4, the solid-state

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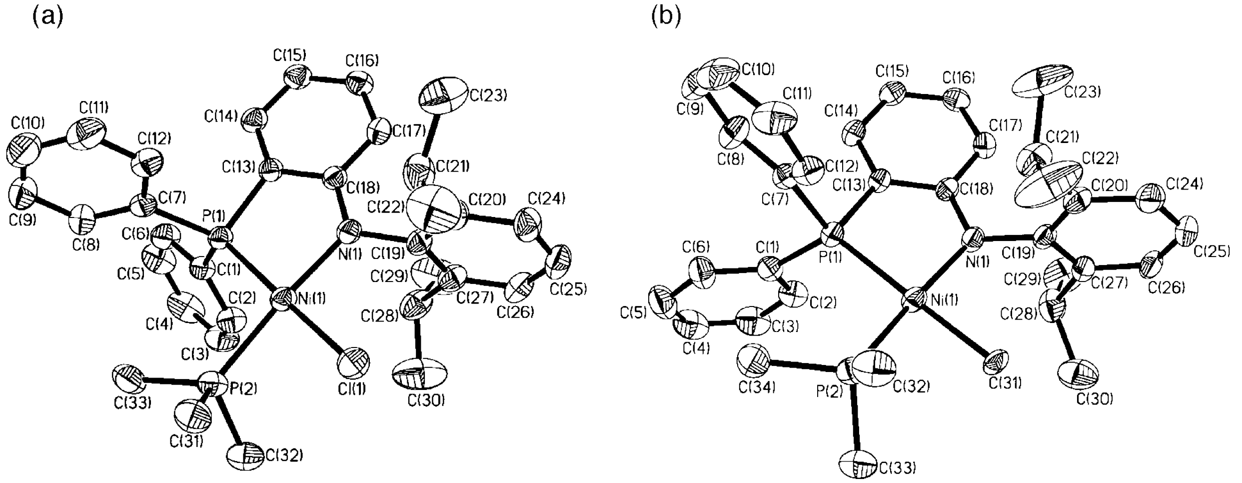

Figure 4. Molecular structures of (a) [^{i}Pr-NP]NiCl(PMe$_3$) and (b) the major isomer of [^{i}Pr-NP]NiMe(PMe$_3$) with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg) for [^{i}Pr-NP]NiCl(PMe$_3$): Ni(1)−N(1) 1.923(3), Ni(1)−P(1) 2.1556(10), Ni(1)−P(2) 2.1941(12), Ni(1)−Cl(1) 2.2006(11), N(1)−Ni(1)−P(1) 85.21(9), N(1)−Ni(1)−P(2) 175.17(10), P(1)−Ni(1)−P(2) 97.51(4), N(1)−Ni(1)−Cl(1) 93.54(9), P(1)−Ni(1)−Cl(1) 177.68(5), P(2)−Ni(1)−Cl(1) 83.88(5). Selected bond distances (Å) and angles (deg) for [^{i}Pr-NP]NiMe(PMe$_3$): Ni(1)−N(1) 1.939(3), Ni(1)−C(31) 2.035(4), Ni(1)−P(2) 2.1475(12), Ni(1)−P(1) 2.2009(12), N(1)−Ni(1)−C(31) 92.15(15), N(1)−Ni(1)−P(2) 173.48(11), C(31)−Ni(1)−P(2) 83.66(12), N(1)−Ni(1)−P(1) 85.02(10), C(31)−Ni(1)−P(1) 176.35(12), P(2)−Ni(1)−P(1) 99.36(5).

structures are consistent with the solution structures observed by NMR spectroscopy. The coordinated PMe$_3$ is cis to the phosphorus donor of the amido phosphine ligand with P−Ni−P angles of 97.51(4)° and 99.36(5)° for [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiMe(PMe$_3$), respectively. The nickel center in both [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiMe(PMe$_3$) lies perfectly on the square plane defined by the four donor atoms. The N(1)−Ni(1)−P(1) bonding angles of 85.21(9)° in [^{i}Pr-NP]NiCl(PMe$_3$) and 85.02(10)° in [^{i}Pr-NP]NiMe(PMe$_3$) are similar to those of the nickel derivatives featuring a five-membered metallacycle such as [(*o*-Ph$_2$PC$_6$H$_4$NHMe)NiCl(PMe$_3$)]PF$_6$ (87.0(1)°)[47] and the SHOP catalyst [Ph$_2$PCH=C(Ph)O]Ni(Ph)(PPh$_3$) (86.5°).[2] The Ni−N distances of ca. 1.93 Å for both molecules are slightly longer than those of nickel diarylamide complexes such as [Ni(NPh$_2$)$_2$]$_2$ (1.828 Å average for terminal amides)[48] and (BQA)NiCl (1.8586(14) Å, BQA = bis(8-quinolinyl)amide),[49] likely implying the significant steric demand of the amido phosphine ligand employed. As expected, the diisopropylphenyl ring is roughly perpendicular to the N−phenylene−P plane with dihedral angles of 93.8° for [^{i}Pr-NP]NiCl(PMe$_3$) and 93.3° for [^{i}Pr-NP]NiMe(PMe$_3$), thus providing steric protection for the axial faces of the nickel center.

