Phosphorus and Olefin Substituent Effects on the Insertion Chemistry of Nickel(II) Hydride Complexes Containing Amido Diphosphine Ligands

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A series of nickel(II) hydride complexes supported by amido diphosphine ligands, including symmetrical $[N(o\text{-}C_6H_4PR_2)_2]^-$ ([R-PNP]$^-$; R = Ph, ^{i}Pr, Cy) and unsymmetrical $[N(o\text{-}C_6H_4PPh_2)(o\text{-}C_6H_4P^iPr_2)]^-$ ([Ph-PNP-^{i}Pr]$^-$), have been prepared for the investigation of olefin insertion chemistry. The unsymmetrical ligand precursor H[Ph-PNP-^{i}Pr] (**1d**) that features different substituents (phenyl and isopropyl) at the two phosphorus donors was prepared in 53% yield as colorless crystals. Treatment of $Ni(COD)_2$ (COD = cycloocta-1,5-diene) with H[R-PNP] (R = Ph (**1a**), ^{i}Pr (**1b**), Cy (**1c**)) or **1d** produced the corresponding four-coordinate nickel hydride complexes **2a**−**d**. Attempts to isolate **2a** led instead to the cyclooct-4-en-1-yl complex [Ph-PNP]Ni(η^1-C_8H_{13}) (**3a**) as a consequence of COD insertion into the Ni−H bond of **2a**. The reactions of **2a**,**d** with ethylene, 1-hexene, and norbornene, respectively, generated cleanly the corresponding ethyl (**4a**,**d**), *n*-hexyl (**5a**,**d**), and 2-norbornyl (**6a**,**d**) complexes. The quantitative formation of **5a**,**d** is indicative of exclusive 1,2-insertion of 1-hexene. In contrast, styrene inserts into the Ni−H bond of **2d** in an exclusively 2,1-manner to afford [Ph-PNP-^{i}Pr]NiCH(Me)Ph (**7d**) quantitatively. The selective 2,1-insertion products [Ph-PNP]NiCH(Me)CO_2Me (**8a**), [^{i}Pr-PNP]NiCH(Me)CO_2Me (**8b**), [Cy-PNP]NiCH(Me)CO_2Me (**8c**), and [Ph-PNP-^{i}Pr]NiCH(Me)CO_2Me (**8d**) were also isolated from the reactions of methyl acrylate with the corresponding nickel hydride complexes **2a**−**d**. The effects of the phosphorus and olefin substituents on the reactivity and regioselectivity of the olefin insertion reactions are discussed. In addition to solution NMR spectroscopic data for all new compounds, X-ray structures of **1d**, **2b**−**d**, **3a**, and **5d**−**7d** are reported.

Introduction

Olefin insertion and β-hydrogen elimination are mutually microscopic reverse; the former represents a valuable C−H or C−C bond forming method for higher alkyl homologue preparation, whereas the latter epitomizes perhaps the most common decomposition pathway for metal alkyl complexes to produce metal hydride derivatives.[1,2] Both processes are particularly relevant to transition-metal-catalyzed olefin polymerization, in that olefin insertion into a metal−hydrogen bond is an essential (re)initiation step while β-hydrogen elimination from a metal alkyl species is a major termination process.[3–35] Isomerization of a propagating alkyl chain in catalytic olefin polymerization is often composed of metal-mediated β-elimination followed by olefin reinsertion.[36–43] The effective control

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of exclusive 1,2- or 2,1-regioselectivity of α-olefin insertion is crucial for the production of transient propagating species with a virtually identical metal-based core structure and thus the resulting poly-α-olefins with well-defined microstructures.[4,6,36,44–52] It has been shown that the regiospecificity of olefin insertion has a dramatic impact on polymer molecular weights,[53] indicating that the reactivity and stability of propagating species derived from 1,2-olefin insertion are different from those of 2,1 -insertion.[54] Such regiospecificity also plays an important role in transition-metal-catalyzed olefin hydroformylation.[55,56]

We are currently exploring reaction chemistry with amido phosphine complexes.[57–64] In particular, a series of nickel(II) alkyl complexes of $[N(o\text{-}C_6H_4PR_2)_2]^-$ ([R-PNP]$^-$; R = Ph, ^{i}Pr, Cy) have been demonstrated to be markedly stable even at elevated temperatures.[65,66] Of particular note is the stability of those containing β-hydrogen atoms. For instance, [Ph-PNP]NiEt, [^{i}Pr-PNP]Ni(*n*-Bu), and [Cy-PNP]Ni(*n*-Bu) do not decompose at all after prolonged heating at 80 °C. Though not uncommon in early-transition-metal chemistry, β-hydrogen-containing alkyl complexes of late transition metals that resist β-elimination at high temperatures are extremely rare. Understanding the decisive factors that control β-hydrogen elimination and olefin insertion is of current interest.[67–71] We thus became interested in examining its microscopic reverse to better understand the inherent nature of this unusual property. To this end, we have set out to prepare a series of nickel hydride complexes supported by these amido diphosphine ligands and study their insertion chemistry with a number of olefins. The interesting unsymmetrical amido diphosphine ligand $[N(o\text{-}C_6H_4PPh_2)(o\text{-}C_6H_4P^iPr_2)]^-$ ([Ph-PNP-^{i}Pr]$^-$), which carries different hydrocarbon substituents at the two phosphorus donors, was designed and employed in this study. The electronic and steric properties of this unsymmetrically substituted ligand are anticipated to lie somewhere in between those of the symmetrical [Ph-PNP]$^-$ and [^{i}Pr-PNP]$^-$, as are those of the corresponding metal derivatives. In this contribution, we describe the reactivity of nickel hydride complexes containing [R-PNP]$^-$ (R = Ph, ^{i}Pr, Cy) or [Ph-PNP-^{i}Pr]$^-$ with olefins featuring divergent electronic and steric characteristics. The effects of the substituents at the phosphorus donors in these tridentate amido diphosphine ligands and those at olefinic substrates on insertion reactivity and regioselectivity are discussed.

Results and Discussion

Following the synthetic protocol established for the symmetrically substituted H[R-PNP] (R = Ph (**1a**), ^{i}Pr (**1b**), Cy (**1c**)),[65,72] the unsymmetrical H[Ph-PNP-^{i}Pr] (**1d**) was prepared successfully as colorless crystals in 53% yield (Scheme 1). This one-pot reaction is essentially clean, as evidenced by the $^{31}P\{^1H\}$ NMR spectrum of a reaction aliquot. The presumed $Li[N(o\text{-}C_6H_4Br)(o\text{-}C_6H_4P^iPr_2)](OEt_2)_x$ intermediate can be observed quantitatively by $^{31}P\{^1H\}$ NMR spectroscopy at −5.34 ppm. The addition sequence of the two chlorodihydrocarbylphosphines is vital, in view of the quantitative formation of **1d**. The reverse addition sequence involving the reaction of chlorodiphenylphosphine prior to chlorodiisopropylphosphine led to a mixture that contains **1a**[65,66] and **1d**, a result that is likely reflective of the electrophilic nature of chlorodiphenylphosphine being higher than that of chlorodiisopropylphosphine. Compound **1d** has been fully characterized by ^1H, ^{13}C,

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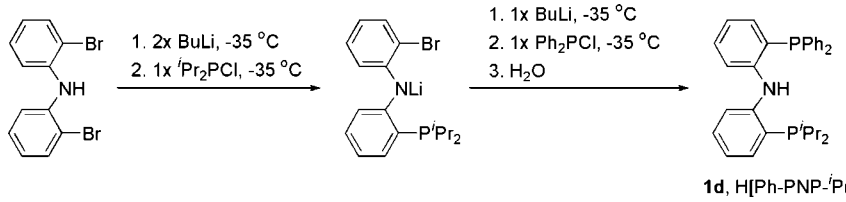
Scheme 1



1d, H[Ph-PNP-^{i}Pr]

and ^{31}P NMR spectroscopy, elemental analysis, and X-ray crystallography. The amino proton is observed as a characteristic doublet of doublets resonance at 7.99 ppm in the ^{1}H NMR spectrum. ^{31}P{^{1}H} NMR spectroscopy reveals two signals at −16.66 and −14.79 ppm for the diphenyl- and the diisopropyl-substituted phosphorus atom, respectively. Interestingly, these ^{31}P chemical shifts are comparable to those found for symmetrically substituted **1a** (−18.62 ppm)[65,66] and **1b** (−13.31 ppm),[65] respectively. Figure 1 depicts the X-ray structure of **1d**. Crystallographic data are summarized in Table 1.

The oxidative addition reactions of Ni(COD)$_2$ (COD = cycloocta-1,5-diene) with **1a**−**d** in benzene at room temperature produced cleanly the corresponding nickel(II) hydride complexes **2a**−**d** (Scheme 2). Nickel hydride complexes supported by a tolyl-derived amido diphosphine ligand have also been prepared similarly.[73] Though it was generated quantitatively, as evidenced by the ^{1}H and ^{31}P{^{1}H} NMR spectra, complex **2a** was not isolable under the conditions employed. This compound, however, can be prepared in situ and used directly for subsequent reactions (vide infra). In contrast, complexes **2b**−**d** were all isolated as crystalline solids. Complexes **2a**−**c** display solution C_{2v} symmetry on the NMR time scale, while **2d** is C_s-symmetric. The nickel-bound hydride ligand in **2a**−**c** appears as a characteristic triplet resonance at ca. −18 ppm with a $^{2}J_{HP}$ value of ca. 63 Hz in the ^{1}H NMR spectra, whereas that in **2d** exhibits a doublet of doublets resonance at −18 ppm with a $^{2}J_{HP^{Ph_2}}$ value of 58 Hz and a $^{2}J_{HP^{i}Pr_2}$ value of 68 Hz. The two distinct $^{2}J_{HP}$ coupling constants for the hydride ligand in **2d** were determined by selective undecoupling of NiH in the ^{31}P{^{1}H} NMR spectra, which revealed two doublet of doublets resonances for the two chemically inequivalent phosphorus donors. The phosphorus atoms in **2a** appear as a singlet resonance in the ^{31}P{^{1}H} NMR spectrum at 33 ppm, a value that is significantly shifted upfield as compared to those of **2b** (56 ppm)[74] and **2c** (47 ppm).[74] The ^{31}P{^{1}H} NMR spectrum of **2d** displays two doublet resonances at 31 ppm for PPh$_2$ and 59 ppm for P^{i}Pr$_2$, values that are very similar to those of symmetrically substituted **2a**,**b**,[74] respectively. The large $^{2}J_{PP}$ value of 244 Hz found for **2d** is indicative of a trans orientation for the two phosphorus donors, suggesting that the tridentate [Ph-PNP-^{i}Pr]$^{-}$ ligand adopts a meridional coordination mode. The ^{13}C{^{1}H} NMR spectra of **2b**,**c** exhibit virtual triplet resonances for the *o*-phenylene carbon atoms,[74] indicating a square-planar geometry for these molecules. On the basis of the solution NMR studies, the structure of **2a** is likely analogous to those of **2b**−**d**.

