Amido Pincer Complexes of Nickel(II): Synthesis, Structure, and Reactivity

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A series of diamagnetic divalent nickel complexes supported by a tridentate amido diphosphine ligand $[N(o\text{-}C_6H_4PR_2)_2]^-$ ([R-PNP]$^-$; R = Ph, ^{i}Pr, Cy) have been prepared and characterized. Deprotonation of H[Ph-PNP], H[^{i}Pr-PNP], and H[Cy-PNP] with *n*-BuLi in ethereal solutions at −35 °C produced the lithium complexes [Ph-PNP]Li(THF)$_2$, [^{i}Pr-PNP]Li(solv) (solv = THF, Et$_2$O), and [Cy-PNP]Li(solv) (solv = THF, Et$_2$O), respectively. The reactions of [R-PNP]Li(solv)$_n$ with NiCl$_2$(DME) in THF at −35 °C generated [R-PNP]NiCl, which was then reacted with a variety of Grignard reagents to afford the corresponding hydrocarbyl complexes [R-PNP]NiR′ (R = Ph, R′ = Me, Et, *n*-Bu, *i*-Bu, *n*-hexyl, CH_2SiMe_3, Ph; R = ^{i}Pr, R′ = Me, Et, *n*-Bu; R = Cy, R′ = Me, Et, *n*-Bu). Of particular interest among the compounds isolated are alkyl complexes that contain β-hydrogen atoms. Treatment of the hydrocarbyl complexes with halogenated hydrocarbons such as dichloromethane, benzyl bromide, and phenyl iodide produced the corresponding nickel halide derivatives. The chloride complexes [Ph-PNP]NiCl, [^{i}Pr-PNP]-NiCl, and [Cy-PNP]NiCl are all active catalyst precursors for Kumada coupling reactions, including those of alkyls containing β-hydrogen atoms. In addition to spectroscopic data for all new compounds, X-ray structures of [Cy-PNP]Li(OEt$_2$), [Ph-PNP]NiCl, [Ph-PNP]NiBr, [Ph-PNP]NiMe, [Ph-PNP]Ni(*n*-Bu), [Ph-PNP]NiCH_2SiMe_3, [^{i}Pr-PNP]NiCl, [^{i}Pr-PNP]NiMe, [^{i}Pr-PNP]Ni(*n*-Bu), and [Cy-PNP]NiMe are presented.

Introduction

β-Hydrogen elimination is one of the primary decomposition pathways for organometallic complexes.[1,2] The search for appropriate methods to effectively control the stability and reactivity of transition metal alkyl complexes that contain β-hydrogen atoms has thus played an essential role in organometallic chemistry. These compounds are often key intermediates that determine reaction mechanisms and scopes such as those found in catalytic olefin polymerization[3−6] and cross-coupling reactions[7−14] mediated by late transition metals. Recent work in our laboratory has focused on the preparation and reactivity exploration of new amido phosphine complexes of both main group[15−17] and transition metals.[18−20] In particular, we found that nickel complexes of the tridentate amido phosphine ligand $[N(o\text{-}C_6H_4PPh_2)_2]^-$, including alkyl complexes that contain β-hydrogen atoms, are thermally stable.[21] In contrast, analogous compounds of the bidentate [*o*-(2,6-^{i}Pr$_2$C$_6$H$_3$N)C$_6$H$_4$PPh$_2$]$^-$ and [*o*-(2,6-Me$_2$C$_6$H$_3$N)C$_6$H$_4$PPh$_2$]$^-$[19] were not synthetically accessible.[22] Notably, NiEt[N(*o*-C$_6$H$_4$-PPh$_2$)$_2$] is the only ethyl complex reported thus far among these and the closely related $[N(SiMe_2CH_2PPh_2)_2]^-$ [23] ligand systems. We were thus interested in organometallic chemistry involving ligands of the general type $[N(o\text{-}C_6H_4PR_2)_2]^-$ ([R-PNP]$^-$; R =

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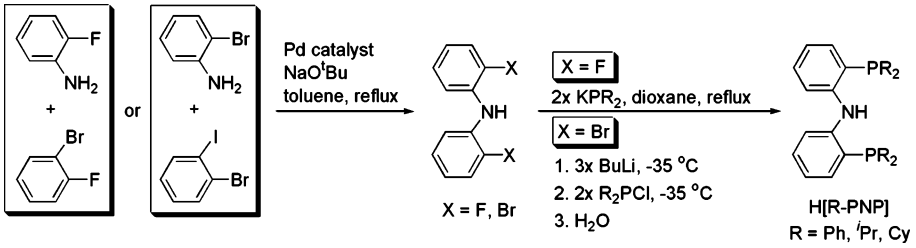
Scheme 1. Preparation of Amido Pincer Ligand Precursors

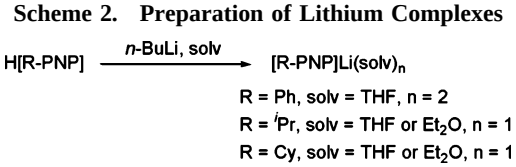


aryl or alkyl). These ligands fall into the category of the popular pincer compounds that are currently under extensive investigation.[24−29] Herein we describe the preparation and characterization of nickel complexes of [Ph-PNP]$^-$, [^{i}Pr-PNP]$^-$, and [Cy-PNP]$^-$ and the reactivity studies of these molecules with respect to catalytic Kumada coupling reactions.

Results and Discussion

Preparation of Ligand Precursors. The preparation of H[Ph-PNP] has been reported independently by Kaska[30] and us[21] with different synthetic approaches. With various substituents at the phosphorus donors, the amido pincer ligands [R-PNP]$^-$ are anticipated to exhibit distinct steric and electronic properties. One elegant precedent in a related ligand system is the silyl-derived [N(SiMe$_2$CH$_2$PR$_2$)$_2$]$^-$ (R = aryl or alkyl) established by Fryzuk and co-workers.[31] Scheme 1 summarizes two strategies for the preparation of the ligand precursors H[Ph-PNP], H[^{i}Pr-PNP], and H[Cy-PNP]. Other similar compounds[32−35] are now available since the preparation of H[Ph-PNP] was reported. Both *o*-fluoro- and *o*-bromo-substituted biphenyl amines were prepared quantitatively from the palladium-catalyzed aryl amination reactions[36,37] of either 2-fluoroaniline with 2-bromofluorobenzene or 2-bromoaniline with 2-bromoiodobenzene. Subsequent reaction of di(2-fluorophenyl)amine with potassium diphenylphosphide in refluxing 1,4-dioxane produced H[Ph-PNP]. Sequential addition of *n*-BuLi and R$_2$PCl (R = Ph, ^{i}Pr, Cy) to a diethyl ether solution of di(2-bromophenyl)amine at −35 °C generated the corresponding H[R-PNP] after anaerobic aqueous workup. These halogenated and phosphanylated diaryl amines were all fully characterized by multinuclear NMR spectroscopy and elemental analysis. The phosphine compounds were all isolated as colorless crystalline solids.

Scheme 2. Preparation of Lithium Complexes



Synthesis and Characterization of Lithium Complexes. Lithium amides are convenient starting materials for metathetical reactions with metal halides. Addition of 1 equiv of *n*-BuLi to H[R-PNP] in ethereal solutions at −35 °C produced the corresponding lithium complexes (Scheme 2). The ^{1}H NMR spectra of these lithium derivatives indicate the presence of coordinated solvent molecules. Consistent with the anticipated steric and electronic properties of substituents at the phosphorus donors, the phenyl-substituted amido pincer complex adopts more coordinated solvent molecules than the isopropyl and cyclohexyl counterparts. While [^{i}Pr-PNP]Li(OEt$_2$) and [Cy-PNP]-Li(OEt$_2$) are considerably stable under reduced pressure, the coordinated ether molecule is notably labile and may be readily replaced by THF, as indicated by ^{1}H NMR spectroscopy.

Table 1 summarizes the selected NMR spectroscopic data. The phosphorus donors in these lithium complexes appear as a signal that is shifted relatively downfield as compared to that of the corresponding ligand precursor. As illustrated in Figure 1, the internuclear coupling observed in the ^{31}P{^{1}H} and ^{7}Li{^{1}H} NMR spectra of the THF adducts is indicative of the coordination of two chemically equivalent phosphorus donors to the quadrupolar lithium-7 center (I = 3/2, natural abundance 92.6%).[38] The coupling constant $^1J_{PLi}$ of 34 Hz for [Ph-PNP]-Li(THF)$_2$ is comparable to those found for lithium phosphine complexes such as [Li(THF)$_2$][*o*-(2,6-^{i}Pr$_2$C$_6$H$_3$N)C$_6$H$_4$PPh$_2$] (38 Hz)[19] and [Li(THF)$_2$][*o*-(2,6-Me$_2$C$_6$H$_3$N)C$_6$H$_4$PPh$_2$] (34 Hz)[19] and the lithium phosphide derivatives [Li(tmeda)]$_2$[1,2-C$_6$H$_4$-(PPh)$_2$] (35 Hz)[39] and [Li(tmeda)]$_2$[1,2-C$_6$H$_4$(PSiMe$_3$)$_2$] (38 Hz),[39] whereas those of [^{i}Pr-PNP]Li(THF) (46 Hz) and [Cy-PNP]Li(THF) (48 Hz) are somewhat larger but similar to that of Li[N(2-P^{i}Pr$_2$-4-Me-C$_6$H$_3$)$_2$](THF) (48 Hz).[40] These values, however, are all notably smaller than that reported for Li[N(*o*-C$_6$H$_4$P^{i}Bu$_2$)$_2$] (61 Hz), which does not incorporate any coordinating solvent molecules.[35] The increasing tendency of $^1J_{PLi}$ following the order [Ph-PNP]Li(THF)$_2$, [^{i}Pr-PNP]Li(THF), and [Cy-PNP]Li(THF) is perhaps a consequence of distinct electronic properties of the substituents at the phosphorus donors or a result of different electrophilicity of the four- and five-coordinate lithium center due to various amounts of coordinated ethereal molecules.

An X-ray crystallographic study of [Cy-PNP]Li(OEt$_2$) established the solid-state structure of this molecule. The crystal-

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Table 1. Selected NMR Spectroscopic Data[a]

compound	δ_P	δ_{Li}	$^1J_{PLi}$	$\delta_{H\alpha}$	$^3J_{PH\alpha}$	$\delta_{C\alpha}$	$^2J_{PC\alpha}$
H[Ph-PNP]	−18.62						
[Ph-PNP]Li(THF)$_2$[b]	−13.60	3.14	34.18				
[Ph-PNP]NiCl	18.77						
[Ph-PNP]NiBr	23.72						
[Ph-PNP]NiI	33.09						
[Ph-PNP]NiMe[c]	27.61			0.13	8.50	−15.37	21.87
[Ph-PNP]NiEt[c]	26.42			1.07		−2.80	19.48
[Ph-PNP]Ni(*n*-Bu)[c]	27.06			1.07		5.24	19.10
[Ph-PNP]Ni(*i*-Bu)[c]	26.80			1.22		18.53	19.54
[Ph-PNP]Ni(*n*-hexyl)	26.78			1.12		6.72	18.85
[Ph-PNP]NiCH$_2$SiMe$_3$[c]	23.90			−0.08	12.00	−12.97	18.83
[Ph-PNP]NiPh[c]	24.45					151.00	28.15
H[^{i}Pr-PNP]	−13.31						
[^{i}Pr-PNP]Li(THF)[b]	−3.95	2.32	46.15				
[^{i}Pr-PNP]Li(OEt$_2$)[b]	−5.07	2.52	NA[d]				
[^{i}Pr-PNP]NiCl	34.68						
[^{i}Pr-PNP]NiMe	35.47			−0.31	9.0	−25.41	25.39
[^{i}Pr-PNP]NiEt	32.07			0.84	11.0[e]	−14.97	22.5
[^{i}Pr-PNP]Ni(*n*-Bu)	32.50			0.76		−6.50	22.0
H[Cy-PNP]	−22.04						
[Cy-PNP]Li(THF)[b]	−12.20	2.41	48.17				
[Cy-PNP]Li(OEt$_2$)[b]	−12.54	3.00	NA[d]				
[Cy-PNP]NiCl	26.77						
[Cy-PNP]NiMe	28.16			−0.13	9.0	−23.60	24.76
[Cy-PNP]NiEt	24.59			1.03	11.0[e]	−13.24	22.40
[Cy-PNP]Ni(*n*-Bu)	25.08			NA[f]	NA[f]	−4.67	22.2

[a] Unless otherwise noted, all spectra were recorded in C_6D_6 at room temperature, chemical shifts in ppm, coupling constants in Hz. [b] Spectra recorded in toluene-d_8. [c] Data selected from ref 21. [d] Not available; a broad singlet rather than a multiplet resonance was observed. [e] Obtained by selective decoupling of β-hydrogen atoms. [f] Not available; the assignment was hampered due to overlap with cyclohexyl signals.