In contrast to [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiMe(PMe$_3$), the phenyl complex [^{i}Pr-NP]NiPh(PMe$_3$) (Scheme 1) possesses the PMe$_3$ ligand exclusively trans to the phosphorus donor of the amido phosphine ligand. ^{31}P{^{1}H} NMR spectroscopy reveals a pair of doublet resonances with $^2J_{PP}$ of 288 Hz. It is interesting to note that the trans relationship for the two phosphorus donors found in [^{i}Pr-NP]NiPh(PMe$_3$) is reminiscent of that of the SHOP catalyst [Ph$_2$PCH=C(Ph)O]Ni(Ph)(PPh$_3$).[2] The C$_\alpha$ atom is observed as a doublet of doublets resonance at 152 ppm with coupling constants $^2J_{CP}$ of 39 and 34 Hz, values that are anticipated for an ipso carbon atom concomitantly experiencing two chemically inequivalent phosphorus donors in the cis positions. Similar to those observed for [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiMe(PMe$_3$), the isopropylmethyl groups in [^{i}Pr-NP]NiPh(PMe$_3$) appear as two doublet resonances in the ^{1}H NMR spectroscopy, again suggesting restricted rotation about the N−Ar bond due to significant steric crowding of these molecules.

Crystals of [^{i}Pr-NP]NiPh(PMe$_3$) suitable for X-ray analysis were grown by layering pentane on a concentrated diethyl ether solution at −35 °C. Figure 5 illustrates the molecular structure that is in accord with that determined by NMR spectroscopy. The Ni−N, Ni−P, and Ni−C distances and the N−Ni−P angle of the amido phosphine ligand in [^{i}Pr-NP]NiPh(PMe$_3$) are all comparable to the corresponding values found in [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiMe(PMe$_3$). Considerable deviation, however, is observed for the phenyl derivative. The P(2) and C(19) atoms are notably displaced from the N−phenylene−P plane by 0.3703 and 0.4093 Å, respectively (Figure 5b). The steric repulsion between the amido substituent and the PMe$_3$ ligand seems significant. As a result, the diisopropylphenyl ring is tilted from the ideal orthogonal orientation with respect to the *o*-phenylene plane (dihedral angle 77.5°). The P−Ni−P angle of 163.76(9)° is thus much smaller than the ideal value of 180°.

Synthesis and Characterization of Nickel η^3-Benzyl Complexes. Prior dissociation or abstraction of the coordinated PMe$_3$ is anticipated to be a prerequisite for [^{i}Pr-NP]NiX(PMe$_3$) (X = Me, Ph) if the catalytic oligomerization or polymerization of olefins is the goal. The preparation of compounds that do not require the coordination of external bases is thus intriguing. The synthesis of [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) was pursued from the reactions of either {[^{i}Pr-NP]NiCl}$_2$ or [^{i}Pr-NP]NiCl(PMe$_3$) with PhCH$_2$MgCl as shown in Scheme 1. Interestingly, the coordinated PMe$_3$ dissoci-

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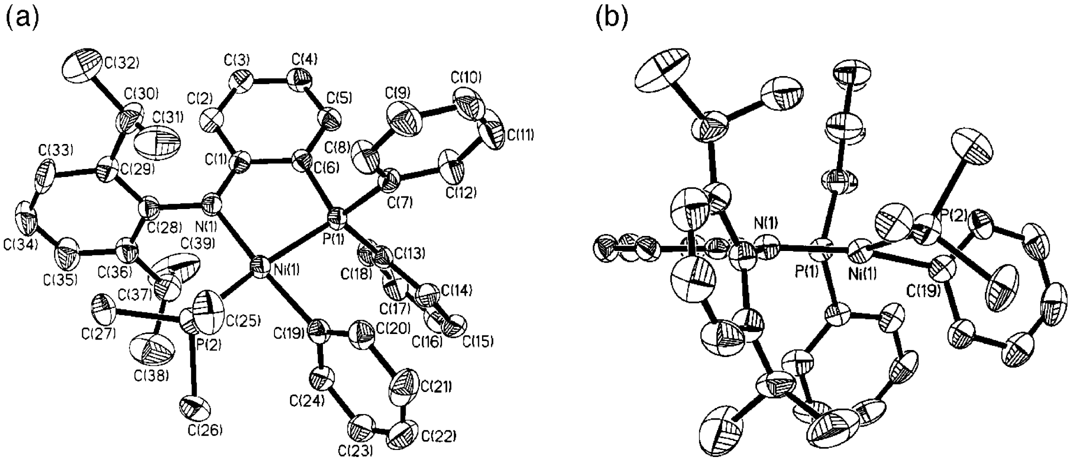
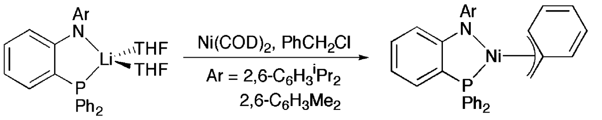


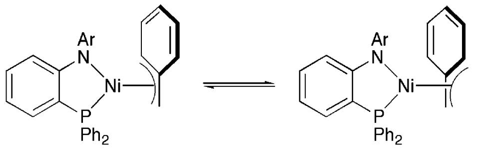
Figure 5. Two views of the molecular structure of [^{i}Pr-NP]NiPh(PMe$_3$) with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Ni(1)−C(19) 1.923(7), Ni(1)−N(1) 1.947(5), Ni(1)−P(1) 2.149(2), Ni(1)−P(2) 2.238(2), C(19)−Ni(1)−N(1) 167.6(3), C(19)−Ni(1)−P(1) 85.7(2), N(1)−Ni(1)−P(1) 85.94(17), C(19)−Ni(1)−P(2) 85.1(2), N(1)−Ni(1)−P(2) 105.14(17), P(1)−Ni(1)−P(2) 163.76(9).

ates from [^{i}Pr-NP]NiCl(PMe$_3$) upon the reaction with PhCH$_2$MgCl. Alternatively, this benzyl complex is accessible in high isolated yield from the reaction of Ni(COD)$_2$ with PhCH$_2$Cl in the presence of [^{i}Pr-NP]Li(THF)$_2$ (eq 4). This strategy takes advantage of facile oxidative addition of benzyl halides to zerovalent nickel[50] and avoids the prerequisite preparation of the chloride precursors, thereby providing a valuable entry to the sterically less bulky [Me-NP]$^-$ derivatives.