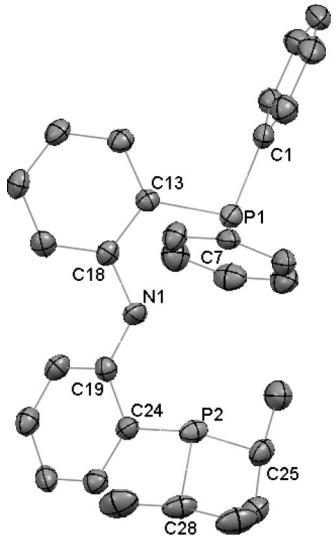


Figure 1. Molecular structure of H[Ph-PNP-^{i}Pr] (**1d**) with thermal ellipsoids drawn at the 35% probability level.

Single crystals of **2b**−**d** suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. As depicted in Figures 2–4, the amido diphosphine ligands all adopt a meridional coordination mode in these nickel hydride species, consistent with the solution structures determined by multinuclear NMR spectroscopy. Selected bond distances and angles are summarized in Tables 2 and 3, respectively. The core structures of **2b**−**d** closely resemble each other, although each has different substituents at the phosphorus donors. In particular, the two Ni−P lengths in **2d** are virtually identical, in spite of bearing different substituents at the two phosphorus donors. These results are likely ascribable to the small size of the hydride ligand. The Ni−N distance of 1.920(3) Å found in **2b** is slightly shorter than that of [^{i}Pr-PNP]NiMe (1.945(3) Å)[65] but slightly longer than that of [^{i}Pr-PNP]NiCl (1.903(2) Å),[65] indicating the trans influence order of Cl < H < Me for these formally anionic ligands. Interestingly, the P−Ni−P angle of 175.05(4)° in **2b** is notably wider than those of [^{i}Pr-PNP]NiCl (168.81(2)°)[65] and [^{i}Pr-PNP]NiMe (166.68(5)°),[65] consistent with the steric repulsion arising from the relatively larger chloride and methyl ligands in the latter complexes. The Ni−P distances in **2b** (2.1373 Å average) are thus slightly shorter than those of [^{i}Pr-PNP]NiCl (2.18985 Å average)[65] and [^{i}Pr-PNP]NiMe (2.1677 Å average).[65] Similar phenomena are also found for **2c** and [Cy-PNP]NiMe.[65] Though **2a** was not crystallographically characterized, its core structure is presumably similar to those of **2b**−**d** on the basis of little deviation observed for the X-ray structures of **2b**−**d**.

Though **2a** could be generated quantitatively from the reaction of Ni(COD)$_2$ with **1a**, attempts to isolate **2a** from the reaction mixture led instead to the cyclooct-4-en-1-yl complex [Ph-PNP]Ni(η^{1}-C$_8$H$_{13}$) (**3a**) in 83% yield as a consequence of COD insertion into the reactive Ni−H bond. Prolonged stirring of the reaction mixture containing the in situ prepared **2a** and liberated COD gave quantitative formation of **3a**, as evidenced by ^{1}H and ^{31}P{^{1}H} NMR spectra. In contrast, no reaction was observed for **2b**−**d**, even in the presence of an excess amount of COD at 25−80 °C. Such a discrepancy in reactivity between **2a** and **2b**−**d** with respect to the COD insertion highlights

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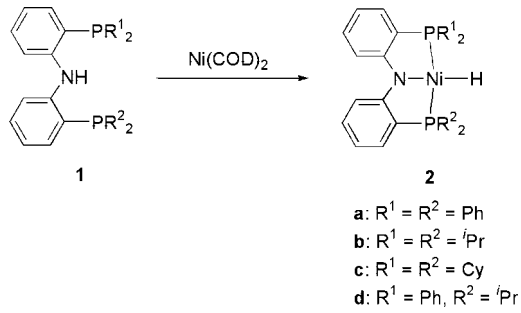
Table 1. Crystallographic Data for 1d, 2b−d, 3a, and 5d−7d

	H[Ph-PNP-^{i}Pr] (**1d**)	[^{i}Pr-PNP]NiH (**2b**)	[Cy-PNP]NiH (**2c**)	[Ph-PNP-^{i}Pr]NiH (**2d**)	{[Ph-PNP]Ni(η^1-C_8H_{13})}(OEt_2) (**3a**)	[Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (**5d**)	{[Ph-PNP-^{i}Pr]Ni (2-norbornyl)}(C_6H_6) (**6d**)	[Ph-PNP-^{i}Pr]NiCH(Me)Ph (**7d**)
formula	$C_{30}H_{33}NP_2$	$C_{24}H_{37}NNiP_2$	$C_{36}H_{53}NNiP_2$	$C_{30}H_{33}NNiP_2$	$C_{48}H_5NNiOP_2$	$C_{36}H_{45}NNiP_2$	$C_{43}H_{49}NNiP_2$	$C_{38}H_{41}NNiP_2$
fw	469.51	460.20	620.44	528.22	778.55	612.38	700.48	632.37
cryst size (mm^3)	018 × 0.17 × 0.05	0.18 × 0.16 × 0.05	0.38 × 0.28 × 0.2	0.3 × 0.2 × 0.07	0.22 × 0.14 × 0.06	0.34 × 0.22 × 0.1	0.29 × 0.2 × 0.12	0.12 × 0.08 × 0.02
D_{calcd} (Mg/m^3)	1.199	1.251	1.074	1.284	1.287	1.249	1.241	1.270
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*
a (Å)	8.4309(3)	9.0510(2)	14.2470(4)	17.9220(3)	10.8520(2)	11.0619(5)	11.1581(2)	10.827(5)
b (Å)	12.8265(5)	16.5150(4)	16.2118(4)	8.0810(5)	12.9860(2)	16.1684(6)	13.0512(3)	16.740(9)
c (Å)	13.2757(6)	16.5300(5)	18.4856(6)	20.6200(7)	15.9410(4)	19.5852(9)	13.3333(3)	36.49(2)
α (deg)	71.000(2)	90	104.5360(10)	90.000(2)	108.9730(10)	111.560(2)	78.4300(10)	90
β (deg)	74.009(2)	98.4750(10)	99.2740(10)	113.8420(10)	95.6310(10)	90.008(2)	81.9720(10)	90
γ (deg)	89.143(2)	90	106.409(2)	90.0000(10)	105.1710(10)	91.929(2)	83.1350(10)	90
V ($Å^3$)	1300.46(9)	2443.88(11)	3838.80(19)	2731.5(2)	2008.65(7)	3255.6(2)	1875.19(7)	6614(6)
Z	2	4	4	4	2	4	2	8
T (K)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	296(2)
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73	Mo Kα (0.710 73	Mo Kα (0.710 73	Mo Kα (0.710 73)
2θ range (deg)	5.04 < 2θ < 51.02	4.86 < 2θ < 50.02	4.14 < 2θ < 50.16	4.32 < 2θ < 50.68	4.36 < 2θ < 50.06	4.10 < 2θ < 50.72	4.56 < 2θ < 50.62	4.86 < 2θ < 50.04
index ranges (*h*; *k*; *l*)	−10 to +10; −15 to +15; −15 to +15	−10 to +10; −19 to +19; −15 to +19	−16 to +16; −19 to +19; −21 to +21	−21 to +21; −9 to +9; −24 to +24	−12 to +12; −15 to +15; −18 to +18	−13 to +13; −19 to +19; −23 to +23	−13 to +13; −15 to +15; −16, to +16	−12 to +10; −19 to +19; −43 to +43
total no. of rflns	17 920	18 757	46 192	30 896	27 482	39 207	28 493	42 157
no. of indep rflns	4745	4296	13 428	4983	7045	11810	6831	5823
R_{int}	0.1302	0.0762	0.1104	0.0735	0.0656	0.1288	0.0638	0.1312
abs coeff (mm^{-1})	0.185	0.934	0.610	0.846	0.600	0.719	0.633	0.710
no. of data/restraints/params	4745/0/299	4296/0/253	13 428/0/722	4983/0/308	7045/0/478	11 810/0/737	6831/0/445	5823/0/379
goodness of fit	1.008	1.053	0.850	1.120	1.083	1.109	1.138	0.959
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0737	R1 = 0.0427	R1 = 0.0814	R1 = 0.0415	R1 = 0.0526	R1 = 0.1013	R1 = 0.0502	R1 = 0.0790
	wR2 = 0.1704	wR2 = 0.0842	wR2 = 0.2152	wR2 = 0.0960	wR2 = 0.1245	wR2 = 0.2229	wR2 = 0.1267	wR2 = 0.1269
R indices (all data)	R1 = 0.1535	R1 = 0.0734	R1 = 0.1305	R1 = 0.0626	R1 = 0.0813	R1 = 0.1909	R1 = 0.0720	R1 = 0.3177
	wR2 = 0.2377	wR2 = 0.1039	wR2 = 0.2467	wR2 = 0.1119	wR2 = 0.1452	wR2 = 0.2833	wR2 = 0.1538	wR2 = 0.1995
residual density ($e/Å^3$)	−0.498 to 0.443	0.479 to 0.320	−0.711 to 1.966	−0.491 to 0.466	−0.455 to 0.455	−1.237 to 0.704	−0.623 to 0.666	−0.417 to 0.345

Scheme 2



particularly the phosphorus substituent effect on the electrophilicity and steric accessibility of the divalent nickel center in these molecules. With the phenyl-substituted phosphorus donors, the nickel center in **2a** is more electrophilic and sterically more accessible than those in **2b**−**d**, leading to facile COD coordination to the former and thus the subsequent insertion reaction to produce **3a**. It should be noted that phosphine dissociation from the nickel center is rather unlikely in view of the markedly thermal stability of nickel alkyl complexes of [Ph-PNP]$^-$,[65,66] particularly for those containing β-hydrogen atoms. Association of COD from the axial faces of square-planar **2a** is thus more possible.[4,42,75,76] For **2b**−**d**, the eight-membered COD ring is perhaps too bulky to access the nickel center in these sterically more demanding molecules. Complex **3a** was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and

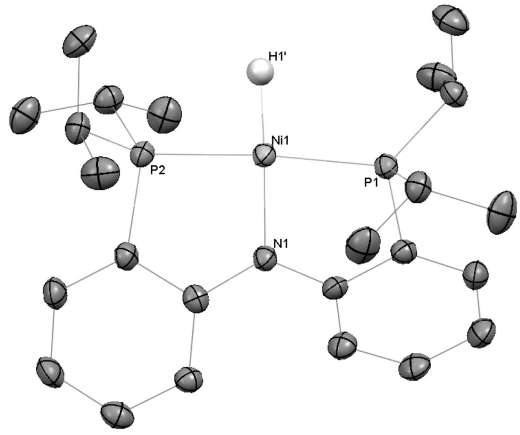


Figure 2. Molecular structure of [^{i}Pr-PNP]NiH (**2b**) with thermal ellipsoids drawn at the 35% probability level.