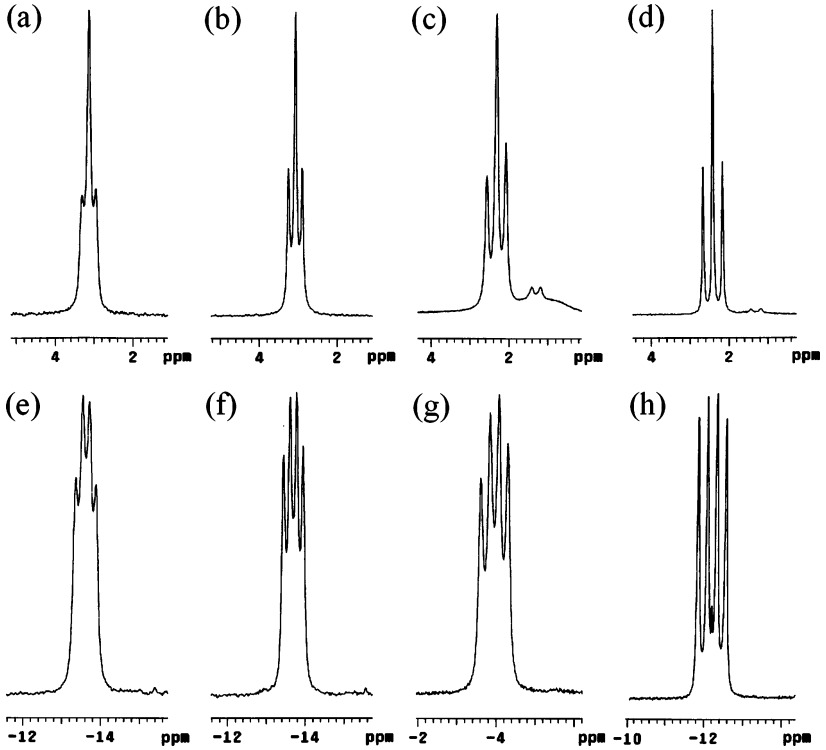


Figure 1. The ^{7}Li{^{1}H} NMR (194 MHz) spectra of (a) [Ph-PNP]Li(THF)$_2$ (toluene-d_8, 25 °C), (b) [Ph-PNP]Li(THF)$_2$ (toluene-d_8, 10 °C), (c) [^{i}Pr-PNP]Li(THF) (toluene-d_8, 25 °C), and (d) [Cy-PNP]Li(THF) (toluene-d_8, 25 °C) and the ^{31}P{^{1}H} NMR (202 MHz) spectra of (e) [Ph-PNP]Li(THF)$_2$ (toluene-d_8, 25 °C), (f) [Ph-PNP]Li(THF)$_2$ (toluene-d_8, 10 °C), (g) [^{i}Pr-PNP]Li(THF) (toluene-d_8, 25 °C), and (h) [Cy-PNP]Li(THF) (toluene-d_8, 25 °C).

lographic data are summarized in Table 2. Consistent with the solution structure determined by NMR spectroscopy, [Cy-PNP]-Li(OEt$_2$) is a four-coordinate species in the solid state (Figure 2). The geometry of the lithium center is best described as distorted tetrahedral with angles ranging from 79.06(11)° to 139.30(13)° (Table 3). As a result, the dihedral angle between two N−Li−P planes of 143.1° in [Cy-PNP]Li(OEt$_2$) is notably smaller than that of 174.6° found in the meridional, five-coordinate [Ph-PNP]Li(THF)$_2$.[21] The Li−P bond distances of [Cy-PNP]Li(OEt$_2$) are slightly shorter than those of [Ph-PNP]-Li(THF)$_2$. The remaining parameters are unexceptional and closely similar to those of Li[N(2-P^{i}Pr$_2$-4-Me-C$_6$H$_3$)$_2$](THF).[40]

Synthesis and Characterization of Nickel Complexes. Addition of the amido pincer lithium complexes to NiCl$_2$-

Table 2. Crystallographic Data for [Cy-PNP]Li(OEt$_2$), [Ph-PNP]NiCl, [^{i}Pr-PNP]NiCl, [Ph-PNP]NiMe, [^{i}Pr-PNP]NiMe, [Cy-PNP]NiMe, [Ph-PNP]Ni(*n*-Bu), [^{i}Pr-PNP]Ni(*n*-Bu), [Ph-PNP]NiCH$_2$SiMe$_3$, and [Ph-PNP]NiBr

	[Cy-PNP]Li(OEt$_2$)	{[Ph-PNP]NiCl}-(C$_6$H$_6$)$_5$	[^{i}Pr-PNP]NiCl	[Ph-PNP]NiMe	[^{i}Pr-PNP]NiMe	[Cy-PNP]NiMe
CCDC ref number	276347	276348	276349	276350	276351	276352
formula	C$_4$0H$_6$2LiNOP$_2$	C$_{66}$H$_{58}$ClNNiP$_2$	C$_{24}$H$_{36}$ClNNiP$_2$	C$_{37}$H$_{31}$NNiP$_2$	C$_{25}$H$_{39}$NNiP$_2$	C$_{37}$H$_{55}$NNiP$_2$
fw	641.79	1021.23	494.64	610.28	474.22	634.47
D_{calc} (g cm^{-3})	1.124	1.193	1.325	1.365	1.256	1.212
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$F2dd$	$P2_1/c$	$Pnca$
a (Å)	10.28900(10)	18.004(3)	12.26400(10)	9.8780(3)	12.2610(3)	18.2850(5)
b (Å)	10.9240(2)	12.8101(18)	9.9710(2)	18.3870(5)	9.9350(2)	18.2850(5)
c (Å)	19.3070(3)	26.044(4)	20.3710(3)	32.6920(10)	20.7080(7)	10.4020(5)
α (deg)	82.5160(10)	90	90	90	90	90
β (deg)	76.7630(10)	108.826(2)	95.6750(10)	90	96.0020(10)	90
γ (deg)	63.9670(10)	90	90	90	90	90
V (Å^3)	1896.98(5)	5685.3(14)	2478.84(6)	5937.7(3)	2508.68(12)	3477.8(2)
Z	2	4	4	8	4	4
T (K)	200(2)	298(2)	100(2)	150(2)	200(2)	293(2)
diffractometer	Kappa CCD	SMART 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
$2\theta_{max}$ (deg)	50.10	56.82	50.06	50.00	50.02	50.04
total no. of reflns	21504	63 576	18 172	5872	15 441	10 336
no. of indep reflns	6680	13 696	4338	2325	4409	3004
R_{int}	0.0471	0.0704	0.0495	0.0416	0.0776	0.0733
abs coeff (mm^{-1})	0.145	0.484	1.030	0.789	0.912	0.675
no. of data/ restraints/ params	6680/0/407	13696/0/640	4338/0/258	2325/1/187	4409/0/263	3004/0/188
goodness of fit	1.053	1.018	1.124	1.090	1.098	0.978
final R indices [$I > 2\sigma(I)$]	R1 = 0.0456	R1 = 0.0543	R1 = 0.0324	R1 = 0.0529	R1 = 0.0583	R1 = 0.0609
	wR2 = 0.1183	wR2 = 0.1261	wR2 = 0.0867	wR2 = 0.1429	wR2 = 0.1330	wR2 = 0.1518
R indices (all data)	R1 = 0.0574	R1 = 0.1454	R1 = 0.0368	R1 = 0.0584	R1 = 0.0957	R1 = 0.1025
	wR2 = 0.1338	wR2 = 0.1748	wR2 = 0.0956	wR2 = 0.1539	wR2 = 0.1581	wR2 = 0.1931

	[Ph-PNP]Ni(*n*-Bu)	[^{i}Pr-PNP]Ni(*n*-Bu)	[Ph-PNP]NiCH$_2$-SiMe$_3$	{[Ph-PNP]NiBr}-(C$_6$H$_6$)$_2$
CCDC ref number	276353	276354	276355	276356
formula	C$_{40}$H$_{37}$NNiP$_2$	C$_{28}$H$_{45}$NNiP$_2$	C$_{40}$H$_{39}$NNiP$_2$Si	C$_{48}$H$_{40}$BrNNiP$_2$
fw	652.401	516.30	682.503	831.37
D_{calc} (g cm^{-3})	1.290	1.199	1.269	1.379
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$C2/c$
a (Å)	17.1579(4)	18.0840(3)	10.9794(2)	24.2880(7)
b (Å)	9.4672(2)	8.5850(2)	15.7917(4)	9.7320(3)
c (Å)	22.0701(6)	19.3230(4)	20.8066(4)	18.4090(7)
α (deg)	90	90	96.604(2)	90
β (deg)	110.4889(9)	107.5760(10)	94.5042(14)	113.0520(10)
γ (deg)	90	90	90.5390(8)	90
V (Å^3)	3358.22(14)	2859.87(10)	3571.89(13)	4003.9(2)
Z	4	4	4	4
T (K)	298(2)	200(2)	298(2)	293(2)
diffractometer	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
$2\theta_{max}$ (deg)	50.06	50.06	50.06	50.00
total no. of reflns	24 984	29 443	33 801	10 438
no. of indep reflns	5870	5051	14 222	3497
R_{int}	0.044	0.0779	0.070	0.0563
abs coeff (mm^{-1})	0.702	0.806	0.69	1.597
no. of data/restraints/ params	5870/0/397	5051/0/290	6528/0/842	3497/0/242
goodness of fit	0.997	1.194	2.962	1.214
final R indices [$I > 2\sigma(I)$]	R1 = 0.0419	R1 = 0.0532	R1 = 0.067	R1 = 0.0654
	wR2 = 0.1269	wR2 = 0.1235	wR2 = 0.162	wR2 = 0.1418
R indices (all data)	R1 = 0.0617	R1 = 0.0804	R1 = 0.150	R1 = 0.1015
	wR2 = 0.1418	wR2 = 0.1491	wR2 = 0.162	wR2 = 0.1803

(DME)[41] suspended in THF at −35 °C resulted in slow dissolution of $NiCl_2$(DME) to give a homogeneous green solution, from which diamagnetic [Ph-PNP]NiCl, [^{i}Pr-PNP]NiCl, and [Cy-PNP]NiCl were isolated as emerald crystals in high yield (Scheme 3). All three chloride complexes are air- and water-stable in both solution and solid state. The $^{31}P\{^1H\}$ NMR spectra of these chloride derivatives reveal a singlet resonance that is shifted downfield from the corresponding ligand precursors and lithium complexes. The $^{13}C\{^1H\}$ NMR spectra exhibit virtual triplet[42] resonances for the *o*-phenylene carbon atoms, consistent with a square-planar geometry for these molecules.

(41) Masotti, H.; Wallet, J. C.; Peiffer, G.; Petit, F.; Mortreux, A.; Buono, G. *J. Organomet. Chem.* **1986**, *308*, 241−252.

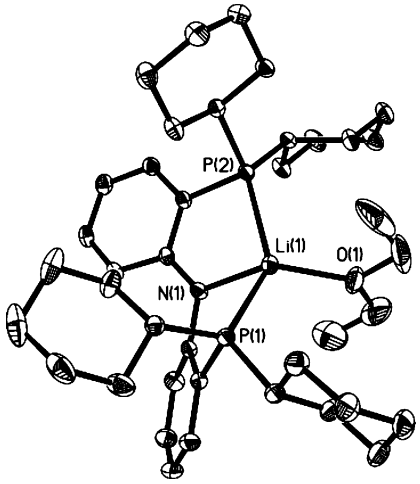


Figure 2. Molecular structure of [Cy-PNP]Li(OEt_2) with thermal ellipsoids drawn at the 35% probability level.