(4)

The solution structures of the benzyl complexes were characterized by multinuclear NMR spectroscopy. The phosphorus donor in [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph) is observed as a sharp singlet resonance at 36.24 and 34.84 ppm, respectively, in the ^{31}P{^{1}H} NMR spectroscopy. Both molecules exhibit a doublet resonance at ca. 1.56 ppm with $^3J_{HP}$ of 4 Hz for the benzylic hydrogen atoms in the ^{1}H NMR spectroscopy and a doublet at ca. 28 ppm with $^2J_{CP}$ of 9 Hz for the benzylic carbon in the ^{13}C{^{1}H} and DEPT ^{13}C NMR spectroscopy. These values are well comparable to those of nickel η^3-benzyl complexes supported by phosphine-derived ligands in which the phosphorus donor is cis to the benzylic methylene group.[4] The η^3 feature of the benzyl ligand[51] maintained in solution is unambiguously elucidated by $^1J_{CH}$ of ca. 152 Hz for the NiCH$_2$ moiety in [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph). The observed coupling constant is significantly larger than the expected $^1J_{CH}$ value of 122 Hz for a normal sp^3 carbon atom. The increased coupling constant parallels a decreased Ni−C$_\alpha$−Ph angle that leads to an increase in the amount of sp^2 character of the C$_\alpha$ atom.[52,53] A variable-temperature ^{1}H NMR study of [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) (42.6 mM in toluene-d_8) revealed that the two benzylic hydrogen atoms are equivalent at temperatures as low as −80 °C, suggesting a rapid suprafacial rearrangement of the benzyl ligand,[54,55] as illustrated in eq 5. The benzyl complexes are thermally stable, even at elevated temperatures. For instance, no decomposition was observed when [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) (24.4 mM in C$_6$D$_6$) was heated to 100 °C for >3 days, as evidenced by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.



(5)

Crystals of [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph) suitable for X-ray diffraction analysis were grown by slow evaporation of concentrated benzene solutions at room temperature. As depicted in Figure 6, the geometry of the nickel center in both molecules is best described as distorted square planar with the C$_\alpha$ atom being cis to the phosphorus donor of the amido phosphine ligand. The hapticity of the benzyl ligand is consistent with that suggested by the NMR spectroscopy. In particular, the acute Ni−C$_\alpha$−Ph angles of 73.6(3)° and 71.8(2)° for [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph), respectively, are markedly smaller than that expected for an sp^3 carbon atom, but well comparable to those found in η^3-benzyl complexes such as [(^{i}PrO)$_3$P]$_2$Rh(η^3-CH$_2$C$_6$Me$_5$) (75°),[55] [Ph$_2$PC$_6$H$_4$C(O-B(C$_6$F$_5$)$_3$)O-κ^2*P*,*O*]Ni(η^3-CH$_2$Ph) (73.6(3)°),[4] and {ArN=C(Me)C=NAr[O-B(C$_6$F$_5$)$_3$]-κ^2*N*,*N′*}Ni(η^3-CH$_2$Ph) (70.6(4)°, Ar = 2,6-C$_6$H$_3$^{i}Pr$_2$).[24] The Ni−C distances to the ipso and ortho carbon atoms are short, although in both

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(51) The ortho protons of the η^3-benzyl group tend to shift upfield at <6.8 ppm in the ^{1}H NMR spectroscopy; for instance, see ref 52. Such signals are observed for both [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph), but assignment of the ortho hydrogen atoms cannot be absolutely certain due to the aromatic signals arising from the amido phosphine ligands.

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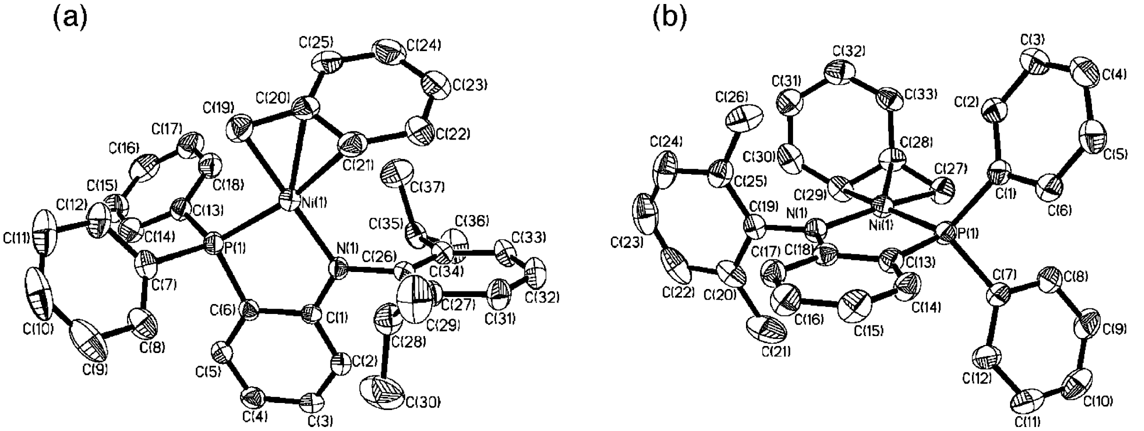