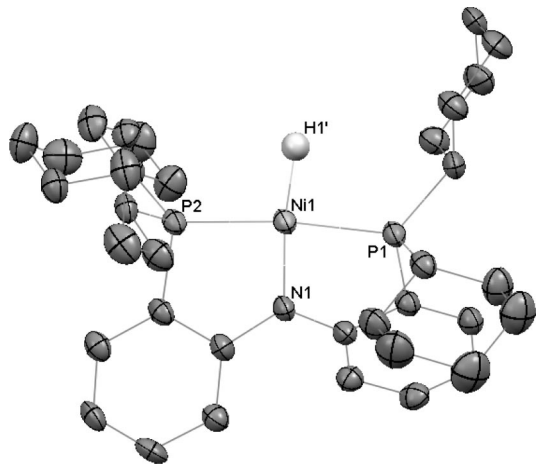


Figure 3. Molecular structure of [Cy-PNP]NiH (**2c**) with thermal ellipsoids drawn at the 35% probability level.

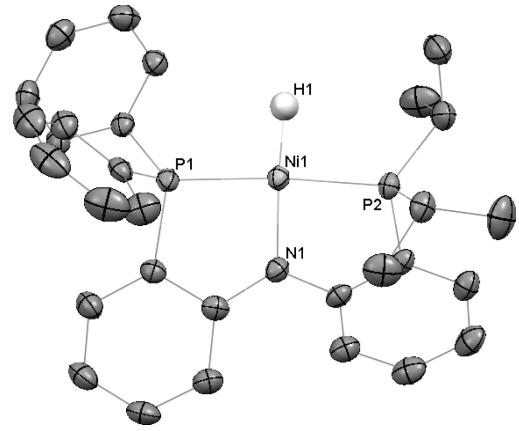


Figure 4. Molecular structure of [Ph-PNP-^{i}Pr]NiH (**2d**) with thermal ellipsoids drawn at the 35% probability level.

Table 2. Selected Bond Distances (Å) for 2b−d, 3a, and 5d−7d

compd	Ni−N	Ni−X[a]	Ni−P
[^{i}Pr-PNP]NiH (**2b**)	1.920(3)		2.137(1), 2.138(1)
[Cy-PNP]NiH (**2c**)[b]	1.918(4)		2.140(1), 2.139(1)
[Ph-PNP-^{i}Pr]NiH (**2**)	1.924(2)		2.1214(7), 2.1235(8)
[Ph-PNP]Ni(5-cyclooctenyl) (**3**)	1.965(3)	1.973(3)	2.136(1), 2.195(1)
[Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (**5d**)[b]	1.961(6)	1.979(7)	2.154(2), 2.198(2)
[Ph-PNP-^{i}Pr]Ni(2-norbornyl) (**6d**)	1.975(2)	1.974(3)	2.1942(8), 2.2006(8)
[Ph-PNP-^{i}Pr]NiCH(Me)Ph (**7d**)	1.949(7)	1.997(9)	2.188(3), 2.196(3)

[a] X represents a hydrogen or an α-carbon atom. [b] The data summarized represent one of the two independent molecules found in the asymmetric unit cell.

X-ray crystallography. Similar to previously reported nickel alkyl complexes of [Ph-PNP]$^-$,[65,66] **3a** displays solution C_{2v} symmetry on the NMR time scale. The phosphorus donors are observed as a singlet resonance at 24.27 ppm in the ^{31}P{^{1}H} NMR spectrum. The cyclooct-4-en-1-yl ligand exhibits a characteristic signal at 5.33 ppm for olefinic protons in the ^{1}H NMR spectrum, consistent with this unsaturated cyclohydrocarbon being bound to nickel in an η^1 rather than an η^3 fashion.[77] The *o*-phenylene carbon atoms are observed as virtual triplet resonances in the ^{13}C{^{1}H} NMR spectrum, consistent with a square-planar geometry for this molecule.

Orange crystals of **3a** suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. The solid-state structure of **3a** is depicted in Figure 5. Unexpectedly, the coordination geometry deviates severely from the ideal square plane by 0.4085 Å. In sharp contrast to those found for square-planar group 10 complexes of [Ph-PNP]$^-$,[65,66,78,79] the dihedral angle of 31.0° between the two N−Ni−P planes in **3a** is notably large and the P(1)−Ni(1)−P(2) angle of 147.37(4)° and the N(1)−Ni(1)−C(37) angle of 163.1(1)° are relatively small. The nickel center is displaced from the mean coordination plane by 0.1220 Å. Both β-methylene groups are tilted toward P(2), leading to Ni(1)−P(2) (2.195(1) Å) being longer than Ni(1)−P(1) (2.136(1) Å) and the N(1)−Ni(1)−P(2) angle (82.76(9)°) being sharper than N(1)−Ni(1)−P(1) (86.78(9)°). The deviation of the core structure of **3a** from the ideally square

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Table 3. Selected Bond Angles (deg) for 2b−d, 3a, and 5d−7d

compd	N−Ni−P	P−Ni−P	P−Ni−X[a]	N−Ni−X[a]
Pr-PNP]NiH (**2b**)	87.44(8), 87.65(9)	175.05(4)		
[Cy-PNP]NiH (2c)[b]	87.2(1), 87.9(1)	172.78(6)		
[Ph-PNP-Pr]NiH (**2d**)	88.41(7), 88.09(7)	174.15(3)		
[Ph-PNP]Ni(5-cyclooctenyl) (**3a**)	86.78(9), 82.76(9)	147.37(4)	95.4(1), 103.5(1)	163.1(1)
[Ph-PNP-Pr]Ni(*n*-hexyl) (**5d**)[b]	84.1(2), 83.5(2)	165.65(9)	93.8(2), 98.9(2)	176.7(3)
[Ph-PNP-Pr]Ni(2-norbornyl) (**6d**)	83.90(7), 83.13(7)	165.08(3)	100.17(9), 92.84(9)	176.7(1)
[Ph-PNP-Pr]NiCH(Me)Ph (**7d**)	82.3(2), 85.1(2)	162.8(1)	99.1(3), 94.6(3)	174.6(4)

[a] X represents a hydrogen or an α-carbon atom. [b] The data summarized represent one of the two independent molecules found in the asymmetric unit cell.

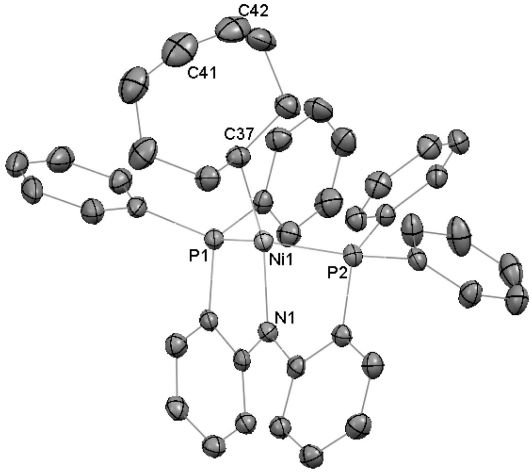

Figure 5. Molecular structure of [Ph-PNP]Ni(η^1-C_8H_{13}) (**3a**) with thermal ellipsoids drawn at the 35% probability level.

planar geometry is thus ascribable to significant steric congestion arising from the cyclooct-4-en-1-yl ligand and the phosphorus-bound phenyl groups. This phenomenon is somewhat consistent with the result that no reaction was found for COD with **2b−d**, as the amido diphosphine ligands in the latter molecules are sterically more demanding than that in **2a**. The C(41)−C(42) distance of 1.304(7) Å in **3a** is characteristic of a C=C double-bond length. The small torsion angle of 2.41° found for C−C(41)−C(42)−C is consistent with C(41) and C(42) atoms having sp^2 hybridization. It is interesting to note that **3a** is resistant to β-hydrogen elimination, in spite of its severely distorted square planar geometry. On the basis of microscopic reverse between β-elimination and olefin insertion, the highly reactive **2a** must be much higher in energy than β-hydrogen-containing alkyl complexes such as **3a**. This result is apparently phenomenal, as nickel hydride species are usually thermally more stable than their alkyl counterparts that bear β-hydrogen atoms.

The in situ prepared **2a** also reacts with other olefins such as ethylene, 1-hexene, and norbornene to generate [Ph-PNP]NiEt (**4a**), [Ph-PNP]Ni(*n*-hexyl) (**5a**), and [Ph-PNP]Ni(2-norbornyl) (**6a**), respectively (Scheme 3). In general, these reactions proceed at room temperature cleanly to produce quantitatively the olefin insertion products. Similar reactions were also found for **2d**, from which [Ph-PNP-^{i}Pr]NiEt (**4d**), [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (**5d**), and [Ph-PNP-^{i}Pr]Ni(2-norbornyl) (**6d**) were isolated upon treating with appropriate olefins. In contrast, no reaction was found for **2b**,**c** under similar conditions or even at elevated temperatures. The lack of ethylene insertion reactivity was also found for a palladium hydride complex supported by a similar amido phosphine ligand.[80] The electrophilicity of the nickel center induced by the phosphorus substituents in **2a−d** likely plays an important role in differentiating the insertion reactivity of these olefins, particularly for those with small sizes such as ethylene. Collectively, the reactivity of **2d** clearly lies in between those of **2a** and **2b**. Consistent with the insertion reactivity, complexes **4−6** are all thermally stable, even at elevated temperatures.