Table 3. Comparison of Selected Bond Distances (Å) and Angles (deg) for the Amido Phosphine Complexes of Lithium

compound	[Cy-PNP]Li(OEt_2)	[Ph-PNP]Li$(THF)_2$[a]
Li−N	1.979(3)	2.039(5)
Li−P	2.578(3), 2.502(3)	2.779(5), 2.824(5)
Li−O	1.979(3)	1.955(5), 1.969(5)
N−Li−P	83.50(12), 79.06(11)	73.35(15), 73.09(15)
P−Li−P	139.30(13)	146.01(18)
P−Li−O	109.17(15), 108.91(14)	105.4(2), 95.26(18), 106.85(19), 94.92(18)
N−Li−O	136.04(19)	118.0(2), 139.7(3)
O−Li−O		102.3(2)

[a] Data selected from ref 21.

Emerald crystals of [Ph-PNP]NiCl suitable for X-ray diffraction analyses were grown from a concentrated benzene solution at room temperature, while those of [^{i}Pr-PNP]NiCl were obtained from an ethereal solution at −35 °C. Figure 3 depicts the solid-state structures of these chloride complexes. As summarized in Tables 4 and 5, the bond distances and angles involving nickel in these molecules are all similar to each other. These parameters are all well within the expected values.[19,23,43] As anticipated, the nickel center in these complexes lies perfectly on the square plane defined by the four donor atoms with the chloride ligand being trans to the amido nitrogen atom. The two *o*-phenylene rings in these molecules are all tilted with respect to the coordination plane due to the steric repulsion between the two CH groups ortho to the amido nitrogen atom. These structures are reminiscent of those of [Ph-PNP]PdCl[44] and [Ph-PNP]PtCl.[45] Consistent with the ionic sizes of divalent group 10 metals, the P−M−P angle decreases on going from [Ph-PNP]NiCl (171.72(4)°) to [Ph-PNP]PdCl (165.27(11)°) and [Ph-PNP]PtCl (167.30(8)°).

Treatment of green [R-PNP]NiCl with a variety of Grignard reagents produced a series of red, diamagnetic nickel alkyl and aryl complexes in high isolated yield. Of particular interest is the preparation of those containing β-hydrogen atoms, as analogous compounds have not been reported for the closely related $[N(SiMe_2CH_2PR_2)_2]^-$,[23] $[o\text{-}(2,6\text{-}Me_2C_6H_3N)C_6H_4PPh_2]^-$,[19] and $[o\text{-}(2,6\text{-}{}^i Pr_2C_6H_3N)C_6H_4PPh_2]^-$ systems.[19,22] In general, the metathetical reactions were completed in ca. 2 h to afford cleanly the desired products as indicated by solution ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. As anticipated, the H_α and C_α atoms in these hydrocarbyl complexes are observed as a triplet resonance in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra. Similar to those found in [R-PNP]NiCl, the *o*-phenylene carbon atoms in [R-PNP]NiR′ appear as virtual triplet resonances, suggestive of a meridional coordination mode for the amido pincer ligands in these square-planar molecules.[42]

The solid-state structures of these hydrocarbyl complexes were investigated by X-ray crystallography. Figures 4−6 illustrate the molecular structures of [R-PNP]NiMe (R = Ph, ^{i}Pr, Cy), [R−PNP]Ni(*n*-Bu) (R = Ph, ^{i}Pr), and [Ph-PNP]NiCH_2-$SiMe_3$, respectively. These structures resemble each other closely. The nickel center in each molecule adopts a square-planar geometry, a result that is in good agreement with that concluded by solution NMR studies. Although the bond distances and angles are all within the expected values, we note that crystallographically characterized, mononuclear nickel complexes of acyclic alkyls that contain β-hydrogen atoms are extremely rare.[46]

The thermal stability of these nickel complexes is remarkable. These compounds are in general thermally stable at elevated temperatures. Of particular note are the β-hydrogen-containing alkyl derivatives. For instance, no decomposition was observed when a benzene solution of [^{i}Pr-PNP]Ni(*n*-Bu) (6 mM) or [Cy-

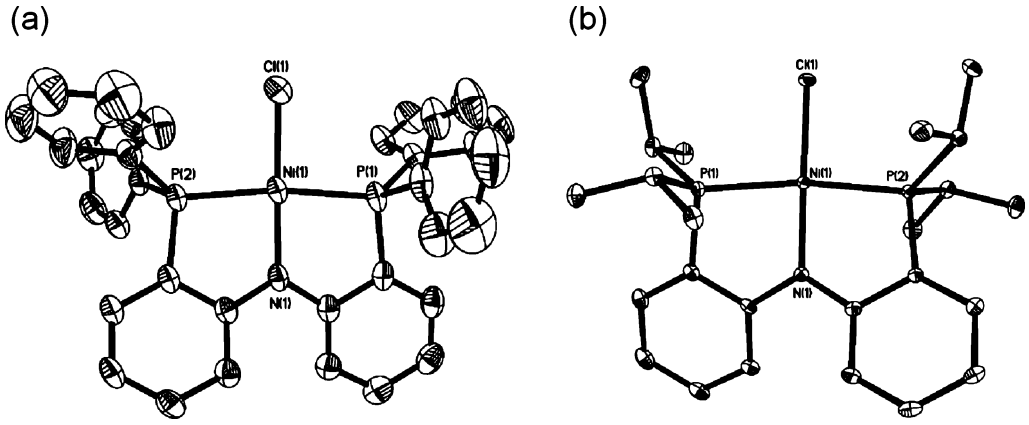


Figure 3. Molecular structures of (a) [Ph-PNP]NiCl and (b) [^{i}Pr-PNP]NiCl with thermal ellipsoids drawn at the 35% probability level.

Scheme 3. Preparation of Nickel Complexes

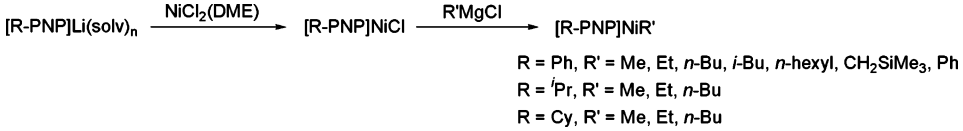


Table 4. Selected Bond Distances (Å) for the Amido Pincer Complexes of Nickel

compound	Ni−N	Ni−X[a]	Ni−P
[Ph-PNP]NiCl	1.895(3)	2.1636(11)	2.1737(9), 2.1879(8)
[Ph-PNP]NiBr	1.912(5)	2.2984(10)	2.1830(12), 2.1830(12)
[Ph-PNP]NiMe	1.967(8)	1.967(11)	2.1776(13), 2.1776(13)
[Ph-PNP]Ni(*n*-Bu)	1.966(2)	1.971(3)	2.1655(8), 2.1811(8)
[Ph-PNP]NiCH_2SiMe_3[b]	1.966(5)	1.944(7)	2.191(2), 2.154(2)
[^{i}Pr-PNP]NiCl	1.9030(17)	2.1834(6)	2.1884(6), 2.1913(6)
[^{i}Pr-PNP]NiMe	1.945(3)	1.965(4)	2.1557(12), 2.1797(12)
[^{i}Pr-PNP]Ni(*n*-Bu)	1.953(3)	1.963(3)	2.1576(9), 2.1966(9)
[Cy-PNP]NiMe	1.947(5)	1.995(7)	2.1677(10), 2.1677(10)

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

Table 5. Selected Bond Angles (deg) for the Amido Pincer Complexes of Nickel

compound	N−Ni−P	P−Ni−P	P−Ni−X[a]	N−Ni−X[a]
[Ph-PNP]NiCl	85.47(7), 86.27(7)	171.72(4)	93.18(4), 95.06(4),	177.88(8)
[Ph-PNP]NiBr	85.14(4), 85.14(4)	170.28(7)	94.86(4), 94.86(4)	180.000(1)
[Ph-PNP]NiMe	84.53(5), 84.53(5)	169.05(9)	95.47(5), 95.47(5)	180.0
[Ph-PNP]Ni(*n*-Bu)	82.84(7), 84.99(7),	163.76(3)	96.45(11), 96.46(11)	175.76(12)
[Ph-PNP]NiCH_2SiMe_3[b]	83.1(2), 84.5(2)	167.51(8)	99.7(2), 92.8(2)	170.6(3)
[^{i}Pr-PNP]NiCl	85.73(6), 84.92(5)	168.81(2)	93.99(2), 95.74(2)	176.24(6)
[^{i}Pr-PNP]NiMe	85.97(10), 84.18(10)	166.68(5)	93.81(14), 96.93(15)	173.90(19)
[^{i}Pr-PNP]Ni(*n*-Bu)	85.58(8), 84.99(8)	168.83(4)	92.86(11), 97.17(11)	173.55(13)
[Cy-PNP]NiMe	85.14(3), 85.14(3)	170.29(7)	94.86(3), 94.86(3)	180.0

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

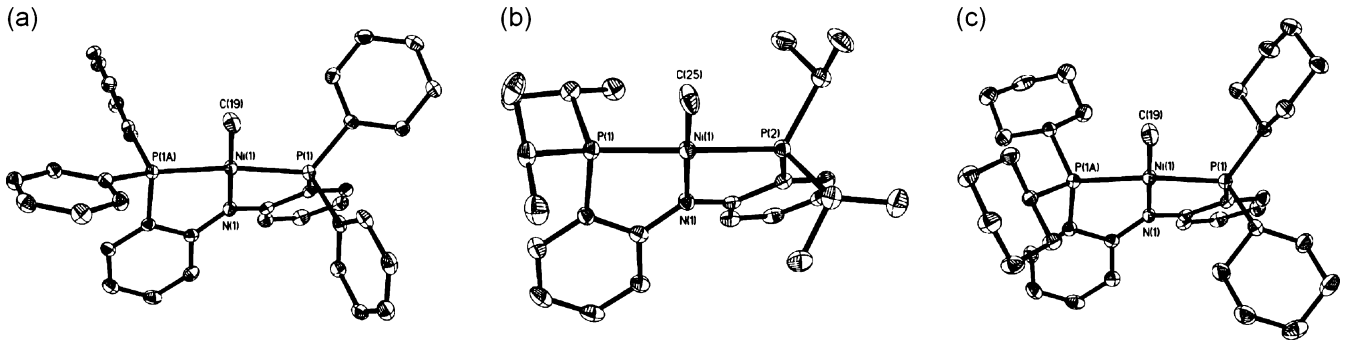


Figure 4. Molecular structures of (a) [Ph-PNP]NiMe, (b) [^{i}Pr-PNP]NiMe, and (c) [Cy-PNP]NiMe with thermal ellipsoids drawn at the 35% probability level.

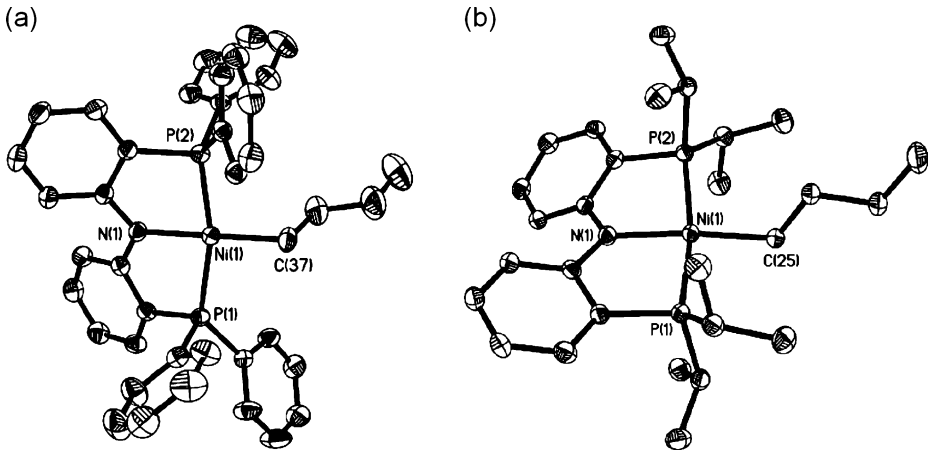


Figure 5. Molecular structures of (a) [Ph-PNP]Ni(*n*-Bu) and (b) [^{i}Pr-PNP]Ni(*n*-Bu) with thermal ellipsoids drawn at the 35% probability level.