Figure 6. Molecular structures of (a) [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and (b) [Me-NP]Ni(η^3-CH$_2$Ph) with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg) for [^{i}Pr-NP]Ni(η^3-CH$_2$Ph): Ni(1)−(1) 1.908(4), Ni(1)−C(19) 1.973(6), Ni(1)−C(20) 2.088(6), Ni(1)−P(1) 2.1231(15), Ni(1)−C(21) 2.192(6), N(1)−Ni(1)−C(19) 173.3(3), N(1)−Ni(1)−C(20) 137.3(2), C(19)−Ni(1)−C(20) 41.3(2), N(1)−Ni(1)−P(1) 88.11(13), C(19)−Ni(1)−P(1) 94.92(19), C(20)−Ni(1)−P(1) 133.59(18), N(1)−Ni(1)−C(21) 104.4(2), C(19)−Ni(1)−C(21) 71.5(3), C(20)−Ni(1)−C(21) 38.1(2), P(1)−Ni(1)−C(21) 162.82(18), C(20)−C(19)−Ni(1) 73.6(3). Selected bond distances (Å) and angles (deg) for [Me-NP]Ni(η^3-CH$_2$Ph): Ni(1)−N(1) 1.900(3), Ni(1)−C(27) 1.973(4), Ni(1)−C(28) 2.039(4), Ni(1)−P(1) 2.1176(11), Ni(1)−C(29) 2.196(4), N(1)−Ni(1)−C(27) 172.51(18), N(1)−Ni(1)−C(28) 136.95(17), C(27)−Ni(1)−C(28) 41.39(19), N(1)−Ni(1)−P(1) 88.36(10), C(27)−Ni(1)−P(1) 95.64(15), C(28)−Ni(1)−P(1) 132.67(14), N(1)−Ni(1)−C(29) 103.25(15), C(27)−Ni(1)−C(29) 71.96(19), C(28)−Ni(1)−C(29) 39.12(17), P(1)−Ni(1)−C(29) 165.93(13), C(28)−C(27)−Ni(1) 71.8(2).

cases longer than that to C$_\alpha$. In accord with the small C$_\alpha$−Ni−C$_{\text{ortho}}$ angles, the N−Ni−P angles of 88.11(13)° for [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and 88.36(10)° for [Me-NP]Ni(η^3-CH$_2$Ph) are slightly wider than those found in [^{i}Pr-NP]NiCl(PMe$_3$), [^{i}Pr-NP]NiMe(PMe$_3$), and [^{i}Pr-NP]NiPh(PMe$_3$).

Conclusions

We have prepared and characterized a series of divalent nickel complexes containing bidentate diarylamido phosphine ligands. The synthetic strategies are versatile, particularly for the diisopropylphenyl derivatives. The exclusive formation of one of the two possible geometric isomers for [^{i}Pr-NP]NiCl(PMe$_3$) and [^{i}Pr-NP]NiPh(PMe$_3$) is unique, which is in contrast to the result obtained for [^{i}Pr-NP]NiMe(PMe$_3$). The benzylic methylene groups in [^{i}Pr-NP]Ni(η^3-CH$_2$Ph) and [Me-NP]Ni(η^3-CH$_2$Ph) are exclusively cis to the phosphorus donor of the amido phosphine ligands. The solution structures of these molecules determined by multinuclear NMR spectroscopy are all in good agreement with the solid-state structures by X-ray crystallography. Of particular interest is the geometric analogy of [^{i}Pr-NP]NiPh(PMe$_3$) to the SHOP catalysts[2] in which the two phosphorus donors are mutually trans. Chemistry involving the catalytic activities of these new molecules will be the subject of further reports.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J) and peak widths at half-height ($\Delta\nu_{1/2}$) are in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C$_6$D$_6$ and δ 2.09 for toluene-d_8 (the most upfield resonance). ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C$_6$D$_6$. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P and ^{7}Li NMR spectra are referenced externally using 85% H$_3$PO$_4$ at δ 0 and LiCl in D$_2$O at δ 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

Materials. Compounds *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H[^{i}Pr-NP]),[38] *N*-(2-diphenylphosphinophenyl)-2,6-dimethylaniline (H[Me-NP]),[39] and [^{i}Pr-NP]Li(THF)$_2$[38] were prepared according to the procedures reported previously. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Table 1 summarizes the crystallographic data for all structurally characterized compounds. Data for compounds H[^{i}Pr-NP] and [Me-NP]Li(THF)$_2$ were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using SHELXTL. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Data for compounds [^{i}Pr-NP]NiCl(PMe$_3$), [^{i}Pr-NP]NiMe(PMe$_3$), [^{i}Pr-NP]NiPh(PMe$_3$), [^{i}Pr-NP]Ni(η^3-CH$_2$Ph), and [Me-NP]Ni(η^3-CH$_2$Ph) were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using the maXus or WinGX crystallographic software package. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions.