With their unsymmetrically substituted amido diphosphine ligands, complexes **4d−6d** display lower solution symmetry than **4a−6a** on the NMR time scale. Unlike the data for the C_{2v}-symmetric **4a** and **5a**, the solution NMR spectroscopic data of **4d** and **5d** are consistent with C_s symmetry for these molecules. For instance, the ^{1}H NMR spectrum of **4d** reveals one signal at 2.16 ppm for the isopropylmethine moieties and two doublet of doublets resonances at 1.29 and 1.08 ppm for the isopropylmethyl groups. The NiCH_2 moiety in **4d** is observed as two signals at 1.42 and 0.96 ppm, indicating a diastereotopic nature for these α-hydrogen atoms. The chemical nonequivalence of these α-hydrogen atoms is ascribable to the lack of symmetry with respect to the internal rotation involving the α-methylene group.[81] Figure 6 depicts a Newman projection of [Ph-PNP-^{i}Pr]NiCH$_2$R (R = Me (**4d**), *n*-pentyl (**5d**)), which features the most stable rotamer of these compounds from a steric viewpoint. Rapid rotation of the alkyl ligand in **4d** and **5d** about the Ni−C bonds should be responsible for the observed solution symmetry.[82] With the stereoactive 2-norbornyl group in **6a**,**d**, the symmetry of these molecules is lower than that of the corresponding **2−5**, as evidenced by their NMR spectroscopic data. Reminiscent of what has been observed for **2d**, the phosphorus donors in **4d−6d** are observed as two doublet resonances with $^2J_{PP}$ values of ca. 270 Hz in the ^{31}P{^{1}H} NMR spectra, consistent with a trans orientation for the two phosphorus donors in these molecules. The regiospecificity of 1-hexene insertion to produce *n*-hexyl complexes **5a** and **5d** is exclusive, as evidenced by the DEPT ^{13}C NMR spectra of these molecules. These results indicate selective 1,2- rather than 2,1-insertion of 1-hexene into the Ni−H bond of **2a** and **2d**.

Single crystals of **5d** and **6d** suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature. Figures 7 and 8 depict the molecular structures of these compounds. The coordination geometry of **5d** and **6d** is best described as square planar. The bond distances and angles are all similar to those of nickel(II) hydrocarbyl complexes of symmetrically substituted [R-PNP]$^-$ (R = Ph, ^{i}Pr, Cy),[65] except for **3a** (vide supra). Consistent with the solution NMR data, **5d** is an *n*-hexyl derivative. In **6d**, the [Ph-PNP-^{i}Pr]Ni fragment occupies one of the exo rather than endo positions in the 2-norbornyl ligand, consistent with what is anticipated from a steric viewpoint. The norbornyl ligand is oriented such that the one-carbon bridge is tilted toward the

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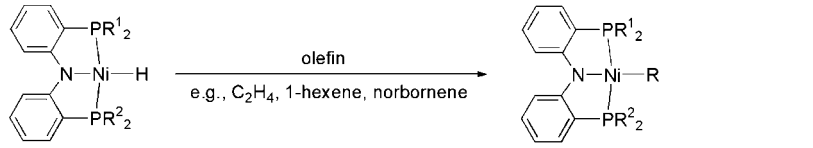
Scheme 3



2

R = Et (**4**), *n*-hexyl (**5**), 2-norbornyl (**6**)
a: $R^1 = R^2 = Ph$
d: $R^1 = Ph$, $R^2 = {}^iPr$

phosphorus donor that contains phenyl instead of isopropyl substituents, so as to minimize the intramolecular steric repulsion. Unlike that of **3a**, the core structure of **6d** deviates only negligibly by 0.0728 Å from the ideal square plane, although both molecules contain a secondary cycloalkyl ligand and the

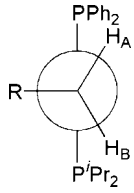


Figure 6. Newman projection of [Ph-PNP-^{i}Pr]NiCH$_2$R (R = Me (**4d**), *n*-pentyl (**5d**)) along the Ni−C$_\alpha$ bond.

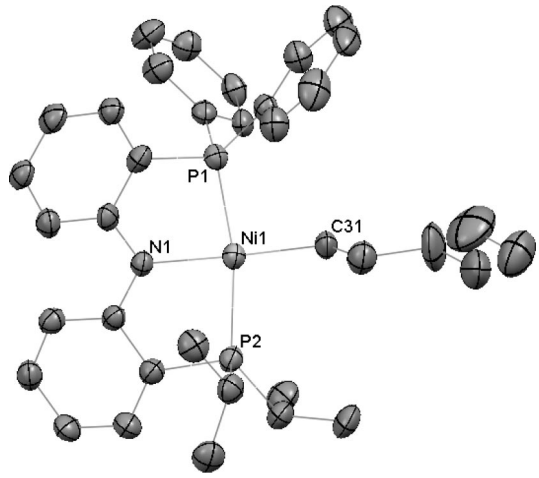


Figure 7. Molecular structure of [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (**5d**) with thermal ellipsoids drawn at the 35% probability level.

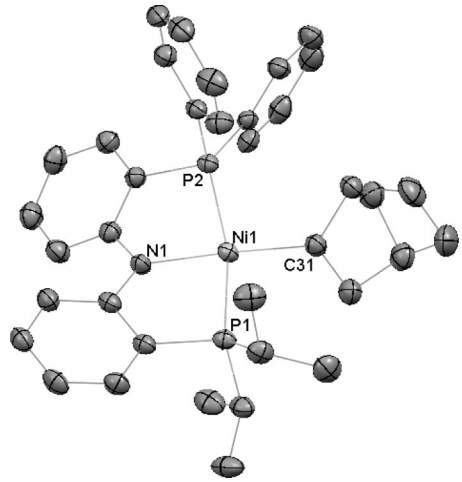
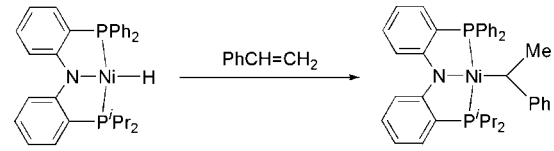


Figure 8. Molecular structure of [Ph-PNP-^{i}Pr]Ni(2-norbornyl) (**6d**) with thermal ellipsoids drawn at the 35% probability level.

Scheme 4



2d **7d**

Ni−C distances are virtually identical (Table 2). It is likely that the steric repulsion arising from the β-CH$_2$ moieties in **3a** is significantly larger than that in **6d**, as evidenced by the Ni−C$_\alpha$−C$_\beta$ bond angles of 94.7(2) and 119.4(3)° for the former, whereas they are 111.2(2) and 123.6(2)° for the latter.

In contrast to the selective 1,2-insertion found for 1-hexene, styrene inserts into the Ni−H bond of **2d** in an exclusively 2,1-manner to afford [Ph-PNP-^{i}Pr]NiCH(Me)Ph (**7d**) (Scheme 4). Such regiospecificity of styrene insertion is reminiscent of what has been reported for $[(\eta^5\text{-}C_5H_4\text{-}CMe_3)_2ZrH_2]_2$,[67] $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$,[83] and $[Y(L)(\mu\text{-}H)]_2$ (L = $(C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2)^{2-}$)[18] but is in contrast with that of $Cp^*_2ZrH_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[67] $Cp^*\{(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}ZrH_2$,[67] and $\{(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrH_2$ (exclusively 1,2-insertion).[67] The DEPT ^{13}C NMR spectrum shows the characteristic α-methine and β-methyl groups. No methylene signal was observed. Consistently, the α-proton appears in the ^{1}H NMR spectra at 3.30 ppm with an intensity corresponding to one hydrogen atom. As a result, the solution symmetry of **7d** is C_1. Similar to the case for other complexes derived from [Ph-PNP-^{i}Pr]$^-$, the phosphorus donors in **7d** are observed as two doublet resonances in the ^{31}P{^{1}H} NMR spectrum. A similar reaction involving the in situ prepared **2a** led to a mixture of **3a** and the presumed styrene insertion product (**7a**; δ_P 23.4 ppm). Attempts to selectively isolate **7a**, however, were not successful. The identity of its regiospecificity was thus indeterminate. No reaction was found for **2b**,**c** under similar or forcing conditions (80 °C).

Red crystals of **7d** suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. As depicted in Figure 9, **7d** is a four-coordinate species containing an α-methylbenzyl ligand, consistent with the result derived from the solution NMR studies. The coordination geometry, and bond distances and angles for the core structure of **7d** are all similar to those of **5d** and **6d**. Consistent with the steric standpoint, both methyl and phenyl substituents at the α-carbon atom in **7d** are tilted toward the phosphorus donor bearing phenyl rather than isopropyl groups.

Though **2b**,**c** do not react with electronically neutral olefins (vide supra), treatment of these nickel hydride complexes with electronically activated olefins such as methyl acrylate afforded quantitatively the corresponding insertion products [^{i}Pr-PNP]NiCH(Me)CO$_2$Me (**8b**) and [Cy-PNP]NiCH(Me)CO$_2$Me

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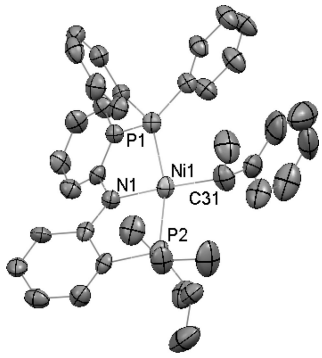
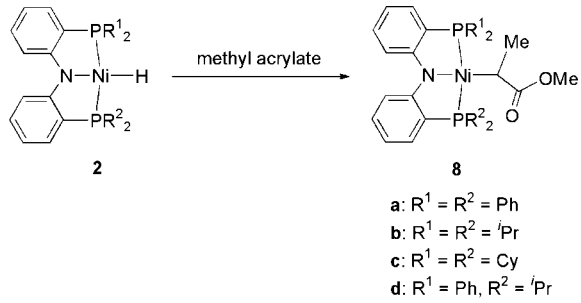


Figure 9. Molecular structure of [Ph-PNP-^{i}Pr]NiCH(Me)Ph (**7d**) with thermal ellipsoids drawn at the 35% probability level.