PNP]Ni(*n*-Bu) (12 mM) was heated to 80 °C for >3 days, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. Attempts to probe whether reversible *β*-hydrogen elimination occurs at high temperatures were not successful. Heating a benzene solution of [^{i}Pr-PNP]Ni(*n*-Bu) (36 mM) or [Ph-PNP]Ni(*n*-Bu) (21 mM) in the presence of an excess amount of 1-hexene at 100 °C for 1 day did not lead to formation of any new compounds, in particular [^{i}Pr-PNP]Ni(*n*-hexyl) and [Ph-PNP]Ni(*n*-hexyl), re-

(42) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: Hoboken, 2005; pp 276−277.
(43) Peters, J. C.; Harkins, S. B.; Brown, S. D.; Day, M. W. *Inorg. Chem.* **2001**, *40*, 5083−5091.
(44) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813−2816.
(45) Liang, L.-C.; Lin, J.-M.; Lee, W.-Y. *Chem. Commun.* **2005**, 2462−2464.

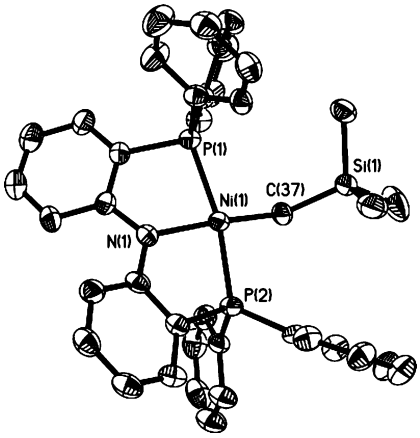
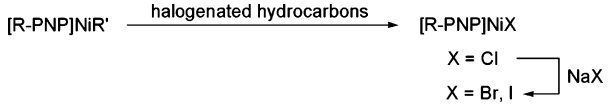


Figure 6. Molecular structure of [Ph-PNP]NiCH$_2$SiMe$_3$ with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two independent molecules; only one is shown for clarity.

Scheme 4. Reactions of Nickel Hydrocarbyl Complexes with Halogenated Hydrocarbons



spectively, as evidenced by ^{1}H NMR and ^{31}P{^{1}H} NMR spectra. Interestingly, the insertion reaction of 1-hexene with [Ph-PNP]-NiH, prepared in situ from the reaction of H[Ph-PNP] with Ni-(COD)$_2$ in benzene,[47] occurs readily even at room temperature to produce [Ph-PNP]Ni(*n*-hexyl) quantitatively. On the basis of these results and the principle of microscopic reversibility of β elimination and olefin insertion, we conclude that the β elimination of [R-PNP]NiCH$_2$C*H*R′R″ species is uphill thermodynamically, at least for [Ph-PNP]$^-$ derivatives.

Reactivity Studies of Nickel Complexes. In general, no reaction was observed for the hydrocarbyl complexes at room temperature with a variety of protic or unsaturated molecules such as water, benzyl alcohol, piperidine, acetone, acetophenone, and trimethylsilylacetylene. These compounds, however, reacted with halogenated hydrocarbons to give corresponding nickel halide complexes (Scheme 4). For instance, the reaction of [Ph-PNP]NiMe with 1 equiv of benzyl bromide in toluene at 100 °C produced tan crystals of [Ph-PNP]NiBr in high yield. Analogous reactions with an excess amount of dichloromethane or benzyl chloride afforded [Ph-PNP]NiCl quantitatively. Treatment of [Ph-PNP]NiMe with chlorobenzene or bromobenzene led to slow but clean formation of [Ph-PNP]NiX (X = Cl, 16% conversion; Br, 86% conversion), whereas the reaction of [Ph-PNP]NiMe with iodobenzene proceeded much faster (100% conversion) to generate a mixture of [Ph-PNP]NiI (80%) and [Ph-PNP]NiPh (20%). We note that the relative reaction rates of [Ph-PNP]NiMe with PhX are consistent with the anticipated reactivity of the aryl halides. The identity of both [Ph-PNP]-NiBr and [Ph-PNP]NiI was further confirmed by independent preparation of these molecules from the reactions of [Ph-PNP]-NiCl with NaBr and NaI, respectively. Figure 7 depicts the X-ray structure of [Ph-PNP]NiBr.

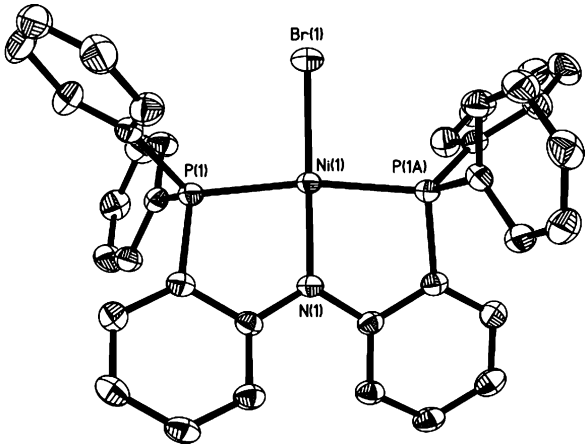
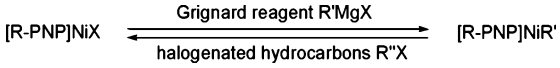


Figure 7. Molecular structure of [Ph-PNP]NiBr with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two benzene molecules, which are omitted for clarity.

Scheme 5. Interconversion between [R-PNP]NiX and [R-PNP]NiR′



It is interesting to note that both [R-PNP]NiX and [R-PNP]-NiR′ can be interconverted to each other in the presence of Grignard reagents and halogenated hydrocarbons, respectively (Scheme 5). Of particular note is the activation of the $C_{sp3}-X$ and $C_{sp2}-X$ (X = Cl, Br, I) bonds promoted by these nickel hydrocarbyl complexes. It thus seems promising that the cross-coupling reactions of Grignard reagents with halogenated hydrocarbons, generally referred to as the Kumada reactions,[48] can be catalyzed by these amido pincer complexes of nickel. As summarized in Table 6, both aryl (entries 1−3) and alkyl (entries 4−9) Griganrd reagents are successfully coupled with phenyl halides in the presence of a catalytic amount of [R-PNP]-NiCl. As anticipated, the catalysis is compatible with alkyl nucleophiles bearing β-hydrogen atoms (entries 4−9), although the reaction conversion and selectivity are relatively unsatisfied. Nevertheless, the successful Kumada couplings of β-hydrogen-containing alkyl groups described herein are remarkable, as preceding examples are rare.[7,9] The formation of the undesired biphenyl product is suggestive of the presence of an [R-PNP]-NiPh intermediate during catalysis, consistent with what we observed in the reaction of [Ph-PNP]NiMe with iodobenzene (vide supra). Although the mechanism is not clear at this stage, the discrepancy for the formation of the undesired [R-PNP]NiPh intermediate in the catalytic reactions involving alkyl rather than aryl Grignard reagents is consistent with the relatively higher inherent reactivity of Ni-alkyl than Ni-aryl with respect to phenyl halides. Attempts to employ decyl halides as electrophiles for Kumada reactions led to insignificant results (ca. 10% yield). As the reactivity of [Ph-PNP]NiCl, [^{i}Pr-PNP]NiCl, and [Cy-PNP]NiCl seems comparable to each other under the conditions employed, it is likely that the rate-determining step in this process is not aryl halide oxidative addition,[49] which would lead instead to a notably higher reactivity for cyclohexyl derivatives. It is also possible that, however, the catalysis described herein may not involve oxidative addition at all. A similar conclusion

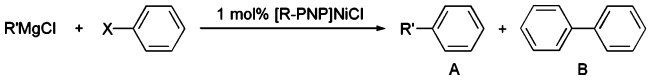
(46) We note that only five examples are available from the Cambridge Structural Database; see: (a) Cotton, F. A.; Frenz, B. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 4820−4825. (b) Hoberg, H.; Gotz, V.; Kruger, C. *J. Organomet. Chem.* **1979**, *169*, 219−224. (c) Conroy-Lewis, F. M.; Mole, L.; Redhouse, A. D.; Litster, S. A.; Spencer, J. L. *Chem. Commun.* **1991**, 1601−1603. (d) Wiencko, H. L.; Kogut, E.; Warren, T. H. *Inorg. Chim. Acta* **2003**, *345*, 199−208. (e) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984−11994.

(47) Attempts to isolate [Ph-PNP]NiH by this route were not successful. ^{31}P{^{1}H} NMR for [Ph-PNP]NiH in C_6D_6: δ 33.

(48) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Ed.; Wiley-VCH: Weinheim, 1998.

(49) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665−1673.

Table 6. Catalytic Kumada Reactions of Grignard Reagents with Aryl Halides[a]



								yield (%)[b]	
entry	R	R′	X	solvent	temp (°C)	*t* (h)	conversion (%)[b]	A	B
1	Ph	4-tolyl[c]	I	toluene	25	12	92	100	0
2	^{i}Pr	4-tolyl[c]	I	toluene	25	39	85	100	0
3	Cy	4-tolyl[c]	I	toluene	25	39	55	100	0
4	Ph	Et	I	THF	60	12	89	59	41
5	^{i}Pr	Et	I	THF	60	12	55	60	40
6	Cy	Et	I	THF	60	12	42	33	67
7	Ph	*n*-Bu	Br	THF	60	12	97	44	56
8	^{i}Pr	*n*-Bu	Br	THF	60	12	57	46	54
9	Cy	*n*-Bu	Br	THF	60	12	47	56	44

[a] Reaction conditions: 1.0 equiv of aryl halide, 1.1 equiv of Grignard reagent, 2 mL of solvent. Reaction times have not been minimized. [b] Determined by GC, based on aryl halides; average of two runs. [c] 4-Tolylmagnesium bromide was used.

has also been deduced for [Ph-PNP]PdCl-catalyzed Heck olefination[44] and $\{[o\text{-}(2,6\text{-}^i Pr_2C_6H_3N)C_6H_4PPh_2]PdCl\}_2$- and $[o\text{-}(2,6\text{-}^i Pr_2C_6H_3N)C_6H_4PPh_2]PdCl(PCy_3)$-catalyzed Suzuki coupling reactions.[20]

Conclusions

In summary, we have prepared a series of lithium and divalent nickel complexes of amido pincer ligands $[R\text{-}PNP]^-$ (R = Ph, ^{i}Pr, Cy) and established their structural characterization by means of solution NMR spectroscopy and X-ray crystallography. The coordination number and geometry of the lithium compounds apparently depend on the characteristics of substituents at the phosphorus donors of these pincer ligands. In contrast, the nickel complexes consistently adopt a square planar geometry. The isolation of nickel alkyl complexes that contain β-hydrogen atoms is intriguing as compared to the closely related $[N(SiMe_2CH_2PR_2)_2]^-$ system.[23] Particularly remarkable is the thermal stability of these β-hydrogen-containing alkyl complexes at elevated temperatures. Consistent with the reactivity studies of the nickel halide and nickel alkyl complexes with Grignard reagents and halogenated hydrocarbons, respectively, the nickel halide complexes of $[R\text{-}PNP]^-$ are all active catalyst precursors for Kumada coupling reactions.