Synthesis of [Me-NP]Li(THF)$_2$. To a solution of H[Me-NP] (2.0 g, 5.24 mmol) in THF (15 mL) at −35 °C was added n-BuLi (3.3 mL, 5.24 mmol, 1 equiv). The reaction mixture was naturally warmed to room temperature and stirred for 3 h. All volatiles were removed in vacuo. The red viscous residue was triturated with pentane (15 mL) to yield a yellow solid. The yellow solid was isolated from the orange solution, washed with pentane (5 mL × 3), and dried in vacuo; yield 2.67 g (99%). Recrystallization of the yellow solid from a concentrated diethyl ether solution at −35 °C gave yellow crystals suitable for X-ray crystallography. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.58 (m, 4, Ar), 7.23 (d, 2, Ar), 7.07−7.16 (m, 8, Ar), 6.97 (m, 1, Ar), 6.38 (m, 1, Ar), 6.33 (m, 1, Ar), 3.23 (m, 8, $\mathrm{OC}H_2\mathrm{CH}_2$), 2.26 (s, 6, CH_3), 1.19 (m, 8, $\mathrm{OCH_2C}H_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ −13.66 (br s, $\Delta\nu_{1/2} = 75$ Hz). ^{31}P{^{1}H} NMR (toluene-d_8, 202 MHz): δ −12.96. ^{31}P{^{1}H} NMR (toluene-d_8, −20 °C, 202 MHz): δ −12.72 (1:1:1:1 q, $^1J_{\mathrm{LiP}} = 34$ Hz). ^{7}Li{^{1}H} NMR (C_6D_6, 194 MHz): δ 1.37 (br s, $\Delta\nu_{1/2} = 21$ Hz). ^{7}Li{^{1}H} NMR (toluene-d_8, 194 MHz): δ 2.08. ^{7}Li{^{1}H} NMR (toluene-d_8, −20 °C, 194 MHz): δ 2.12 (d, $^1J_{\mathrm{LiP}} = 34$ Hz). ^{13}C NMR (C_6D_6, 125.5 MHz): δ 163.88 ($J_{\mathrm{CP}} = 21.63$, *C*P), 154.81, 138.20 (PC*C*N), 135.69 (CH), 134.38 ($J_{\mathrm{CP}} = 16.25$, CH), 134.06, 132.74 (CH), 129.00 (CH), 128.88 ($J_{\mathrm{CP}} = 6.63$, CH), 128.68 (CH), 120.65 (CH), 114.00 ($J_{\mathrm{CP}} = 3.75$ Hz), 113.01 (CH), 110.47 (CH), 68.70 ($\mathrm{O}C\mathrm{H_2CH_2}$), 25.61 ($\mathrm{OCH_2}C\mathrm{H_2}$), 19.73 ($CH_3$).

Synthesis of {[^{i}Pr-NP]NiCl}$_2$. Method 1: Solid $\mathrm{NiCl_2}$(DME) (400 mg, 1.818 mmol) was suspended in THF (60 mL) and cooled to −35 °C. To this was added dropwise a solution of [^{i}Pr-NP]Li(THF)$_2$ (1.0672 g, 1.818 mmol) in THF (20 mL) at −35 °C. Upon addition, the reaction mixture became red in color and the suspended $\mathrm{NiCl_2}$(DME) dissolved. The solution was stirred at room temperature overnight. All volatiles were removed in vacuo. The resulting viscous, reddish-brown residue was dissolved in $\mathrm{CH_2Cl_2}$ (15 mL) and passed through a pad of Celite, which was further washed with $\mathrm{CH_2Cl_2}$ (2 mL) until the washings were colorless. The filtrate was evaporated in vacuo to dryness to give the product as a deep red solid, which was gently washed with diethyl ether (3 mL × 2) and dried in vacuo; yield 780.6 mg (81%). Method 2: Solid $\mathrm{NiCl_2}$(DME) (100 mg, 0.454 mmol) was suspended in THF (15 mL) at room temperature. To this was added a THF solution (5 mL) of H[^{i}Pr-NP] (198.9 mg, 0.454 mmol). The reaction mixture was stirred at room temperature for 30 min, and $\mathrm{NEt_3}$ (0.095 mL, 0.681 mmol, 1.5 equiv) was added. After being stirred for 1 h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was triturated with pentane (2 mL × 2). The product was extracted with $\mathrm{CH_2Cl_2}$ (10 mL) and filtered through a pad of Celite. Solvent was removed in vacuo to afford the crude product as a brick-red solid. The product was purified by dissolving the solid in a minimal amount of THF (ca. 1 mL) followed by addition of pentane (3 mL) to induce the precipitation of a red solid. The red solid was isolated by decantation of the solution, washed with pentane, and dried in vacuo; yield 150 mg (62%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.75 (m, 4, Ar), 7.09 (m, 3, Ar), 7.00−7.04 (m, 6, Ar), 6.79 (m, 1, Ar), 6.64 (t, 1, Ar), 6.09 (t, 1, Ar), 5.85 (d, 1, Ar), 3.94 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.51 (d, 6, $\mathrm{CH}Me_2$), 1.11 (d, 6, $\mathrm{CH}Me_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 32.45 (br s, $\Delta\nu_{1/2} = 80$ Hz). ^{31}P{^{1}H} NMR (THF, 121.4 MHz): δ 33.06 (br s). ^{13}C NMR (C_6D_6, 125.5 MHz): δ 167.63, 147.92, 145.77, 133.88 (CH), 133.64 (CH), 132.81 (CH), 131.27 (CH), 129.92 ($J_{\mathrm{CP}} = 44.80$), 129.26 (CH), 125.93 (CH), 124.12 (CH), 116.71 (CH), 114.05 (CH), 117.5 ($J_{\mathrm{CP}} = 37.65$). Anal. Calcd for $(\mathrm{C_{30}H_{31}ClNNiP})_2$: C, 67.90; H, 5.89; N, 2.64. Found: C, 68.12; H, 6.44; N, 2.51.