Scheme 5



(**8c**) (Scheme 5). A similar reaction employing **2d** produced [Ph-PNP-^{i}Pr]NiCH(Me)CO_2Me (**8d**) cleanly. Reminiscent of that with styrene, the reaction of the in situ prepared **2a** with methyl acrylate gave a mixture of **3a** and [Ph-PNP]NiCH(Me)CO_2Me (**8a**). Recrystallization of the reaction mixture from a diethyl ether solution at −35 °C, however, selectively afforded **8a** as a red crystalline solid in 71% yield. Similar to that of **7d**, the DEPT ^{13}C NMR spectra of **8a**−**d** reveal a characteristic methine rather than methylene signal for the nickel-bound carbon atom in these molecules ($^2J_{CP}$ = ca. 18 Hz), indicating an exclusive 2,1-insertion product for these reactions. The α-proton is observed in the ^{1}H NMR spectra of **8a**−**d** at ca. 2.4 ppm with intensity corresponding to one hydrogen atom. Complexes **8a**−**d** are thus chiral and the two phosphorus donors in these molecules are chemically inequivalent. Notably, two isopropylmethine signals are observed for **8b** (Figure S1, Supporting Information). This result is intriguing, particularly for compounds derived from symmetrically substituted [R-PNP]$^-$. It is interesting to note that the generation of a chiral center at the α-carbon atom by olefin insertion is relevant to stereoregular polymerization via a chain-end control mechanism.[84] The ^{31}P{^{1}H} NMR spectrum of **8b** at room temperature reveals two broad singlet resonances with equal intensity at 33.4 ppm ($\Delta\nu_{1/2}$ = 638 Hz) and 31.4 ppm ($\Delta\nu_{1/2}$ = 657 Hz). A variable-temperature ^{31}P{^{1}H}NMR study of **8b** (in toluene-d_8) indicated that the two broad signals coalesce at 310 K and become sharper to give a singlet resonance at temperatures higher than 330 K. When the temperature is lowered to 280 K, the two broad signals resolve to give two doublet resonances with a $^2J_{PP}$ value of 253 Hz, a value that is comparable to those of unsymmetrically substituted [Ph-PNP-^{i}Pr]$^-$ derivatives such as **4d** ($^2J_{PP}$ = 271 Hz), **5d** ($^2J_{PP}$ = 273 Hz), **6d** ($^2J_{PP}$ = 258 Hz), **7d** ($^2J_{PP}$ = 259 Hz), and **8d** ($^2J_{PP}$ = 268 Hz). The large coupling constant found between the two phosphorus atoms in **8b** is indicative of a trans orientation for these donors. These results are consistent with a hindered rotation of the nickel-bound, asymmetric −CH(Me)CO_2Me group about the Ni−C bond. Similar phenomena were also found for **8a**,**c**. Consistent with the insertion reactivity, **8a**−**d** are all thermally stable and resistant to β-elimination even at elevated temperatures (80 °C, 3 days).

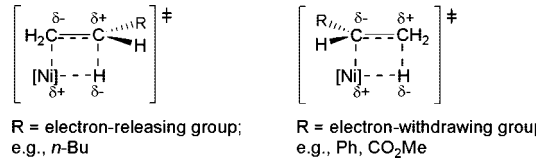


Figure 10. Proposed four-membered cyclic transition states which contain electron-releasing (left) or electron-withdrawing (right) substituents.

It is interesting to note that **2a** is most reactive toward olefin insertion among the nickel hydride species investigated. The reaction times in all cases are short, as compared to those of the corresponding reactions involving **2b**−**d**. The electronic and steric properties of **2a** derived from the phenyl-substituted amido diphosphine ligand are thus comparatively superior in this regard. The reactivity of **2b**,**c** with methyl acrylate is in sharp contrast to that with electronically neutral olefins (vide supra). The regioselectivity of methyl acrylate (in reactions with **2a**,**d**) and styrene (in a reaction with **2d**) also is in contrast with that of 1-hexene (in reactions with **2a**,**d**) under similar conditions. These results highlight the olefin substituent effect. The reactivity discrepancy between methyl acrylate and electronically neutral olefins such as ethylene with respect to **2b**,**c** underscores the significance of the enhanced back-π-acceptor nature of the former, which encourages coordination to the nickel center. The divergent regioselectivities of 1-hexene versus styrene and methyl acrylate insertion, however, suggest two different cyclic transition states in these reactions, where the electropositive charge of the coordinated olefins is likely localized at the β-carbon atom for the former, whereas it is at the α-carbon for the latter (Figure 10). This hypothesis is consistent with the anticipated electron-releasing character of an *n*-butyl group and electron-withdrawing nature of a phenyl or ester substituent. In accord with these results, Cundari and Holland also reported that the relative ratio of α-methylbenzyl to isomeric phenylethyl complexes in a β-diketiminate iron(II) system decreases as the electron-releasing ability of the para substituents increases.[68] The distinct regiospecificities of 1-hexene versus styrene and methyl acrylate insertion described herein are reminiscent of what has been found for early-transition-metal chemistry such as [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$[85] with 1-hexene and styrene. The divergent insertion regiospecificities are also relevant to those of polymer microstructures derived from copolymerization of α-olefins with styrene or acrylates. For instance, Proto and co-workers have shown that the microstructure of propylene−styrene multiblock copolymer prepared by a bis-phenolate titanium catalyst is composed of 2,1-styrene units and 1,2-propylene building blocks.[49]

Conclusions

In summary, we have demonstrated that the reactivity and regioselectivity of olefin insertion into a Ni−H bond can be effectively manipulated by the electronic and steric properties of substituents at the olefinic substrates and the phosphorus

(84) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252.

(85) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228–243.

donors of the amido diphosphine ligands. With various substituents at the phosphorus donors, the electronic and steric characteristics of the derived nickel(II) hydride complexes are finely tunable. The unsymmetrically substituted **2d** is unique, as it exhibits reactivity resembling that of **2a** and/or **2b**, depending on the olefinic substrates employed. Among the nickel hydride complexes investigated, **2a** is the most reactive due to its higher electrophilic and sterically more accessible nickel center. Remarkably, exclusive 1,2-insertion products were generated from reactions with 1-hexene, whereas selective 2,1-insertion occurs for reactions involving styrene and methyl acrylate. The creation of a chiral center at the nickel-bound hydrocarbyl ligand by 2,1-insertion is intriguing, particularly for those derived from symmetrically substituted amido diphosphine ligands. Consistent with the insertion reactivity described herein, the hydrocarbyl complexes containing β-hydrogen atoms are all thermally stable and resistant to β-elimination, even at elevated temperatures. These results suggest that the hydride species **2a**−**d** are higher in energy than their corresponding olefin insertion products on the basis of the microscopic reverse between β-elimination and olefin insertion.

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. Coupling constants (J) and peak widths at half-height ($\Delta\nu_{1/2}$) are listed in hertz. ^{1}H and ^{13}C NMR spectra are referenced using the residual solvent peaks at δ 7.16 and 128.39, respectively, for C_6D_6. The assignment of the carbon atoms for all new compounds is based on DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. 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. The compounds H[Ph-PNP] (**1a**)[65,66] and [R-PNP-]NiH (R = ^{i}Pr (**2b**), Cy (**2c**))[74] were prepared according to the procedures reported previously. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Crystals of **2b**,**c** suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. Table 1 summarizes the crystallographic data for all structurally characterized compounds. Data 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 H[Ph-PNP-^{i}Pr] (1d). *n*-BuLi (1.94 mL, 1.6 M in hexane solution, 311 mmol, 2 equiv) was added dropwise to a diethyl ether solution (50 mL) of bis(2-bromophenyl)amine (508 mg, 155 mmol) at −35 °C. The reaction solution was stirred at room temperature for 3 h and cooled to −35 °C again. To this was added dropwise a cold diethyl ether solution (2 mL) of chlorodiisopropylphosphine (237 mg, 155 mmol) at −35 °C. The reaction mixture was stirred at room temperature overnight and cooled to −35 °C before addition of *n*-BuLi (0.97 mL, 1.6 M in hexane, 155 mmol) dropwise. The solution was stirred at room temperature for 3 h and cooled to −35 °C again, and a cold (−35 °C) diethyl ether solution (2 mL) of chlorodiphenylphosphine (324 mg, 155 mmol) was added dropwise. The reaction solution was subsequently stirred at room temperature overnight, filtered through a pad of Celite, and evaporated to dryness under reduced pressure. The resulting solid residue was dissolved in diethyl ether (15 mL), and deionized water (10 mL) was added at room temperature. The solution was then dried over $MgSO_4$, filtered, and evaporated to dryness under reduced pressure. The oily residue thus obtained was dissolved in a mixture of diethyl ether (5 mL) and pentane (1 mL). The solution was cooled to −35 °C to afford the product as a pale yellow solid, which was isolated and dried in vacuo. Crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C: yield 390 mg (53%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.99 (dd, 1, J_{HP} = 10.5 and 3.5, NH), 7.56 (m, 5, Ar), 7.39 (dd, 1, Ar), 7.28 (m, 5, Ar), 7.14 (m, 6, Ar), 6.87 (dt, 2, Ar), 1.95 (m, 2, C*H*Me$_2$), 1.10 (dd, 6, CH*Me*$_2$), 0.95 (dd, 6, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ −14.79 (br s, P^{i}Pr$_2$), −16.66 (d, J_{PP} = 9.10, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 149.96 (d, J_{CP} = 19.20, C), 147.20 (d, J_{CP} = 19.20, C), 137.13 (d, J_{CP} = 10.4, C), 134.99 (s, CH), 134.85 (d, J_{CP} = 20.08, CH), 133.95 (s, CH), 130.29 (d, J_{CP} = 16.44, CH), 129.31 (d, J_{CP} = 6.40, CH), 129.24 (s, CH), 129.13 (d, J_{CP} = 10.92, C), 128.68 (s, CH), 122.77 (s, CH), 122.60 (d, J_{CP} = 15.56, C), 120.46 (s, CH), 119.33 (s, CH), 117.04 (d, J_{CP} = 2.76, CH), 23.71 (d, J_{CP} = 10.92, *C*HMe$_2$), 20.63 (d, J_{CP} = 19.20, CH*Me*$_2$), 19.38 (d, J_{CP} = 9.16, CH*Me*$_2$). Anal. Calcd for $C_{30}H_{33}NP_2$: C, 76.74; H, 7.08; N, 2.98. Found: C, 77.03; H, 7.23; N, 3.03.

In Situ Synthesis of [Ph-PNP]NiH (2a). A solid mixture of H[Ph-PNP] (10 mg, 0.019 mmol) and Ni(COD)$_2$ (5 mg, 0.019 mmol) was dissolved in C_6D_6 (0.6 mL) at room temperature. The reaction solution was transferred to an NMR tube, and the ^{1}H and ^{31}P{^{1}H} NMR spectra were taken in 10 min. The spectroscopic data indicate quantitative formation of [Ph-PNP]NiH along with 2 equiv of liberated COD. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.88 (d, 2, Ar), 7.69 (m, 8, Ar), 7.25 (m, 4, Ar), 6.97 (m, 12, Ar), 6.48 (t, 2, Ar), −18.31 (t, $^2J_{HP}$ = 62, NiH). ^{31}P{^{1}H} NMR (C_6D_6, 80.95 MHz): δ 32.65. Liberated COD molecules present in the reaction aliquot: ^{1}H NMR (C_6D_6, 200 MHz) δ 5.58 (s, 8, CH═C*H*CH$_2$), 2.23 (s, 16, CH═CHC*H*$_2$).