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*) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_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_6D_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_3PO_4 at δ 0, and LiCl in D_2O 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 $NiCl_2(DME)$,[41] $[Ph\text{-}PNP]Li(THF)_2$,[21] and [Ph-PNP]NiR′ (R′ = Me, Et, *n*-Bu, *i*-Bu, CH_2SiMe_3, Ph)[21] were prepared according to the procedures reported previously. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Table 2 summarizes the crystallographic data for all structurally characterized compounds. Crystals of [Ph-PNP]NiMe suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at −35 °C, while those of [Ph-PNP]Ni(*n*-Bu) and $[Ph\text{-}PNP]NiCH_2SiMe_3$ were grown by slow evaporation of a concentrated benzene solution at room temperature. Data were collected on a Bruker-Nonius Kappa CCD or a Bruker AXS SMART APEX 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 Di(2-fluorophenyl)amine. A Schlenk flask was charged with 2-fluoroaniline (5.55 g, 50 mmol), 1-bromo-2-fluorobenzene (8.75 g, 50 mmol), $Pd(OAc)_2$ (0.020 g, 0.089 mmol, 0.5% equiv), DPEPhos (0.216 g, 0.401 mmol, 0.75% equiv), NaO^{t}Bu (7.185 g, 74.84 mmol, 1.4 equiv), and toluene (45 mL) under nitrogen. The reaction mixture was heated to reflux with stirring. The reaction was monitored by GC, which showed complete formation of the desired product in 1 day. After being cooled to room temperature, the reaction was quenched with deionized water (45 mL). The organic portion was separated from the aqueous layer, which was further extracted with toluene (10 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. All volatiles were removed in vacuo to yield a red oil, which was directly used for the subsequent reaction; yield 9.38 g (91.4%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (m, 2, Ar), 7.25 (m, 2, Ar), 7.20 (m, 2, Ar), 7.04 (m, 2, Ar), 6.03 (br s, 1, NH). ^{19}F NMR ($CDCl_3$, 470.5 MHz): δ −133.07. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 153.45 (t, J_{CF} = 241, *C*F), 130.45 (t, J_{CF} = 11.75, *C*N), 124.14 (t, J_{CF} = 3.63, *C*H), 121.38 (t, J_{CF} = 7.25, *C*H), 117.98 (s, *C*H), 115.45 (t, J_{CF} = 19.00, *C*H). LR-MS (EI): calcd for $C_{12}H_9F_2N$ *m*/*z* 205, found *m*/*z* 205. Anal. Calcd for $C_{12}H_9F_2N$: C, 70.24; H, 4.42; N, 6.83. Found: C, 70.13; H, 4.52; N 6.69.

Synthesis of Di(2-bromophenyl)amine. A Schlenk flask was charged with 2-bromoaniline (5.26 g, 30.58 mmol), 1-bromo-2-iodobenzene (8.65 g, 30.58 mmol), $Pd(OAc)_2$ (0.034 g, 0.15 mmol, 0.5% equiv), DPEPhos (0.123 g, 0.23 mmol, 0.75% equiv), NaO^{t}Bu (4.11 g, 42.81 mmol, 1.4 equiv), and toluene (20 mL) under nitrogen. In the absence of light, the reaction mixture was heated to reflux with stirring. The reaction was monitored by GC-MS, which showed quantitative formation of the desired product in 15 h. After being cooled to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. The solid residue was dissolved in deionized water (30 mL) and CH_2Cl_2 (60 mL). The organic portion was separated from the aqueous layer, which was further extracted with dichloromethane (40 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. The

solvent was removed in vacuo to yield a dark brown oil, which was subjected to flash column chromatography on neutral Al_2O_3 using Et_2O as the eluant. The first band (pale yellow) was collected and solvent was removed in vacuo, affording the product as pale yellow oil; yield 9.21 g (92%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (dd, 2, Ar), 7.30 (dd, 2, Ar), 7.22 (td, 2, Ar), 6.85 (td, 2, Ar), 6.48 (br s, 1, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.70 MHz): δ 139.87 (s, C), 133.13 (s, CH), 128.00 (s, CH), 122.44 (s, CH), 117.82 (s, CH), 114.16 (s, C). HRMS (EI): Calcd for $C_{12}H_9Br_2N$ *m*/*z* 324.9102, found *m*/*z* 324.9101. Anal. Calcd for $C_{12}H_9Br_2N$: C, 44.07; H, 2.77; N, 4.28. Found: C, 44.21; H, 2.80; N, 4.27.

Synthesis of Bis(2-diphenylphosphinophenyl)amine (H[Ph-PNP]). Method 1. A 100 mL Schlenk flask equipped with a condenser was flashed with nitrogen thoroughly. To this flask was added $KPPh_2$ (20 mL, 0.5 M in THF solution, 10 mmol). THF was removed in vacuo, and a solution of di(2-fluorophenyl)amine (1.00 g, 4.88 mmol) in 1,4-dioxane (8 mL) was added with a syringe. The transparent, ruby reaction solution was heated to reflux with stirring. The reaction condition was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which revealed the completion of reaction in 2 days. The resulting yellow solution was evaporated to dryness in vacuo. The residue was treated with degassed deionized water (50 mL), and the product was extracted with deoxygenated dichloromethane (15 mL). The dichloromethane solution was separated from the aqueous layer, from which the product was further extracted with dichloromethane (15 mL × 3). The combined organic solution was dried over $MgSO_4$ and filtered. All volatiles were removed in vacuo to yield the product as a pale yellow crystalline solid; yield 2.1 g (80%). **Method 2.** *n*-BuLi (2.5 mL, 1.6 M in hexane, 4.0 mmol, 3 equiv) was added dropwise to a solution of di(2-bromophenyl)-amine (440 mg, 1.35 mmol) in diethyl ether (15 mL) at −35 °C. The reaction solution was naturally warmed to room temperature and stirred for 1 h, providing a pale yellow solution along with a significant amount of off-white precipitate. The reaction mixture was cooled to −35 °C again, and chlorodiphenylphosphine (0.5 mL, 2.69 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 18 h. The reaction was quenched with 2-propanol (0.2 mL) and filtered through a pad of Celite, which was further washed with diethyl ether (4 mL). The combined diethyl ether solution was evaporated to dryness under reduced pressure to afford a pale yellow oil. The oil was dissolved in a mixture of CH_2Cl_2 (2 mL) and pentane (5 mL) and cooled to −35 °C, affording the product as an off-white solid; yield 450 mg (62%, 2 crops). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10−7.23 (m, 24, Ar), 6.69−6.76 (m, 5, Ar and NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −19.58. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ −18.62. $^{31}P\{^1H\}$ NMR (Et_2O, 121.5 MHz): δ −18.62. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 146.51 (d, J_{CP} = 21.1), 135.78 (d, J_{CP} = 8.0), 134.14 (s), 133.72 (d, J_{CP} = 21.1), 129.64 (s), 128.53 (d, J_{CP} = 12.0), 128.46 (d, J_{CP} = 7.5), 126.34 (d, J_{CP} = 10.1), 121.51 (s), 118.16 (s). Anal. Calcd for $C_{36}H_{29}NP_2$: C, 80.43; H, 5.44; N, 2.61. Found: C, 80.04; H, 5.56; N, 2.69.

Synthesis of Bis(2-diisopropylphosphinophenyl)amine (H[^{i}Pr-PNP]). *n*-BuLi (2.9 mL, 1.6 M in hexane, 4.68 mmol, 3 equiv) was added dropwise to a solution of di(2-bromophenyl)amine (510 mg, 1.56 mmol) in diethyl ether (13 mL) at −35 °C. The reaction solution was naturally warmed to room temperature and stirred for 1 h, providing a pale yellow solution along with a significant amount of off-white precipitate. The reaction mixture was cooled to −35 °C again, and chlorodiisopropylphosphine (0.5 mL, 3.12 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 16 h. Degassed deionized water (10 mL) and diethyl ether (10 mL) were added. The diethyl ether portion was separated from the aqueous solution, which was further extracted with diethyl ether (5 mL × 2). The diethyl ether solutions were combined, dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford a yellow oil. The yellow oil was dissolved in degassed ethanol (1 mL) and cooled to −40 °C to give the product as an off-white crystalline solid; yield 344 mg (55%). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.48 (t, 1, J_{HP} = 8.3, NH), 7.41 (d, 2, Ar), 7.26 (d, 2, Ar), 7.06 (t, 2, Ar), 6.82 (t, 2, Ar), 1.97 (m, 4, C*H*Me$_2$), 1.09 (dd, 12, CH*Me*$_2$), 0.93 (dd, 12, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (Et_2O, 80.95 MHz): δ −11.86. $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ −12.07. $^{31}P\{^1H\}$ NMR (toluene, 80.95 MHz): δ −13.07. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ −13.31.$^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 149.55 (d, J_{CP} = 20.1, C), 134.14 (s, CH), 130.14 (s, CH), 123.79 (d, J_{CP} = 16.6, C), 120.74 (s, CH), 117.36 (s, CH), 23.73 (d, J_{CP} = 11.1, *C*HMe$_2$), 20.70 (d, J_{CP} = 19.4, CH*Me*$_2$), 19.44 (d, J_{CP} = 9.2, *C*H*Me*$_2$). Anal. Calcd for $C_{24}H_{37}NP_2$: C, 71.79; H, 9.29; N, 3.49. Found: C, 71.50; H, 9.15; N, 3.56.

Synthesis of Bis(2-dicyclohexylphosphinophenyl)amine (H[Cy-PNP]). *n*-BuLi (5.8 mL, 1.6 M in hexane, 9.3 mmol, 3 equiv) was added dropwise to a solution of di(2-bromophenyl)amine (1.0 g, 3.1 mmol) in diethyl ether (30 mL) at −35 °C. The reaction solution was naturally warmed to room temperature and stirred for 1 h, providing a pale yellow solution along with a significant amount of off-white precipitate. The reaction mixture was cooled to −35 °C again, and a diethyl ether solution (3 mL) of chlorodiisopropylphosphine (933 mg, 6.1 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 16 h and evaporated to dryness under reduced pressure to give an orange viscous oil. Degassed deionized water (30 mL) and dichloromethane (50 mL) were added. The dichloromethane portion was separated from the aqueous solution, which was further extracted with dichloromethane (20 mL × 2). The dichloromethane solutions were combined, dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford a white cloudy oil. Pentane (5 mL) was added. The solution was vigorously stirred at room temperature to give the product as an off-white solid, which was isolated by decantation of the solution and dried in vacuo; yield 1.32 g (77%). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.51 (t, 1, J_{HP} = 7.3, NH), 7.48 (dd, 2, Ar), 7.40 (d, 2, Ar), 7.09 (td, 2, Ar), 6.85 (td, 2, Ar), 2.00 (m, 8, Cy), 1.70 (t, 8, Cy), 1.60 (d, 4, Cy), 1.53 (d, 4, Cy), 1.36 (qt, 4, Cy), 1.23 (m, 8, Cy),1.15 (dt, 4, Cy), 1.07 (tt, 4, Cy). $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ −19.56. $^{31}P\{^1H\}$ NMR (toluene, 80.95 MHz): δ −20.86. $^{31}P\{^1H\}$ NMR (Et_2O, 80.95 MHz): δ −20.62. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ −22.04 ($\Delta\nu_{1/2}$ = 491 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 149.75 (d, J_{CP} = 19.2, C), 134.68 (s, CH), 130.13 (s, CH), 123.76 (d, J_{CP} = 16.2, C), 120.78 (s, CH), 117.46 (s, CH), 33.96 (d, J_{CP} = 11.4, CH), 31.31 (d, J_{CP} = 17.4, CH_2), 29.72 (d, J_{CP} = 8.2, CH_2), 27.86 (d, J_{CP} = 10.4, CH_2), 27.67 (d, J_{CP} = 7.4, CH_2), 27.10 (s, CH_2). Anal. Calcd for $C_{36}H_{53}NP_2$: C, 76.97; H, 9.51; N, 2.49. Found: C, 77.43; H, 9.69; N, 2.06.