Synthesis of [^{i}Pr-NP]NiCl(PMe$_3$). $\mathrm{PMe_3}$ (0.38 mL, 1.0 M in THF, Aldrich, 0.38 mmol, 1 equiv per nickel) was added to a red solution of {[^{i}Pr-NP]NiCl}$_2$ (200 mg, 0.19 mmol) in THF (8 mL) at room temperature. The solution became green in color over the course of 30 min. After being stirred at room temperature overnight, the solution was evaporated to dryness under reduced pressure. The product was isolated as a green solid, which was spectroscopically pure by ^{31}P{^{1}H} NMR spectroscopy; yield 186.8 mg (81.6%). Emerald cubic crystals of [^{i}Pr-NP]NiCl(PMe$_3$) suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated THF solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.81 (m, 4, Ar), 7.34 (m, 3, Ar), 7.03 (m, 2, Ar), 6.99 (m, 4, Ar), 6.79 (t, 1, Ar), 6.71 (m, 1, Ar), 6.21 (t, 1, Ar), 6.08 (m, 1, Ar), 3.94 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.65 (d, 6, $\mathrm{CH}Me_2$), 1.20 (d, 6, $\mathrm{CH}Me_2$), 0.74 (d, 9, $^2J_{\mathrm{HP}} = 9.5$, PMe$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 47.29 (d, $^2J_{\mathrm{PP}} = 88$ Hz), −16.98 (d, $^2J_{\mathrm{PP}} = 88$ Hz). ^{31}P{^{1}H} NMR (THF, 121.4 MHz): δ 46.89 (d, $^2J_{\mathrm{PP}} = 88$ Hz), −15.75 (d, $^2J_{\mathrm{PP}} = 88$ Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 146.47, 134.24, 134.12, 134.05, 131.91, 131.44, 129.37, 129.20, 125.60, 124.09, 116.20,113.66, 29.14 ($C\mathrm{HMe_2}$), 25.27 ($\mathrm{CH}Me_2$), 24.97 ($\mathrm{CH}Me_2$), 16.08 (dd, $^1J_{\mathrm{CP}} = 30.92$, $^3J_{\mathrm{CP}} = 9.17$, PMe$_3$). Anal. Calcd for $\mathrm{C_{33}H_{40}ClNNiP_2}$: C, 65.32; H, 6.64; N, 2.31. Found: C, 64.72; H, 6.71; N, 2.35.

Synthesis of [^{i}Pr-NP]NiMe(PMe$_3$). Solid [^{i}Pr-NP]NiCl(PMe$_3$) (56.7 mg, 0.094 mmol) was dissolved in THF (3 mL) and cooled to −35 °C. To this was added MeMgCl (0.03 mL, 3 M in THF, Aldrich, 0.094 mmol) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. An aliquot was taken and examined by ^{31}P{^{1}H} NMR spectroscopy, which indicated complete consumption of [^{i}Pr-NP]NiCl(PMe$_3$) and exhibited two pairs of doublet resonances with the relative intensities of ca. 9:1 ($^2J_{\mathrm{PP}} = 30$ Hz for major and $^2J_{\mathrm{PP}} = 302$ Hz for minor). All volatiles were removed in vacuo. The red residue thus obtained was triturated with pentane (2 mL × 2), extracted with benzene (6 mL), and filtered through a pad of Celite. The Celite pad was further washed with benzene (1 mL × 2) until the washings became colorless. Solvent was removed in vacuo to give the product as a ruby solid. Crystals suitable for X-ray crystallography were grown by slow evaporation of a concentrated benzene solution at room temperature; yield 43.6 mg (79%). The ^{1}H and ^{31}P{^{1}H} NMR spectra of the X-ray quality crystals indicated the presence of two geometric isomers in a ratio of ca. 3:1 with the major corresponding to a cis relationship between the two phosphorus donors. Spectroscopic data for the major isomer: ^{1}H NMR (C_6D_6, 500 MHz): δ 7.78 (m, 4, Ar), 7.40 (m, 3, Ar), 7.08 (m, 2, Ar), 7.05 (m, 4, Ar), 6.92 (dt, 1, Ar), 6.87 (dt, 1, Ar), 6.28 (t, 1, Ar), 6.12 (dd, 1, Ar), 3.90 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.46 (d, 6, $\mathrm{CH}Me_2$), 1.24 (d, 6, $\mathrm{CH}Me_2$), 0.70 (d, 9, $^2J_{\mathrm{HP}} = 9$ Hz, PMe$_3$), −0.12 (dd, 3, $^3J_{\mathrm{HP}}{}^{\mathrm{NP}} = 4.0$ Hz, $^3J_{\mathrm{HP}}{}^{\mathrm{PMe3}} = 7.5$ Hz, NiMe). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 35.60 (d, $^2J_{\mathrm{PP}} = 25.49$ Hz, NP), −7.46 (d, $^2J_{\mathrm{PP}} = 25.49$ Hz, PMe$_3$). ^{31}P{^{1}H} NMR (THF, 80.953 MHz): δ 35.25 (d, $^2J_{\mathrm{PP}} = 29.95$ Hz, NP), −6.26 (d, $^2J_{\mathrm{PP}} = 29.95$ Hz, PMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.678 MHz):[56] δ 28.55 (s, $C\mathrm{HMe_2}$), 25.62 (s, $\mathrm{CH}Me_2$), 24.65 (s, $\mathrm{CH}Me_2$), 17.03 (dd, $^1J_{\mathrm{CP}} = 30$ Hz, $^3J_{\mathrm{CP}} = 5$ Hz, PMe$_3$), 11.13 (dd, $^2J_{\mathrm{CP}}{}^{\mathrm{PMe3}} = 38.84$ Hz, $^2J_{\mathrm{CP}}{}^{\mathrm{NP}} = 58.69$ Hz, NiMe). Spectroscopic data for the minor isomer: ^{1}H NMR (C_6D_6, 500 MHz):[56] δ 3.84 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.30 (d, 6, $\mathrm{CH}Me_2$), 1.18 (d, 6, $\mathrm{CH}Me_2$), 0.55 (dd, 9, $^2J_{\mathrm{HP}} = 7$ Hz, $^4J_{\mathrm{HP}} = 1$ Hz, PMe$_3$), −0.42 (dd, 3, $^3J_{\mathrm{HP}}{}^{\mathrm{NP}} = 12$ Hz, $^3J_{\mathrm{HP}}{}^{\mathrm{PMe3}} = 7.5$ Hz, NiMe). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 38.95 (d, $^2J_{\mathrm{PP}} = 301.04$ Hz, NP), −17.96 (d, $^2J_{\mathrm{PP}} = 301.04$ Hz, PMe$_3$). ^{31}P{^{1}H} NMR (THF, 80.953 MHz): δ 38.66 (d, $^2J_{\mathrm{PP}} = 302.3$ Hz, NP), −17.10 (d, $^2J_{\mathrm{PP}} = 302.3$ Hz, PMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.678 MHz):[56] δ 28.85 (s, $C\mathrm{HMe_2}$), 24.96 (s, $\mathrm{CH}Me_2$), 24.21 (s, $\mathrm{CH}Me_2$), 13.45 (d, $^1J_{\mathrm{CP}} = 23$ Hz, PMe$_3$), NiMe not found. Anal. Calcd for $\mathrm{C_{34}H_{43}NNiP_2}$: C, 69.65; H, 7.39; N, 2.39. Found: C, 69.32; H, 7.35; N, 2.37.