Synthesis of [Ph-PNP-^{i}Pr]NiH (2d). Benzene (6 mL) was added to a solid mixture of [Ph-PNP-^{i}Pr]NiH (60 mg, 0.128 mmol) and Ni(COD)$_2$ (35 mg, 0.128 mmol) at room temperature. The red reaction solution was stirred at room temperature for 10 min and evaporated to dryness under reduced pressure. The oily residue was washed with pentane (1 mL × 2) to remove liberated COD and dried in vacuo, affording the product as a dark red solid: yield 60 mg (89%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.92 (dd, 1, Ar), 7.88 (dd, 1, Ar), 7.79 (m, 4, Ar), 7.26 (td, 1, Ar), 7.06 (m, 4, Ar), 7.00 (m, 5, Ar), 6.56 (t, 1, Ar), 6.48 (t, 1, Ar), 2.01 (m, 2, C*H*Me$_2$), 1.21 (dd, 6, CH*Me*$_2$), 0.93 (dd, 6, CH*Me*$_2$), −18.22 (dd, 1, $J_{HP^iPr_2}$ = 68, J_{HPPPh_2} = 58, NiH). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 58.97 (d, J_{PP} = 243.78, P^{i}Pr$_2$), 31.27 (d, J_{PP} = 243.78, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 163.55 (dd, J_{CP} = 21.59, J_{CP} = 4.14, C), 162.92 (dd, J_{CP} = 25.60, J_{CP} = 3.26, C), 135.20 (s, CH), 134.20 (d, J_{CP} = 12.30, CH), 134.17 (d, J_{CP} = 44.80, C), 133.03 (s, CH), 132.15 (d, J_{CP} = 48.95, CH), 130.34 (d, J_{CP} = 1.88, CH), 129.11 (d, J_{CP} = 10.17, CH), 128.68 (s, CH), 125.56 (d, J_{CP} = 42.55, C), 123.21 (d, J_{CP} = 34.76, C), 116.79 (d, J_{CP} = 6.40, CH), 116.40 (d, J_{CP} = 6.02, CH), 116.27 (d, J_{CP} = 10.04, CH), 115.68 (d, J_{CP} = 11.42, CH), 24.01 (d, J_{CP} = 25.98, *C*HMe$_2$), 19.90 (d, J_{CP} = 6.02, CH*Me*$_2$), 18.65 (s, CH*Me*$_2$). Anal. Calcd for $C_{30}H_{33}NNiP_2$: C, 68.21; H, 6.30; N, 2.65. Found: C, 68.06; H, 6.38; N, 2.65.

Synthesis of [Ph-PNP]Ni(η^1-C_8H_{13}) (3a). A solid mixture of H[Ph-PNP] (50 mg, 0.093 mmol) and Ni(COD)$_2$ (25 mg, 0.093 mmol) was dissolved in benzene (1 mL) at room temperature. The reaction solution was stirred at room temperature for 1 min and evaporated to dryness under reduced pressure. The solid thus obtained was washed with pentane (1 mL) and dried in vacuo to

give the product as a yellowish orange powder (52 mg, 83%). Orange crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.99 (m, 4, Ar), 7.72 (m, 4, Ar), 7.66 (dt, 2, Ar), 7.24 (m, 2, Ar), 7.07 (m, 12, Ar), 6.94 (t, 2, Ar), 6.45 (t, 2, Ar), 5.33 (m, 2, HC═C*H*), 2.36 (d, 1, cyclooctenyl), 2.00 (m, 1, cyclooctenyl), 1.82 (m, 1, cyclooctenyl), 1.67 (m, 3, cyclooctenyl), 1.53 (m, 1, cyclooctenyl), 1.28 (m, 2, cyclooctenyl), 0.99 (m, 1, cyclooctenyl), 0.85 (m, 1, cyclooctenyl). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 24.27. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 162.25 (t, J_{CP} = 13.2, C), 134.61 (t, J_{CP} = 6.7, CH), 134.08 (t, J_{CP} = 5.7, CH), 133.81 (t, J_{CP} = 6.54, C), 133.76 (s, CH), 133.70 (t, J_{CP} = 5.7, C), 132.01 (s, CH), 130.80 (s, CH), 130.60 (s, CH), 130.13 (s, CH), 129.75 (s, CH), 129.16 (t, J_{CP} = 4.8, CH), 128.96 (t, J_{CP} = 4.7, CH), 116.85 (s, CH), 116.33 (s, CH), 39.38 (t, J_{CP} = 5.7, CH_2), 33.48 (t, J_{CP} = 3.8, CH_2), 30.33 (s, CH_2), 28.88 (s, CH_2), 25.40 (s, CH_2), 20.82 (t, $^2J_{CP}$ = 14.2, NiCH). Anal. Calcd for $C_{44}H_{41}NNiP_2$: C, 75.02; H, 5.87; N, 1.99. Found: C, 74.65; H, 5.53; N, 1.62.

Synthesis of [Ph-PNP]NiEt (4a). A benzene solution (1 mL) of [Ph-PNP]NiH was prepared in situ from H[Ph-PNP] (10 mg, 0.019 mmol) and $Ni(COD)_2$ (5 mg, 0.019 mmol) as described above. The solution was transferred to a reaction vessel and degassed with three freeze−pump−thaw cycles. Ethylene (1 atm) was introduced. The reaction solution was stirred at room temperature for 1 day and evaporated to dryness under reduced pressure to afford the product as a red solid: yield 10 mg (83%). The NMR spectroscopic data are all identical with those obtained from the reaction of [Ph-PNP]NiCl with EtMgCl, as reported previously.[66]

Synthesis of [Ph-PNP-^{i}Pr]NiEt (4d). A reaction vessel was charged with a solution of [Ph-PNP-^{i}Pr]NiH (20 mg, 0.038 mmol) in benzene (2 mL). The solution was degassed with three freeze−pump−thaw cycles, and ethylene (1 atm) was introduced. The reaction solution was stirred at room temperature for 3 days. The resulting yellow solution was evaporated to dryness under reduced pressure to afford the product as a yellowish brown solid: yield 20 mg (95%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.80 (m, 4, Ar), 7.74 (dd, 1, J = 5.0 and 8.5, Ar), 7.65 (dd, 1, J = 4.0 and 8.5, Ar), 7.18 (dt, 1, Ar), 7.05 (m, 7, Ar), 6.99 (dt, 1, Ar), 6.95 (dt, 1, Ar), 6.51 (t, 1, J = 7.5, Ar), 6.42 (t, 1, J = 7.5, Ar), 2.16 (m, 2, C*H*Me$_2$), 1.42 (m, 1, NiC*H*$_A$CH$_B$Me), 1.29 (dd, 6, J = 7.0 and 15.5, CH*Me*$_2$), 1.08 (dd, 6, J = 7.0 and 15.5, CH*Me*$_2$), 0.96 (m, 1, NiCH$_A$C*H*$_B$Me), 0.92 (m, 3, NiCH$_2$*Me*). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 34.68 (d, J_{PP} = 271.30, P^{i}Pr$_2$), 27.18 (d, J_{PP} = 271.30, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 163.24 (dd, J_{CP} = 20.08 and 4.02, C), 162.91 (dd, J_{CP} = 23.85 and 3.64, C), 134.34 (s, CH), 134.09 (d, J_{CP} = 11.42, CH), 132.91 (dd, J_{CP} = 39.78 and 1.76, C), 132.49 (s, CH), 132.29 (d, J_{CP} = 1.38, CH), 131.54 (d, J_{CP} = 1.88, CH), 130.38 (d, J_{CP} = 1.88, CH), 129.11 (d, J_{CP} = 9.66, CH), 125.88 (d, J_{CP} = 45.68, C), 121.87 (d, J_{CP} = 37.15, C), 116.65 (d, J_{CP} = 9.16, CH), 116.48 (d, J_{CP} = 6.40, CH), 116.18 (d, J_{CP} = 6.02, CH), 115.66 (d, J_{CP} = 10.04, CH), 24.02 (dd, J_{CP} = 19.58 and 1.76, *C*HMe$_2$), 19.25 (d, J_{CP} = 5.02, CH*Me*$_2$), 18.10 (d, J_{CP} = 0.88, CH*Me*$_2$), 15.78 (t, J_{CP} = 2.39, NiCH$_2$*Me*), −8.51 (vt, J_{CP} = 20.58, Ni*C*H$_2$Me). Anal. Calcd for $C_{32}H_{37}NNiP_2$: C, 69.09; H, 6.70; N, 2.52. Found: C, 68.92; H, 6.57; N, 2.50.

Synthesis of [Ph-PNP]Ni(*n*-hexyl) (5a). To a solid mixture of H[Ph-PNP] (10 mg, 0.019 mmol) and $Ni(COD)_2$ (5 mg, 0.019 mmol) was added 1-hexene (25 mg, 0.297 mmol, 16 equiv) followed by benzene (1 mL) at room temperature. The reaction solution was transferred to an NMR tube, and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, which showed quantitative formation of [Ph-PNP]Ni(*n*-hexyl) in 1 day. The NMR spectroscopic data are all identical with those obtained from the reaction of [Ph-PNP]NiCl with *n*-hexylmagnesium chloride, as reported previously.[65]

Synthesis of [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (5d). Neat 1-hexene (64 mg, 0.757 mmol, 4 equiv) was added to a solution of [Ph-PNP-^{i}Pr]NiH (100 mg, 0.189 mmol) in benzene (2 mL) at room temperature. The red reaction solution was stirred at room temperature for 45 h and evaporated to dryness under reduced pressure, affording the product as a red solid: yield 100 mg (86%). 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 7.80 (m, 4, Ar), 7.72 (dd, 1, Ar), 7.62 (dd, 1, Ar), 7.20 (t, 1, Ar), 7.06 (br s, 6, Ar), 7.00 (m, 2, Ar), 6.95 (t, 1, Ar), 6.51 (t, 1, Ar), 6.43 (t, 1, Ar), 2.22 (m, 2, C*H*Me$_2$), 1.33 (dd, 6, CH*Me*$_2$), 1.19 (m, 4, Ni(C*H*$_2$)$_5$Me), 1.13 (m, 10, CH*Me*$_2$ and Ni(C*H*$_2$)$_5$Me), 0.85 (m, 5, Ni(C*H*$_2$)$_5$Me and Ni(CH$_2$)$_5$*Me*). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 34.56 (d, J_{PP} = 273.12, P^{i}Pr$_2$), 27.38 (d, J_{PP} = 273.12, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 163.20 (dd, J_{CP} = 20.08, J_{CP} = 3.64, C), 162.91 (dd, J_{CP} = 24.72, J_{CP} = 3.64, C), 134.27 (s, CH), 134.11 (d, J_{CP} = 10.92, CH), 132.92 (dd, J_{CP} = 39.78, J_{CP} = 1.88, C), 132.48 (s, CH), 132.31 (d, J_{CP} = 1.38, CH), 131.55 (d, J_{CP} = 1.38, CH), 130.39 (d, J_{CP} = 1.88, CH), 129.06 (d, J_{CP} = 9.16, CH), 125.95 (d, J_{CP} = 45.31, C), 121.88 (d, J_{CP} = 37.02, C), 116.58 (d, J_{CP} = 9.16, CH), 116.46 (d, J_{CP} = 6.90, CH), 116.15 (d, J_{CP} = 5.52, CH), 115.67 (d, J_{CP} = 10.54, CH), 35.41 (s, CH_2), 32.36 (s, CH_2), 31.69 (s, CH_2), 24.10 (d, J_{CP} = 20.08, *C*HMe$_2$), 23.53 (s, CH_2), 19.25 (s, CH*Me*$_2$), 18.13 (s, CH*Me*$_2$), 14.83 (s, CH_3), 0.17 (vt, J_{CP} = 20.58, Ni*C*H$_2$). Anal. Calcd for $C_{36}H_{45}NNiP_2$: C, 70.61; H, 7.41; N, 2.29. Found: C, 70.22; H, 7.26; N, 2.24.