Synthesis of [^{i}Pr-PNP]Li(THF). Solid H[^{i}Pr-PNP] (69 mg, 0.17 mmol) was dissolved in THF (3 mL) and cooled to −35 °C. To this was added *n*-BuLi (0.11 mL, 1.6 M in hexane, 0.17 mmol) dropwise. The reaction solution was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure to give an orange-yellow oil. Pentane (2 mL) was added and evaporated in vacuo, affording the product as a yellow oil; yield 80 mg (97%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.53 (t, 2, Ar), 7.16 (td, 2, Ar), 7.11 (td, 2, Ar), 6.60 (t, 2, Ar), 3.40 (t, 4, OC*H*$_2$CH$_2$), 1.99 (m, 4, C*H*Me$_2$), 1.25 (t, 4, OCH$_2$C*H*$_2$), 1.12 (dd, 12, CH*Me*$_2$), 1.05 (dd, 12, CH*Me*$_2$). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.51 (t, 2, Ar), 7.09 (m, 4, Ar), 6.57 (t, 2, Ar), 3.40 (t, 4, OC*H*$_2$CH$_2$), 1.97 (m, 4, C*H*Me$_2$), 1.27 (t, 4, OCH$_2$C*H*$_2$), 1.11 (dd, 12, CH*Me*$_2$), 1.03 (dd, 12, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ −7.95. $^{31}P\{^1H\}$ NMR (Et_2O, 80.95 MHz): δ −4.66. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ −4.43 ($\Delta\nu_{1/2}$ = 59 Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8, 202.31 MHz): δ −3.95 (1:1:1:1 q, $^1J_{LiP}$ = 46.15 Hz). $^7Li\{^1H\}$ NMR (C_6D_6, 194.20 MHz): δ 2.48 ($\Delta\nu_{1/2}$ = 53 Hz). $^7Li\{^1H\}$ NMR (toluene-d_8, 194.20 MHz): δ 2.32 (t, $^1J_{LiP}$ = 46.15 Hz). $^{13}C\{^1H\}$

NMR (C_6D_6, 125.70 MHz): δ 163.71 (br s, C), 133.25 (s, CH), 130.85 (s, CH), 120.75 (br s, C), 117.51 (br s, CH), 114.46 (s, CH), 68.61 (s, OCH_2CH_2), 25.73 (s, OCH_2CH_2), 23.26 (br s, $CHMe_2$), 20.66 (d, J_{CP} = 13.7, $CHMe_2$), 20.10 (d, J_{CP} = 8.7, $CHMe_2$).

Synthesis of [^{i}Pr-PNP]Li(OEt$_2$). Solid H[^{i}Pr-PNP] (90 mg, 0.22 mmol) was dissolved in diethyl ether (3 mL) and cooled to −35 °C. To this was added *n*-BuLi (0.14 mL, 1.6 M in hexane, 0.22 mmol) dropwise. The reaction solution was naturally warmed to room temperature with stirring for 10 min, evaporated to dryness under reduced pressure, and triturated with pentane (2 mL) to afford the product as a yellow oil; yield 100 mg (93%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.61 (t, 2, Ar), 7.17 (m, 4, Ar), 6.65 (t, 2, Ar), 3.09 (q, 4, OCH_2CH_3), 1.99 (m, 4, $CHMe_2$), 1.11 (dd, 12, $CHMe_2$), 1.04 (dd, 12, $CHMe_2$), 0.93 (t, 6, OCH_2CH_3). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.50 (dd, 2, Ar), 7.08 (m, 4, Ar), 6.57 (t, 2, Ar), 3.13 (q, 4, OCH_2CH_3), 1.95 (m, 4, $CHMe_2$), 1.10 (dd, 12, $CHMe_2$), 1.01 (dd, 12, $CHMe_2$), 0.95 (t, 6, OCH_2CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −4.91 ($\Delta_{1/2}$ = 77 Hz). ^{31}P{^{1}H} NMR (diethyl ether, 80.95 MHz): δ −5.03. ^{31}P{^{1}H} NMR (toluene-d_8, 202.31 MHz): δ −5.07 ($\Delta_{1/2}$ = 116 Hz). ^{7}Li{^{1}H} NMR (C_6D_6, 194.2 MHz): δ 2.79 ($\Delta_{1/2}$ = 40 Hz). ^{7}Li{^{1}H} NMR (toluene-d_8, 194.2 MHz): δ 2.52 ($\Delta_{1/2}$ = 49 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 163.42 (d, J_{CP} = 19.23, C), 133.30 (d, J_{CP} = 1.89, CH), 131.02 (s, CH), 120.24 (d, J_{CP} = 1.06, C), 117.34 (br s, CH), 114.58 (s, CH), 66.71 (s, OCH_2CH_3), 23.12 (d, $^1J_{CP}$ = 14.20, $CHMe_2$), 20.66 (d, $^2J_{CP}$ = 13.32, $CHMe_2$), 20.17 (d, $^2J_{CP}$ = 8.67, $CHMe_2$), 14.91 (s, OCH_2CH_3).

Synthesis of [Cy-PNP]Li(THF). Solid H[Cy-PNP] (128 mg, 0.228 mmol) was dissolved in THF (3 mL) and cooled to −35 °C. To this was added *n*-BuLi (0.14 mL, 1.6 M in hexane, 0.228 mmol) dropwise. The reaction solution was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure to give a bright yellow solid, which was triturated with pentane (2 mL), affording the product as a yellow solid; yield 139 mg (95%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.63 (t, 2, Ar), 7.26 (t, 2, Ar), 7.18 (t, 2, Ar), 6.66 (t, 2, Ar), 3.42 (t, 4, OCH_2CH_2), 1.93 (m, 12, Cy), 1.69 (t, 8, Cy), 1.61 (d, 4, Cy), 1.39 (q, 4, Cy), 1.23 (m, 16, Cy and OCH_2CH_2), 1.13 (t, 4, Cy). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.53 (dd, 2, Ar), 7.21 (m, 2, Ar), 7.12 (t, 2, Ar), 6.60 (t, 2, Ar), 3.46 (t, 4, OCH_2CH_2), 1.90 (m, 12, Cy), 1.70 (t, 8, Cy), 1.61 (d, 4, Cy), 1.35 (q, 4, Cy), 1.25 (m, 16, Cy and OCH_2CH_2), 1.13 (t, 4, Cy). ^{31}P{^{1}H} NMR (THF, 80.95 MHz): δ −15.63. ^{31}P{^{1}H} NMR (Et_2O, 80.95 MHz): δ −12.81. ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −12.12 (1:1:1:1 q, $^1J_{PLi}$ = 46.13). ^{31}P{^{1}H} NMR (toluene-d_8, 202.31 MHz): δ −12.20 (1:1:1:1 q, $^1J_{LiP}$ = 48.17). ^{7}Li{^{1}H} NMR (C_6D_6, 194.20 MHz): δ 2.58 (t, $^1J_{LiP}$ = 46.13). ^{7}Li{^{1}H} NMR (toluene-d_8, 194.20 MHz): δ 2.41 (t, $^1J_{LiP}$ = 48.17). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 163.42 (d, J_{CP} = 19.2, C), 133.18 (s, CH), 130.81 (s, CH), 120.15 (d, J_{CP} = 10.6, C), 117.12 (s, CH), 114.38 (s, CH), 68.75 (s, OCH_2CH_2), 33.39 (s, CH), 31.06 (d, J_{CP} = 11.8, CH_2), 30.35 (d, J_{CP} = 7.8, CH_2), 28.14 (d, J_{CP} = 10.9, CH_2), 28.03 (d, J_{CP} = 9.1, CH_2), 27.32 (s, CH_2), 25.71 (s, OCH_2CH_2). Anal. Calcd for $C_{40}H_{60}LiNOP_2$: C, 75.09; H, 9.45; N, 2.19. Found: C, 73.09; H, 9.22; N, 2.15. Satisfactory analysis could not be obtained due to moisture sensitivity of this compound.

Synthesis of [Cy-PNP]Li(OEt$_2$). Method 1. *n*-BuLi (2.13 mL, 1.6 M in hexane, 3.39 mmol, 3 equiv) was added dropwise to a solution of di(2-bromophenyl)amine (370 mg, 1.13 mmol) in diethyl ether (13 mL) at −35 °C. The reaction solution was naturally warmed to room temperature and stirred for 1 h, providing a pale yellow solution along with a significant amount of off-white precipitate. The reaction mixture was cooled to −35 °C again, and chlorodicyclohexylphosphine (0.5 mL, 2.26 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 16 h and filtered through a pad of Celite, which was further washed with diethyl ether (4 mL). The diethyl ether solution was combined and evaporated to dryness under reduced pressure. The resulting oily residue was dissolved in pentane (1 mL) and cooled to −35 °C to afford the product as a yellow solid; yield 570 mg (79%, 2 crops). **Method 2.** *n*-BuLi (0.1 mL, 1.6 M in hexane, 0.16 mmol) was added dropwise to a solution of H[Cy-PNP] (90 mg, 0.16 mmol) in diethyl ether (3 mL) at −35 °C. The reaction solution was stirred at room temperature for 10 min, evaporated to dryness under reduced pressure, and triturated with pentane (2 mL) to afford the product as a yellow solid; yield 96 mg (94%). Yellow crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a diethyl ether solution at room temperature. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.62 (m, 2, Ar), 7.24 (m, 2, Ar), 7.17 (t, 2, Ar), 6.66 (t, 2, Ar), 3.17 (q, 4, OCH_2CH_3), 1.91 (m, 12, Cy), 1.70 (m, 8, Cy), 1.62 (d, 4, Cy), 1.36 (qt, 4, Cy), 1.24 (m, 12, Cy), 1.12 (q, 4, Cy), 1.02 (t, 6, OCH_2CH_3). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.46 (m, 2, Ar), 7.18 (m, 2, Ar), 7.10 (t, 2, Ar), 6.60 (t, 2, Ar), 3.18 (q, 4, OCH_2CH_3), 1.88 (m, 12, Cy), 1.66 (m, 12, Cy), 1.10−1.35 (m, 20, Cy), 0.98 (t, 6, OCH_2CH_3). ^{31}P{^{1}H} NMR (diethyl ether, 80.95 MHz): δ −13.29. ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −12.97 (br s, $\Delta\nu_{1/2}$ = 127 Hz). ^{31}P{^{1}H} NMR (toluene-d_8, 202.31 MHz): δ −12.54 (br s, $\Delta\nu_{1/2}$ = 90 Hz). ^{7}Li{^{1}H} NMR (C_6D_6, 194.20 MHz): δ 2.90 (br s, $\Delta\nu_{1/2}$ = 54 Hz). ^{7}Li{^{1}H} NMR (toluene-d_8, 194.20 MHz): δ 3.00 (br s, $\Delta\nu_{1/2}$ = 49 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 163.58 (m, C), 133.34 (s, CH), 130.85 (s, CH), 120.00 (br s, C), 117.48 (br s, CH), 114.62 (s, CH), 66.70 (s, OCH_2CH_3), 33.57 (br s, PCH), 31.29 (d, J_{CP} = 11.94, CH_2), 30.43 (d, J_{CP} = 7.29, CH_2), 28.12 (d, J_{CP} = 11.94, CH_2), 28.03 (d, J_{CP} = 10.94, CH_2), 27.29 (s, CH_2), 15.16 (s, OCH_2CH_3). Anal. Calcd for $C_{40}H_{62}LiNOP_2$: C, 74.85; H, 9.74; N, 2.18. Found: C, 73.03; H, 9.59; N, 2.10. Satisfactory analysis could not be obtained due to moisture sensitivity of this compound.