Synthesis of [^{i}Pr-NP]NiPh(PMe$_3$). Solid [^{i}Pr-NP]NiCl(PMe$_3$) (110 mg, 0.181 mmol) was dissolved in THF (6 mL) and cooled to −35 °C. To this was added PhMgCl (0.09 mL, 2.05 M in THF, Strem, 0.181 mmol) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. All volatiles were removed in vacuo. The red solid residue was extracted with benzene (3 mL) and filtered through a pad of Celite, which was further washed with benzene (1 mL × 2) until the washings became colorless. Solvent was removed in vacuo to give the product as a brownish red solid; yield 100.8 mg (86%). Crystals suitable for X-ray analysis were grown by layering pentane on a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.65 (m, 4, Ar), 7.46 (m, 1, Ar), 7.22 (m, 6, Ar), 7.04

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(56) The complete assignment was hampered by the complicated aromatic signals, primarily due to the relatively small intensities of the minor isomer. Only aliphatic signals are reported.

(m, 6, Ar), 6.87 (td, 1, Ar), 6.65 (t, 2, Ar), 6.24 (t, 1, Ar), 5.99 (dd, 1, Ar), 4.11 (septet, 2, C*H*Me$_2$), 1.44 (d, 6, CH*Me*$_2$), 1.25 (d, 6, CH*Me*$_2$), 0.38 (d, 9, $^2J_{HP} = 8$, PMe$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 33.00 (d, $^2J_{PP} = 288$, NP), -22.32 (d, $^2J_{PP} = 288$, PMe$_3$). ^{31}P{^{1}H} NMR (THF, 121.42 MHz): δ 33.16 (d, $^2J_{PP} = 286$, NP), -21.24 (d, $^2J_{PP} = 293$, PMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.679 MHz): δ 168.56 (d, $J_{CP} = 33.68$), 151.90 (dd, $^2J_{CP} = 39.1$, $^2J_{CP} = 33.7$, NiC), 147.99, 145.89, 139.00 (CH), 134.7 (CH), 133.72 (CH), 133.18 (CH), 132.98 (d, $J_{CP} = 50.90$), 130.19 (CH), 128.67 (CH), 128.20 (CH), 126.73 (CH), 124.95 (CH), 121.97 (CH), 115.14 (d, $J_{CP} = 44.62$), 114.53 (d, $J_{CP} = 12.69$, CH), 112.54 (d, $J_{CP} = 7.29$, CH), 29.13 (*C*HMe$_2$), 25.04 (CH*Me*$_2$), 24.31 (CH*Me*$_2$), 13.45 (d, $^1J_{CP} = 23.6$, PMe$_3$).