Synthesis of [Ph-PNP]Ni(2-norbornyl) (6a). To a solid mixture of H[Ph-PNP] (100 mg, 0.19 mmol) and $Ni(COD)_2$ (51 mg, 0.19 mmol) was added a toluene solution of norbornene (245 mg, 50 wt %, 1.3 mmol, 6.8 equiv) and benzene (3 mL) at room temperature. The reaction solution was stirred at room temperature for 14 h and evaporated to dryness under reduced pressure. The solid thus obtained was washed with pentane (2 mL × 2) and dried in vacuo to give the product as a brownish red powder: yield 118 mg (92%). Layering diethyl ether on a concentrated THF solution at room temperature afforded a red microcrystalline solid. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.92 (m, 8, Ar), 7.53 (dt, 2, Ar), 7.14 (m, 2, Ar), 7.06 (m, 12, Ar), 6.88 (t, 2, Ar), 6.40 (t, 2, Ar), 2.01 (br s, 1, norbornyl), 1.80 (t, 1, norbornyl), 1.62 (m, 1, norbornyl), 1.50 (quintet, 1, norbornyl), 1.23 (m, 1, norbornyl), 1.03 (m, 2, norbornyl), 0.90 (m, 2, norbornyl), 0.68 (t, 1, norbornyl), 0.62 (d, 1, norbornyl). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz): δ 25.32. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 161.94 (t, J_{CP} = 13.1, C), 134.62 (t, J_{CP} = 6.0, CH), 134.53 (t, J_{CP} = 6.0, CH), 133.77 (s, CH), 133.39 (t, J_{CP} = 20.1, C), 133.16 (t, J_{CP} = 20.1, C), 132.11 (s, CH), 130.43 (s, CH), 129.04 (t, J_{CP} = 4.8, CH), 126.76 (t, J_{CP} = 23.5, C), 116.87 (t, J_{CP} = 3.0, CH), 116.40 (t, J_{CP} = 4.4, CH), 45.79 (t, J_{CP} = 6.0, CH), 42.22 (t, J_{CP} = 4.8, CH_2), 38.72 (s, CH), 38.58 (s, CH_2), 34.70 (s, CH_2), 30.21 (s, CH_2), 25.00 (t, $^2J_{CP}$ = 16.6, NiCH). Anal. Calcd for $(C_{43}H_{39}NNiP_2)_3(THF)_2$: C, 74.26; H, 6.05; N, 1.90. Found: C, 73.94; H, 5.73; N, 1.90.

Synthesis of [Ph-PNP-^{i}Pr]Ni(2-norbornyl) (6d). Neat norbornene (36 mg, 0.379 mmol, 2 equiv) was added to a solution of [Ph-PNP-^{i}Pr]NiH (100 mg, 0.189 mmol) in benzene (4 mL) at room temperature. The red reaction solution was stirred at room temperature for 23 h and evaporated to dryness under reduced pressure, affording the product as a red solid: yield 80 mg (68%). Red 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 8.16 (t, 2, Ar), 7.62 (t, 2, Ar), 7.55 (dd, 1, Ar), 7.42 (dd, 1, Ar), 7.13 (t, 1, Ar), 7.03 (m, 7, Ar), 6.96 (t, 1, Ar), 6.83 (t, 1, Ar), 6.42 (q, 2, Ar), 2.23 (m, 1, C*H*Me$_2$), 1.98 (br s, 1, norbornyl), 1.82 (m, 1, C*H*Me$_2$), 1.54 (m, 1, norbornyl), 1.47 (dd, 3, CH*Me*$_2$), 1.42 (m, 1, norbornyl), 1.38 (dt, 1, norbornyl), 1.30 (dd, 3, CH*Me*$_2$), 1.27 (dd, 3, CH*Me*$_2$), 1.21 (m, 1, norbornyl), 1.91 (m, 2, norbornyl), 1.03 (dd, 3, CH*Me*$_2$), 0.91 (m, 3, norbornyl),

0.56 (d, 1, norbornyl). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz): δ 29.62 (d, J_{PP} = 257.54, P^{i}Pr$_2$), 25.76 (d, J_{PP} = 257.54, PPh$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 163.27 (dd, J_{CP} = 4.14 and 18.70, C), 162.28 (dd, J_{CP} = 3.64 and 21.46, C), 134.99 (d, J_{CP} = 11.92, CH), 134.66 (d, J_{CP} = 10.04, CH), 134.49 (d, J_{CP} = 4.14, C), 133.82 (d, J_{CP} = 2.26, C), 133.76 (s, CH), 133.55 (d, J_{CP} = 2.26, C), 132.07 (s, CH), 131.90 (d, J_{CP} = 1.38, CH), 131.57 (d, J_{CP} = 1.88, CH), 130.62 (d, J_{CP} = 1.88, CH), 129.96 (d, J_{CP} = 1.76, CH), 129.03 (d, J_{CP} = 9.16, CH), 128.93 (s, CH), 120.65 (d, J_{CP} = 38.40, C), 116.72 (d, J_{CP} = 6.40, CH), 116.54 (d, J_{CP} = 8.66, CH), 116.09 (d, J_{CP} = 8.28, CH), 115.62 (d, J_{CP} = 5.52, CH), 46.63 (dd, J_{CP} = 2.26 and 12.80, norbornyl CH), 42.25 (d, J_{CP} = 3.26, norbornyl CH$_2$), 38.51 (s, norbornyl CH$_2$), 38.06 (s, norbornyl CH$_2$), 35.17 (s, norbornyl CH$_2$), 30.44 (s, norbornyl CH$_2$), 25.21 (dd, J_{CP} = 2.76 and 15.06, Ni*C*H), 23.13 (dd, J_{CP} = 1.88 and 20.58, *C*HMe$_2$), 20.22 (d, J_{CP} = 5.90, CH*Me*$_2$), 18.46 (d, J_{CP} = 3.64, CH*Me*$_2$), 18.53 (d, J_{CP} = 3.26, CH*Me*$_2$), 17.24 (dd, J_{CP} = 2.76, CH*Me*$_2$), 15.94 (vt, J_{CP} = 18.70, *C*HMe$_2$). Anal. Calcd for $C_{37}H_{43}NNiP_2$: C, 71.40; H, 6.96; N, 2.25. Found: C, 71.03; H, 7.00; N, 1.88.

Synthesis of [Ph-PNP-^{i}Pr]NiCH(Me)Ph (7d). Neat styrene (24 mg, 0.23 mmol) was added to a solution of [Ph-PNP-^{i}Pr]NiH (100 mg, 0.189 mmol) in benzene (2 mL) at room temperature. The reaction solution was stirred at room temperature for 18 h and evaporated to dryness under reduced pressure. Diethyl ether (10 mL) was added. The solution was filtered through a pad of Celite, concentrated under reduced pressure, and cooled to −35 °C to afford the product as a red crystalline solid: yield 107 mg (90%). ^1H NMR (C_6D_6, 500 MHz): δ 7.70 (m, 2, Ar), 7.54 (dd, 1, Ar), 7.45 (dd, 1, Ar), 7.20 (m, 2, Ar), 7.05 (m, 6, Ar), 6.94 (m, 9, Ar), 6.46 (t, 1, Ar), 6.33 (t, 1, J = 7, Ar), 3.30 (m, 1, Ni*C*H(Me)Ph), 2.32 (m, 1, C*H*Me$_2$), 2.08 (m, 1, C*H*Me$_2$), 1.39 (d, 3, NiCH(*Me*)Ph), 1.37 (dd, 3, CH*Me*$_2$), 1.27 (dd, 3, CH*Me*$_2$), 1.17 (dd, 3, CH*Me*$_2$), 1.10 (dd, 3, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 30.67 (d, J_{PP} = 259.16, P^{i}Pr$_2$), 22.85 (d, J_{PP} = 259.16, PPh$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 162.97 (dd, J_{CP} = 19.20 and 3.64, C), 162.15 (dd, J_{CP} = 21.96 and 3.26, C), 155.90 (d, J_{CP} = 6.90, C), 134.90 (d, J_{CP} = 11.04, CH), 134.04 (d, J_{CP} = 11.42, CH), 133.64 (s, CH), 132.24 (dd, J_{CP} = 35.64 and 2.26, C), 132.01 (d, CH), 131.81 (s, CH), 131.66 (d, J_{CP} = 1.38, CH), 131.50 (dd, J_{CP} = 32.88 and 2.26, C), 130.29 (d, J_{CP} = 1.88, CH), 129.86 (d, J_{CP} = 1.88, CH), 128.79 (d, J_{CP} = 9.16, CH), 128.63 (d, J_{CP} = 12.30, CH), 128.54 (s, CH), 127.38 (d, J_{CP}= 47.56, C), 126.91 (s, CH), 122.85 (s, CH), 121.2 (d, J_{CP} = 39.78, C), 117.19 (d, J_{CP} = 8.66, CH), 116.67 (d, J_{CP} = 6.90, CH), 116.16 (d, J_{CP} = 6.02, CH), 115.62 (d, J_{CP} = 9.16, CH), 24.91 (d, J_{CP} = 18.20, *C*HMe$_2$), 23.27 (d, J_{CP} = 20.58, *C*HMe$_2$), 19.80 (d, J_{CP} = 5.90, CH$_3$), 19.60 (d, J_{CP} = 4.14, CH$_3$), 18.95 (d, J_{CP} = 4.14, CH$_3$), 18.02 (s, CH$_3$), 17.87 (s, CH$_3$), 7.40 (dd, J_{CP} = 17.82 and 13.68, NiCH). Anal. Calcd for $C_{38}H_{41}NNiP_2$: C, 72.16; H, 6.54; N, 2.22. Found: C, 72.17; H, 6.77; N, 2.03.