Synthesis of [Ph-PNP]NiCl. Method 1. Solid $NiCl_2$(DME) (172.7 mg, 0.785 mmol) was suspended in THF (10 mL) and cooled to −35 °C. A cold solution of [Ph-PNP]Li(THF)$_2$ (540 mg, 0.785 mmol) in THF (10 mL) at −35 °C was added dropwise to the suspension to result in gradual dissolution of solid $NiCl_2$(DME), and a homogeneous dark green solution formed. The reaction mixture was stirred at room temperature for 2 h. All volatiles were removed in vacuo. The solid residue was extracted with CH_2Cl_2 (20 mL). The green CH_2Cl_2 solution was filtered through a pad of Celite and evaporated to dryness, providing the product as a green solid, yield 464 mg (93.6%). **Method 2.** A J. Young tube containing a toluene solution (0.5 mL) of [Ph-PNP]NiMe (4 mg, 0.006 mmol) and benzyl chloride (20 mg, 0.158 mmol, 26.3 equiv) was immersed into an oil bath at 110 °C. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, which indicated quantitative formation of [Ph-PNP]NiCl in 43 h. **Method 3.** A J. Young tube containing a toluene solution (0.5 mL) of [Ph-PNP]NiMe (1.0 mg, 0.002 mmol) and CH_2Cl_2 (130 mg, 1.531 mmol, 765.5 equiv) was immersed into an oil bath at 110 °C. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, which indicated quantitative formation of [Ph-PNP]-NiCl in 113 h. **Method 4.** A J. Young tube containing a toluene solution (0.5 mL) of [Ph-PNP]NiMe (4 mg, 0.006 mmol) and PhCl (17 mg, 0.151 mmol, 25.2 equiv) was immersed into an oil bath at 110 °C. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, which indicated the presence of [Ph-PNP]NiCl (16%) and [Ph-PNP]-NiMe (84%) in 168 h. 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 7.92−7.95 (m, 8, Ar), 7.61 (d, 2, Ar), 6.96−7.04 (m, 14, Ar), 6.83 (t, 2, Ar), 6.35 (t, 2, Ar). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ 18.77. ^{31}P{^{1}H} NMR (THF, 121 MHz): δ 17.82. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 163.31 (t, J_{CP} = 14.43), 135.15 (s, CH), 134.38 (t, J_{CP} = 5.90, CH), 132.38 (s, CH), 130.95 (s, CH), 130.69 (t, J_{CP} = 23.97), 129.29 (t, J_{CP} = 4.89, CH), 123.65 (t, J_{CP} = 23.47), 118.51 (t, J_{CP} = 3.14, CH), 117.87 (t, J_{CP} = 5.90, CH). Anal. Calcd for

$C_{36}H_{28}ClNNiP_2$: C, 68.56; H, 4.47; N, 2.22. Found: C, 68.36; H, 4.57; N, 2.18.

Synthesis of [Ph-PNP]NiBr. Method 1. This experiment was conducted under aerobic conditions. Solid NaBr (10.7 mg, 0.104 mmol, 2.6 equiv) was suspended in acetone (30 mL) and added to a green solution of [Ph-PNP]NiCl (25 mg, 0.040 mmol) in acetone (8 mL) at room temperature. After being stirred at room temperature for 24 h, the reaction mixture was evaporated to dryness in vacuo. The residue was extracted with CH_2Cl_2 (6 mL) and filtered through a pad of Celite. Solvent was removed in vacuo to yield the product as a tan solid; yield 26.6 mg (99%). **Method 2.** A toluene solution (10 mL) containing [Ph-PNP]NiMe (100 mg, 0.164 mmol) and benzyl bromide (0.02 mL, 0.164 mmol) was heated to 100 °C in an oil bath for 2 days. All volatiles were removed in vacuo. The tan solid residue was subject to recrystallization from benzene to give the desired product as tan crystals; yield 79 mg (72%). **Method 3.** A J. Young tube containing a toluene solution (0.5 mL) of [Ph-PNP]NiMe (4 mg, 0.006 mmol) and PhBr (14 mg, 0.089 mmol, 15 equiv) was immersed into an oil bath at 110 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which indicated the presence of [Ph-PNP]NiBr (86%) and [Ph-PNP]NiMe (14%) in 221 h. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature. ^1H NMR (C_6D_6, 499.767 MHz): δ 7.92 (m, 8, Ar), 7.62 (m, 2, Ar), 6.99 (m, 14, Ar), 6.84 (t, 2, Ar), 6.35 (t, 2, Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 23.72. $^{31}P\{^1H\}$ NMR (CH_3COCH_3, 80.953 MHz): δ 24.31. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 80.95 MHz): δ 23.50. $^{31}P\{^1H\}$ NMR (toluene, 121.42 MHz): δ 23.46. $^{31}P\{^1H\}$ NMR (THF, 121.42 MHz): δ 23.18. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.68 MHz): δ 163.14 (t, J_{CP} = 14.58 Hz, C), 135.25 (s, CH), 134.56 (t, J_{CP} = 5.9 Hz, CH), 132.41 (s, CH), 130.97 (s, CH), 130.89 (t, J_{CP} = 24.57 Hz, C), 129.23 (t, J_{CP} = 5.03 Hz, CH), 124.37 (t, J_{CP} = 23.19 Hz, C), 118.58 (s, CH), 117.71 (t, J_{CP} = 4.96 Hz, CH). Anal. Calcd for $C_{36}H_{28}BrNNiP_2$: C, 64.04; H, 4.18; N, 2.07. Found: C, 64.51; H, 4.33; N, 2.12.

Synthesis of [Ph-PNP]NiI. Method 1. The experiment was conducted under aerobic condition. At room temperature, an acetone solution (8 mL) of NaI (62 mg, 0.41 mmol, 2.6 equiv) was added to a green solution of [Ph-PNP]NiCl (100 mg, 0.159 mmol) dissolved in acetone (20 mL). Upon addition, the reaction solution became red in color and a considerable amount of a red solid formed. After being stirred at room temperature for 16 h, the reaction mixture was evaporated to dryness under reduced pressure. The solid residue was extracted with CH_2Cl_2 (10 mL) and filtered to remove the remaining solid halides. Solvent was removed in vacuo to yield the desired product as a brick-red solid; yield 102 mg (89%). **Method 2.** A J. Young tube containing a toluene solution (0.5 mL) of [Ph-PNP]NiMe (4 mg, 0.006 mmol) and PhI (36 mg, 0.176 mmol, 29 equiv) was immersed into an oil bath at 110 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which indicated the presence of [Ph-PNP]NiI (80%) and [Ph-PNP]NiPh (20%) in 1 h. ^1H NMR (C_6D_6, 500 MHz): δ 7.91 (m, 6, Ar), 7.64 (m, 2, Ar), 6.99 (m, 16, Ar), 6.86 (t, 2, Ar), 6.34 (t, 2, Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 33.09. $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ 32.19. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 121.42 MHz): δ 32.37. $^{31}P\{^1H\}$ NMR (toluene, 80.95 MHz): δ 32.76. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.68 MHz): δ 162.79 (t, J_{CP} = 14.14 Hz, C), 135.38 (s, CH), 134.84 (s, CH), 132.44 (s, CH), 131.47 (t, J_{CP} = 25.01 Hz, C), 131.00 (s, CH), 129.12 (s, CH), 125.53 (t, J_{CP} = 22.69 Hz, C), 118.67 (s, CH), 117.32 (s, CH). Anal. Calcd for $C_{36}H_{28}INNiP_2$: C, 59.87; H, 3.91; N, 1.94. Found: C, 60.48; H, 4.29; N, 1.73.

Synthesis of [^{i}Pr-PNP]NiCl. Solid $NiCl_2$(DME) (45.6 mg, 0.21 mmol) was suspended in THF (3 mL) and cooled to −35 °C. To this was added dropwise a prechilled solution of [^{i}Pr-PNP]Li(THF) (100 mg, 0.21 mmol) in THF (3 mL) at −35 °C. Upon addition, the reaction solution became emerald in color. The reaction mixture was stirred at room temperature overnight. All volatiles were removed in vacuo. The solid residue was triturated with pentane (3 mL × 2) and extracted with toluene (6 mL). The toluene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure, affording the product as a green solid; yield 96 mg (93%). Emerald crystals suitable for X-ray diffraction analysis were grown from a concentrated THF/Et_2O (ca. 1:9) solution at −35 °C; yield 81 mg (84%). ^1H NMR (C_6D_6, 500 MHz): δ 7.55 (d, 2, Ar), 6.97 (br s, 2, Ar), 6.88 (t, 2, Ar), 6.43 (t, 2, Ar), 2.21 (m, 4, C*H*Me$_2$), 1.50 (dt, 12, CH*Me*$_2$), 1.21 (dt, 12, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 34.68. $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ 35.17. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 164.45 (t, J_{CP} = 13.7, C), 132.53 (s, CH), 131.71 (s, CH), 121.17 (t, J_{CP} = 18.4, C), 117.29 (t, J_{CP} = 5.5, CH), 117.25 (t, J_{CP} = 2.6, CH), 24.32 (t, J_{CP} = 11.9, *C*HMe$_2$), 18.90 (s, CH*Me*$_2$), 18.00 (s, CH*Me*$_2$). Anal. Calcd for $C_{24}H_{36}ClNNiP_2$: C, 58.28; H, 7.34; N, 2.83. Found: C, 58.05; H, 7.35; N, 2.78.

Synthesis of [Cy-PNP]NiCl. Solid $NiCl_2$(DME) (34 mg, 0.16 mmol) was suspended in THF (3 mL) and cooled to −35 °C. To this was added dropwise a prechilled solution of [Cy-PNP]Li(THF) (100 mg, 0.16 mmol) in THF (3 mL) at −35 °C. Upon addition, the reaction solution became emerald in color. The reaction mixture was stirred at room temperature for 7 h. All volatiles were removed in vacuo. The solid residue was triturated with pentane (3 mL × 2) and extracted with toluene (5 mL). The toluene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure, affording the product as a green solid; yield 860 mg (85%). ^1H NMR (C_6D_6, 500 MHz): δ 7.62 (d, 2, Ar), 7.13 (m, 2, Ar), 6.91 (t, 2, Ar), 6.47 (t, 2, Ar), 2.61 (d, 4, Cy), 2.24 (m, 4, Cy), 1.97 (m, 8, Cy), 1.86 (m, 4, Cy), 1.70 (m, 4, Cy), 1.62 (m, 4, Cy), 1.51 (m, 4, Cy), 1.22 (m, 4, Cy), 1.10 (m, 8, Cy). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 26.77. $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ 27.58. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 164.62 (t, J_{CP} = 13.7, C), 132.71 (s, CH), 131.60 (s, CH), 121.59 (t, J_{CP} = 19.4, C), 117.30 (t, J_{CP} = 5.5, CH), 117.29 (t, J_{CP} = 2.6, CH), 33.81 (t, $^1J_{CP}$ = 10.9, PCH), 29.02 (s, CH_2), 28.42 (s, CH_2), 27.72 (t, $^2J_{CP}$ = 6.4, CH_2), 27.57 (t, $^2J_{CP}$ = 5.4, CH_2), 26.75 (s, CH_2). Anal. Calcd for $C_{36}H_{52}ClNNiP_2$: C, 66.02; H, 8.00; N, 2.14. Found: C, 65.73; H, 8.14; N, 2.06.

Synthesis of [Ph-PNP]Ni(*n*-hexyl). Method 1. Solid [Ph-PNP]-NiCl (50 mg, 0.08 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this was added *n*-hexylmagnesium chloride (0.04 mL, 2 M in diethyl ether, 0.08 mmol) dropwise. Upon addition, the green solution became red in color. The reaction mixture was stirred at room temperature for 10 min, and 1,4-dioxane (0.02 mL, 0.22 mmol) was added. The solid thus precipitated was removed by filtration through a pad of Celite from the reaction solution, which was then evaporated to dryness under reduced pressure and triturated with pentane (2 mL × 2) to afford the product as a red solid; yield 53 mg (100%). **Method 2.** 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 $^{31}P\{^1H\}$ NMR spectroscopy, which showed quantitative formation of [Ph-PNP]Ni(*n*-hexyl) in 1 day. ^1H NMR (C_6D_6, 500 MHz): δ 7.780 (m, 10, Ar), 7.200 (m, 2, Ar), 7.039 (m, 12, Ar), 6.965 (t, 2, Ar), 6.442 (t, 2, Ar), 1.116 (t, 2, CH_2), 0.993−1.097 (m, 4, CH_2), 0.945 (m, 4, CH_2), 0.753 (t, 3, CH_3). $^{31}P\{^1H\}$ NMR (toluene, 80.953 MHz): δ 26.533. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 26.782.$^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 163.576 (t, J_{CP} = 13.70, C), 135.444 (s, CH), 135.149 (t, J_{CP} = 6.03, CH), 133.840 (t, J_{CP} = 20.99, C), 133.297 (s, CH), 131.409 (s, CH), 130.148 (t, J_{CP} = 23.76, CH), 126.510 (t, J_{CP} = 22.88, C), 118.017 (t, J_{CP} = 3.14, CH), 117.372 (t, J_{CP} = 5.03, CH), 36.155 (s, CH_2), 33.275 (s, CH_2), 32.003 (s, CH_2), 24.246 (s, CH_2), 15.743

(s, CH_3), 6.718 (t, $^2J_{CP}$ = 18.85, Ni*C*H_2). Anal. Calcd for $C_{42}H_{41}NNiP_2$: C, 74.14; H, 6.07; N, 2.06. Found: C, 74.50; H, 6.04; N, 1.59.