Synthesis of [^{i}Pr-NP]Ni(η^3-CH$_2$Ph). Method 1: Solid {[^{i}Pr-NP]NiCl}$_2$ (500 mg, 0.47 mmol) was dissolved in THF (5 mL) and cooled to −35 °C. To this was added dropwise a solution of $PhCH_2MgCl$ (0.94 mL, 1.0 M Et_2O solution, Aldrich, 0.94 mmol, 1 equiv per nickel). The reaction mixture was stirred at room temperature overnight and evaporated to dryness. The resulting residue was dissolved in CH_2Cl_2 (5 mL) and filtered through a pad of Celite. All volatiles were removed in vacuo to give a brownish red solid; yield 519 mg (94%). Method 2: Solid [^{i}Pr-NP]NiCl(PMe$_3$) (76.6 mg, 0.126 mmol) was dissolved in THF (2 mL) and cooled to −35 °C. To this was added dropwise a solution of $PhCH_2MgCl$ (0.13 mL, 1.0 M Et_2O solution, Aldrich, 0.13 mmol). The reaction mixture was stirred at room temperature overnight and evaporated to dryness under reduced pressure. The resulting residue was dissolved in benzene (5 mL) and filterd through a pad of Celite. All volatiles were removed in vacuo to give a brownish red solid; yield 63.8 mg (86%). Method 3: A solid mixture of [^{i}Pr-NP]-Li(THF)$_2$ (200 mg, 0.341 mmol) and Ni(COD)$_2$ (93.72 mg, 0.341 mmol) was dissolved in THF (6 mL) at room temperature. To this was added a toluene solution of $PhCH_2Cl$ (3.41 mL, 0.1 M, 0.341 mmol) at room temperature. After being stirred at room temperature for 3 h, the reaction mixture was evaporated to dryness under reduced pressure. The reddish brown solid residue was extracted with benzene (6 mL) and filtered through a pad of Celite. Solvent was removed in vacuo to afford the product as a brownish red solid; yield 178.5 mg (89%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.67 (m, 4, Ar), 7.22 (m, 3, Ar), 7.06 (m, 7, Ar), 6.85 (t, 1, Ar), 6.66 (t, 1, Ar), 6.57 (t, 2, Ar), 6.24 (t, 1, Ar), 6.14 (d, 2, Ar), 6.04 (t, 1, Ar), 3.46 (septet, 2, C*H*Me$_2$), 1.56 (d, 2, $^3J_{HP} = 4$, NiC*H*$_2$Ph), 1.12 (d, 12, CH*Me*$_2$). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.64 (m, 4, Ar), 7.14 (m, 4, Ar), 7.07 (m, 4, Ar), 7.00 (m, 2, Ar), 6.80 (t, 1, Ar), 6.63 (m, 1, Ar), 6.55 (t, 2, Ar), 6.18 (t, 1, Ar), 6.11 (d, 2, Ar), 5.96 (t, 1, Ar), 3.41 (septet, 2, $J = 7.5$, C*H*Me$_2$), 1.52 (d, 2, $^3J_{HP} = 3.5$, NiCH$_2$), 1.12 (d, 6, $J = 7.5$, CH*Me*$_2$), 1.09 (d, 6, $J = 7.5$, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 36.24. ^{31}P{^{1}H} NMR (THF, 121.4 MHz): δ 36.27. ^{13}C NMR (C_6D_6, 125.5 MHz): δ 168.11, 150.87, 145.36, 134.58 (CH), 134.35, 134.12, 133.30 (CH), 133.21 (CH), 130.62 (CH), 129.24 ($J_{CP} = 9.91$, CH), 126.82 (CH), 124.42 (CH), 123.97 (CH), 117.45, 114.82 (CH), 114.73 (CH), 112.42 ($J_{CP} = 7.28$, CH), 110.28 ($J_{CP} = 5.52$, CH), 28.71 (*C*HMe$_2$), 28.53 ($^2J_{CP} = 9.04$, $^1J_{CH} = 152$, Ni*C*H$_2$Ph), 24.26 (CH*Me*$_2$). Anal. Calcd for $C_{37}H_{38}NNiP$: C, 75.79; H, 6.53; N, 2.39. Found: C, 75.76; H, 6.75; N, 2.33.

Synthesis of [Me-NP]Ni(η^3-CH$_2$Ph). Diethyl ether (6 mL) was added to a solid mixture of [Me-NP]Li(THF)$_2$ (200 mg, 0.38 mmol) and Ni(COD)$_2$ (103.5 mg, 0.38 mmol). To this suspension was added $PhCH_2Cl$ (3.8 mL, 0.1 M stock solution in diethyl ether, 0.38 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 h. All volatiles were removed in vacuo. The product was extracted from the resulting solid residue with benzene (3 mL × 2). The deep brown solution was filtered through a pad of Celite, which was further washed with benzene (2 mL) until the washings were colorless. The combined filtrate was evaporated to dryness in vacuo to afford the product as a red solid; yield 188.2 mg (100%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.76−7.80 (m, 4, Ar), 7.23 (d, 2, Ar), 7.12−7.20 (m, 7, Ar), 7.07 (t, 1, Ar), 6.92 (m, 1, Ar), 6.65 (m, 1, Ar), 6.56 (t, 2, Ar), 6.32 (t, 1, Ar), 6.10 (dd, 1, Ar), 6.06 (d, 2, Ar), 2.17 (s, 6, CH$_3$), 1.55 (d, 2, $^3J_{HP} = 4$, NiC*H*$_2$Ph). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ 34.84. ^{13}C NMR (C_6D_6, 125.5 MHz): δ 166.67 ($J_{CP} = 26.13$), 151.91, 135.73, 134.63 ($J_{CP} = 50.5$), 134.06 (CH), 133.93 (CH), 133.49 (CH), 133.20 ($J_{CP} = 11.75$, CH), 130.57 ($J_{CP} = 2.75$, CH), 129.31 ($J_{CP} = 10.75$, CH), 128.68 (CH), 127.11 ($J_{CP} = 2.63$, CH), 123.42 (CH), 116.00, 114.69 ($J_{CP} = 50.5$), 112.50 ($J_{CP} = 26.13$, CH), 112.48 ($J_{CP} = 8.13$, CH), 110.60 ($J_{CP} = 6.25$, CH), 28.24 ($^2J_{CP} = 9.13$, $^1J_{CH} = 154$, Ni*C*H$_2$Ph), 18.92 ($^1J_{CH} = 122$, CH$_3$). Anal. Calcd for $C_{33}H_{30}NNiP$: C, 74.75; H, 5.70; N, 2.64. Found: C, 73.73; H, 5.87; N, 2.63.

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Supporting Information Available: X-ray crystallographic data in CIF format for H[^{i}Pr-NP], [Me-NP]Li(THF)$_2$, [^{i}Pr-NP]NiCl(PMe$_3$), [^{i}Pr-NP]NiMe(PMe$_3$), [^{i}Pr-NP]NiPh(PMe$_3$), [^{i}Pr-NP]Ni(η^3-CH$_2$Ph), and [Me-NP]Ni(η^3-CH$_2$Ph). This material is available free of charge via the Internet at http://pubs.acs.org.

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