Synthesis of [Ph-PNP]NiCH(Me)CO$_2$Me (8a). A benzene solution (3 mL) of [Ph-PNP]NiH was prepared in situ from H[Ph-PNP] (100 mg, 0.19 mmol) and Ni(COD)$_2$ (51 mg, 0.19 mmol) as described above. Neat methyl acrylate (245 mg, 2.85 mmol) was added. The reaction mixture was stirred at room temperature for 15 min. All volatiles were removed in vacuo. Diethyl ether (10 mL) was added. The solution was filtered through a pad of Celite, concentrated under reduced pressure until the volume became ca. 4 mL, and cooled to −35 °C to afford the product as a deep red crystalline solid: yield 90 mg (71%). ^1H NMR (C_6D_6, 500 MHz): δ 8.22 (q, 4, Ar), 7.74 (q, 4, Ar), 7.64 (d, 2, Ar), 7.17 (m, 6, Ar), 7.00 (m, 8, Ar), 6.88 (t, 2, Ar), 6.37 (t, 2, Ar), 2.94 (s, 3, O*Me*), 2.19 (m, 1, C*H*Me), 0.90 (d, 3, J = 7, CH*Me*). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 26.78. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 183.37 (t, J_{CP} = 4.14, CO), 162.52 (t, J_{CP} = 13.30, C), 135.06 (t, J = 6.02, CH), 134.65 (s, CH), 133.94 (t, J_{CP} = 5.90, CH), 132.26 (s, CH), 131.95 (t, J = 22.84, C), 131.26 (t, J = 20.96, C), 130.76 (s, CH), 130.46 (s, CH), 129.19 (d, J = 5.02, CH), 129.04 (d, J = 4.52, CH), 125.98 (t, J_{CP} = 24.22, C), 117.65 (t, J_{CP} = 3.26, CH), 116.85 (t, J_{CP} = 4.52, CH), 50.12 (s, OCH$_3$), 15.93 (s, NiCH(*C*H$_3$)), 9.61 (t, J_{CP} = 16.06, NiCH). Anal. Calcd for $(C_{40}H_{35}NNiO_2P_2)(OEt_2)_{0.5}$ (confirmed by integration of ^1H NMR): C, 70.10; H, 5.61; N, 1.95. Found: C, 70.40; H, 5.90; N, 1.79.

Synthesis of [^{i}Pr-PNP]NiCH(Me)CO$_2$Me (8b). Benzene (1 mL) was added to a mixture of solid [^{i}Pr-PNP]NiH (50 mg, 0.10 mmol) and methyl acrylate (87 mg, 0.86 mmol, 8.6 equiv) at room temperature. The reaction solution was stirred at room temperature for 2 h to give a red solution, which was evaporated to dryness under reduced pressure, triturated with pentane (2 mL × 2), and dried in vacuo to afford the product as a red solid: yield 58 mg (95%). ^1H NMR (C_6D_6, 500 MHz): δ 7.55 (d, 2, Ar), 7.02 (br s, 2, Ar), 6.92 (t, 2, Ar), 6.45 (t, 2, Ar), 3.49 (s, 3, OMe), 2.47 (br s, 2, C*H*Me$_2$), 2.41 (qt, 1, $^3J_{HP}$ = 13, $^3J_{HH}$ = 7, Ni*CH*), 2.22 (br s, 2, C*H*Me$_2$), 1.42 (br s, 12, CH*Me*$_2$), 1.33 (d, 3, J_{HP} = 7, NiCH(C*H*$_3$)), 1.16 (dd, 6, CH*Me*$_2$), 1.10 (dd, 6, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz): δ 33.36 (br s, $\Delta\nu_{1/2}$ = 638 Hz), 31.42 (br s, $\Delta\nu_{1/2}$ = 657 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz): δ 184.18 (C═O), 163.78 (m, C), 132.53 (m, CH), 131.51 (s, CH), 121.51 (m, C), 116.72 (s, CH), 116.32 (t, J_{CP} = 2.77, CH), 50.11 (s, OMe), 24.19 (m, *C*HMe$_2$), 23.89 (br s, *C*HMe$_2$), 19.76 (br s, CH$_3$), 19.51 (br s, CH$_3$), 17.95 (m, CH$_3$), 17.88 (s, NiCH(*C*H$_3$)), −0.11 (t, $^2J_{CP}$ = 18.35, Ni*C*H). IR (Nujol): 1697 cm^{-1} (C═O). Anal. Calcd for $C_{28}H_{43}NNiO_2P_2$: C, 61.56; H, 7.93; N, 2.56. Found: C, 62.75; H, 8.08; N, 2.30. Multiple attempts to obtain satisfactory analysis data were not successful.

Synthesis of [Cy-PNP]NiCH(Me)CO$_2$Me (8c). Benzene (3 mL) was added to a mixture of [Cy-PNP]NiH (60 mg, 0.096 mmol) and methyl acrylate (110 mg, 1.056 mmol, 11 equiv) at room temperature. The reaction solution was stirred at room temperature for 24 h and evaporated to dryness under reduced pressure. The solid residue was washed with pentane (2 mL × 2) to afford the product as a red solid: yield 68 mg (96%). ^1H NMR (C_6D_6, 500 MHz): δ 7.66 (d, 2, Ar), 7.22 (br s, 2, Ar), 6.95 (t, 2, Ar), 6.49 (t, 2, Ar), 3.56 (s, 3, OMe), 2.51 (m, 5, Ni*CH* and Cy), 1.86 (m, 4, Cy), 1.68 (m, 20, Cy), 1.47 (d, 3, NiCH(*Me*)), 1.25 (m, 12, Cy), 1.11 (m, 4, Cy). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz): δ 25.45 ($\Delta\nu_{1/2}$ = 58.84 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz): δ 184.31 (s, C═O), 164.07 (t, J_{CP} = 9.18, C), 132.72 (m, CH), 131.35 (m, CH), 122.06 (m, C), 116.79 (s, CH), 116.30 (s, CH), 50.42 (s, OMe), 34.53 (t, $^1J_{CP}$ = 9.18, PCH), 28.72 (s, CH$_2$), 28.12 (m, CH$_2$), 27.80 (s, CH$_2$), 26.96 (s, CH$_2$), 26.78 (s, CH$_2$), 17.55 (s, NiCH(*Me*)), 0.74 (t, $^2J_{CP}$ = 18.35, Ni*C*H(Me)). IR (Nujol): 1690 cm^{-1} (C═O). Anal. Calcd for $C_{40}H_{59}NNiO_2P_2$: C, 68.00; H, 8.42; N, 1.98. Found: C, 68.07; H, 8.55; N, 1.85.

Synthesis of [Ph-PNP-^{i}Pr]NiCH(Me)CO$_2$Me (8d). Neat methyl acrylate (32 mg, 0.378 mmol, 2 equiv) was added to a solution of [Ph-PNP-^{i}Pr]NiH (100 mg, 0.189 mmol) in benzene (2 mL) at room temperature. The red reaction solution was stirred at room temperature for 24 h and evaporated to dryness under reduced pressure, affording the product as a red solid: yield 100 mg (84%). ^1H NMR (C_6D_6, 500 MHz): δ 8.10 (m, 2, Ar), 7.91 (m, 2, Ar), 7.58 (dd, 1, Ar), 7.47 (dd, 1, Ar), 7.13 (m, 2, Ar), 7.06 (m, 6, Ar), 6.88 (m, 2, Ar), 6.47 (t, 1, Ar), 6.36 (t, 1, Ar), 3.26 (s, 3, OMe), 2.42 (m, 1, C*H*Me$_2$), 2.34 (m, 1, C*H*Me$_2$), 2.14 (m, 1, Ni*CH*(Me)CO$_2$Me), 1.43 (dd, 3, CH*Me*$_2$), 1.38 (dd, 3, CH*Me*$_2$), 1.28 (dd, 3, CH*Me*$_2$), 1.09 (dd, 3, CH*Me*$_2$), 1.07 (d, 3, NiCH(*Me*)CO$_2$Me). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz): δ 35.99 (d, J_{PP} = 268 Hz, P^{i}Pr$_2$), 24.62 (d, J_{PP} = 268 Hz, PPh$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 183.24 (d, J_{CP} = 5.90, C), 163.40 (dd, J_{CP} = 3.64 and 20.08, C), 162.49 (dd, J_{CP} = 2.76 and 22.84, C), 134.71 (dd, J_{CP} = 96.64, J_{CP} = 10.54, CH), 133.91 (s, CH), 133.09 (d, J_{CP} = 40.29, C), 132.05 (s, CH), 131.83 (d, J_{CP} = 44.80, CH), 130.53 (dd, J_{CP} = 41.16, J_{CP} = 1.76, CH), 129.05 (d, J_{CP} = 10.04, CH), 128.92 (s, CH), 127.18 (d, J_{CP} = 47.57, C), 121.39 (d, J_{CP} = 39.78, C), 117.54 (d, J_{CP} = 9.16, CH), 117.15 (d, J_{CP} = 6.40, CH), 116.75 (d, J_{CP} = 5.90,

CH), 115.85 (d, J_{CP} = 9.54, CH), 50.18 (s, OMe), 24.41 (d, J_{CP} = 20.58, *C*HMe$_2$), 24.04 (d, J_{CP} = 23.34, *C*HMe$_2$), 19.69 (d, J_{CP} = 4.64, CH*Me*$_2$), 18.89 (d, J_{CP} = 3.26, CH*Me*$_2$), 18.08 (s, CH*Me*$_2$), 17.75 (s, CH*Me*$_2$), 15.88 (d, J_{CP} = 5.52, NiCH(*Me*)CO$_2$Me), 3.70 (vt, J_{CP} = 16.69, Ni*C*H(Me)CO$_2$Me). Anal. Calcd for $C_{34}H_{39}NNiO_2P_2$: C, 66.48; H, 6.40; N, 2.28. Found: C, 66.59; H, 6.27; N, 2.10.

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Supporting Information Available: A figure giving the ^{1}H NMR spectrum of **8b** and CIF files giving X-ray crystallographic data for **1d**, **2b**−**d**, **3a**, and **5d**−**7d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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