Synthesis of [*i*Pr-PNP]NiMe. Solid [*i*Pr-PNP]NiCl (100 mg, 0.2 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this was added MeMgCl (0.07 mL, 3 M in THF, 0.2 mmol) dropwise. Upon addition, the green solution became brownish-red in color. The reaction solution was naturally warmed to room temperature with stirring for 1 h and evaporated to dryness under reduced pressure. The solid residue was triturated with pentane (2 mL × 2), and the product was extracted with toluene (4 mL). The toluene solution was filtered through a pad of Celite and evaporated to dryness to afford the product as a red solid; yield 87 mg (91%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.77 (d, 2, Ar), 7.09 (m, 2, Ar), 7.01 (t, 2, Ar), 6.50 (t, 2, Ar), 2.12 (m, 4, C*H*Me$_2$), 1.25 (dd, 12, CH*Me*$_2$), 1.12 (dd, 12, CH*Me*$_2$), −0.31 (t, 3, $^3J_{HP}$ = 9.0, NiMe). ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 35.31. ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 35.47. ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 163.94 (t, J_{CP} = 12.70, C), 132.45 (s, CH), 131.52 (s, CH), 122.24 (t, J_{CP} = 18.60, C), 116.01 (t, J_{CP} = 4.90, CH), 115.84 (t, J_{CP} = 2.89, CH), 24.18 (t, J_{CP} = 11.69, *C*HMe$_2$), 19.24 (t, J_{CP} = 2.45, CH*Me*$_2$), 18.34 (s, CH*Me*$_2$), −25.41 (t, $^2J_{CP}$ = 25.39, NiMe). Anal. Calcd for $C_{25}H_{39}NNiP_2$: C, 63.32; H, 8.29; N, 2.95. Found: C, 62.79; H, 8.33; N, 2.87.

Synthesis of [*i*Pr-PNP]NiEt. Solid [*i*Pr-PNP]NiCl (59 mg, 0.12 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this green solution was added EtMgCl (0.06 mL, 2 M in diethyl ether, 0.12 mmol) dropwise. Upon naturally warming to room temperature with stirring, the reaction solution gradually became brownish-red in color in 15 min. 1,4-Dioxane (0.01 mL, 0.12 mmol) was added. The solid thus precipitated was removed by filtration through a pad of Celite. All volatiles were removed in vacuo, and the solid residue was triturated with pentane (1 mL) to give the product as a red powder; yield 45 mg (78%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.71 (d, 2, Ar), 7.03 (m, 2, Ar), 6.99 (t, 2, Ar), 6.49 (t, 2, Ar), 2.17 (m, 4, C*H*Me$_2$), 1.30 (dd, 12, CH*Me*$_2$), 1.23 (t, 3, $^3J_{HH}$ = 7.5, NiCH$_2$C*H*$_3$), 1.10 (dd, 12, CH*Me*$_2$), 0.84 (tq, 2, $^3J_{HP}$ = 11, $^3J_{HH}$ = 7.5, NiC*H*$_2$CH$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 32.07. ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 32.00. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 163.77 (t, J_{CP} = 12.3, C), 132.42 (s, CH), 131.49 (s, CH), 121.84 (t, J_{CP} = 18.4, C), 115.96 (t, J_{CP} = 4.5, CH), 115.73 (t, J_{CP} = 2.8, CH), 24.01 (t, $^1J_{CP}$ = 10.9, *C*HMe$_2$), 19.25 (t, $^2J_{CP}$ = 2.3, CH*Me*$_2$), 18.04 (s, CH*Me*$_2$), 17.01 (t, $^3J_{CP}$ = 2.3, NiCH$_2$*C*H$_3$), −14.97 (t, $^2J_{CP}$ = 22.5, Ni*C*H$_2$CH$_3$). Anal. Calcd for $C_{26}H_{41}NNiP_2$: C, 63.96; H, 8.46; N, 2.87. Found: C, 63.94; H, 8.66; N, 2.85.

Synthesis of [*i*Pr-PNP]Ni(*n*-Bu). Solid [*i*Pr-PNP]NiCl (59 mg, 0.12 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this green solution was added *n*-BuMgCl (0.06 mL, 2 M in diethyl ether, 0.12 mmol) dropwise. Upon naturally warming to room temperature with stirring, the reaction solution gradually became brownish-red in color in 15 min. 1,4-Dioxane (0.01 mL, 0.12 mmol) was added. The solid thus precipitated was removed by filtration through a pad of Celite. All volatiles were removed in vacuo to give the product as a red powder; yield 59 mg (95%). Red crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.71 (d, 2, Ar), 7.04 (m, 2, Ar), 6.99 (t, 2, Ar), 6.49 (t, 2, Ar), 2.19 (m, 4, C*H*Me$_2$), 1.64 (m, 2, NiCH$_2$(C*H*$_2$)$_2$CH$_3$), 1.49 (m, 2, NiCH$_2$(C*H*$_2$)$_2$CH$_3$), 1.31 (dd, 12, CH*Me*$_2$), 1.10 (dd, 12, CH*Me*$_2$), 1.08 (t, 3, NiCH$_2$(CH$_2$)$_2$C*H*$_3$), 0.76 (m, 2, NiCH$_2$). ^{31}P-{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 32.50. ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 32.12. ^{31}P{^{1}H} NMR (pentane, 80.95 MHz): δ 31.82. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 163.79 (t, J_{CP} = 11.8, C), 132.41 (s, CH), 131.50 (s, CH), 121.85 (t, J_{CP} = 18.4, C), 115.99 (t, J_{CP} = 4.5, CH), 115.77 (t, J_{CP} = 3.6, CH), 35.14 (s, NiCH$_2$-(*C*H$_2$)$_2$CH$_3$), 28.47 (s, NiCH$_2$(*C*H$_2$)$_2$CH$_3$), 24.11 (t, $^1J_{CP}$ = 10.9, *C*HMe$_2$), 19.27 (t, $^2J_{CP}$ = 2.8, CH*Me*$_2$), 18.05 (s, CH*Me*$_2$), 14.62 (s, NiCH$_2$(CH$_2$)$_2$*C*H$_3$), −6.50 (t, $^2J_{CP}$ = 22.0, Ni*C*H$_2$). Anal. Calcd for $C_{28}H_{45}NNiP_2$: C, 65.14; H, 8.78; N, 2.71. Found: C, 64.95; H, 8.76; N, 2.68.

Synthesis of [Cy-PNP]NiMe. Solid [Cy-PNP]NiCl (39 mg, 0.06 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this was added MeMgCl (0.02 mL, 3 M in THF, 0.06 mmol) dropwise. Upon addition, the green solution became red in color. The reaction mixture was stirred at room temperature for 30 min, evaporated to dryness under reduced pressure, and triturated with pentane (2 mL × 2). The product was extracted with toluene (2 mL) and filtered through a pad of Celite. The toluene solution was evaporated to dryness and triturated with pentane (2 mL × 2) to afford the product as an orange solid; yield 36 mg (92%). 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 7.84 (d, 2, Ar), 7.24 (m, 2, Ar), 7.04 (t, 2, Ar), 6.54 (t, 2, Ar), 2.33 (d, 4, Cy), 2.14 (m, 4, Cy), 1.84 (m, 4, Cy), 1.75 (m, 4, Cy), 1.64 (m, 12, Cy), 1.53 (m, 4, Cy), 1.20 (m, 4, Cy), 1.07 (qt, 8, Cy), −0.13 (t, 3, $^3J_{HP}$ = 9, NiMe). ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 27.99. ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 28.16.^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 164.08 (t, J_{CP} = 12.82, C), 132.62 (s, CH), 131.43 (s, CH), 122.65 (t, J_{CP} = 18.35, C), 116.02 (t, J_{CP} = 5.02, CH), 115.89 (t, J_{CP} = 3.14, CH), 34.05 (t, $^1J_{CP}$ = 6.53, CH), 29.69 (s, CH$_2$), 28.79 (s, CH$_2$), 27.96 (t, J_{CP} = 6.41, CH$_2$), 27.71 (t, J_{CP} = 5.03, CH$_2$), 26.95 (s, CH$_2$), −23.60 (t, J_{CP} = 24.76, NiCH$_3$). Anal. Calcd for $C_{37}H_{55}NNiP_2$: C, 70.04; H, 8.74; N, 2.21. Found: C, 70.48; H, 9.25; N, 1.78.

Synthesis of [Cy-PNP]NiEt. Solid [Cy-PNP]NiCl (100 mg, 0.15 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this was added EtMgCl (0.08 mL, 2.0 M in diethyl ether, 0.16 mmol) dropwise. The green reaction solution became brownish-red in color upon addition. The reaction mixture was stirred at room temperature for 2 h and filtered through a pad of Celite, which was further washed with toluene (2 mL) until the washings were colorless. The toluene filtrate was evaporated to dryness under reduced pressure. The solid residue was triturated with pentane (2 mL × 2) to afford the product as a brownish-red solid; yield 81 mg (82%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.81 (d, 4, Ar), 7.20 (m, 2, Ar), 7.02 (t, 2, Ar), 6.53 (t, 2, Ar), 2.41 (d, 4, Cy), 2.20 (tt, 4, Cy), 1.84 (m, 4, Cy), 1.67 (m, 18, Cy), 1.52 (d, 4, Cy), 1.41 (t, 3, CH$_2$C*H*$_3$), 1.20 (qt, 4, Cy), 1.09 (m, 6, Cy), 1.03 (m, 2, $^3J_{HP}$ = 11, NiCH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 24.59. ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 24.67. ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 163.99 (t, J_{CP} = 12.3, C), 132.55 (s, CH), 131.40 (s, CH), 122.29 (t, J_{CP} = 18.4, C), 116.02 (t, J_{CP} = 4.7, CH), 115.80 (t, J_{CP} = 3.1, CH), 34.01 (t, J_{CP} = 10.9, PCH), 29.67 (s, CH$_2$), 28.41 (s, CH$_2$), 28.10 (t, J_{CP} = 6.0, CH$_2$), 27.72 (t, J_{CP} = 5.0, CH$_2$), 26.87 (s, CH$_2$), 17.10 (s, NiCH$_2$*C*H$_3$), −13.24 (t, J_{CP} = 22.4, Ni*C*H$_2$). Anal. Calcd for $C_{38}H_{57}NNiP_2$: C, 70.38; H, 8.86; N, 2.16. Found: C, 69.95; H, 8.56; N, 1.94.

Synthesis of [Cy-PNP]Ni(*n*-Bu). Solid [Cy-PNP]NiCl (90 mg, 0.14 mmol) was dissolved in toluene (3 mL) and cooled to −35 °C. To this was added *n*-BuMgCl (0.07 mL, 2.0 M in diethyl ether, 0.14 mmol) dropwise. The green reaction solution became brownish-red in color upon addition. The reaction mixture was stirred at room temperature for 2 h and filtered through a pad of Celite, which was further washed with toluene (2 mL) until the washings were colorless. The toluene filtrate was evaporated to dryness under reduced pressure. The solid residue was triturated with pentane (2 mL × 2) to afford the product as a brownish-red solid; yield 70 mg (75%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.80 (d, 4, Ar), 7.21 (m, 2, Ar), 7.02 (t, 2, Ar), 6.53 (t, 2, Ar), 2.41 (d, 4, Cy), 2.20 (tt, 4, Cy), 1.84 (m, 4), 1.66 (m, 18), 1.52 (d, 4), 1.22 (m, 4), 1.17 (t, 3, CH$_3$), 1.05 (m, 8), 0.92 (m, 4); the complete assignment for the

upfield aliphatic signals was hampered due to the overlap of *n*-Bu with cyclohexyl groups. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 25.08. $^{31}P\{^1H\}$ NMR (toluene, 80.953 MHz): δ 24.65. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 163.96 (t, J_{CP} = 12.3, C), 132.54 (s, CH), 131.41 (s, CH), 122.38 (t, J_{CP} = 18.9, C), 116.01 (t, J_{CP} = 4.5, CH), 115.80 (t, J_{CP} = 3.1, CH), 35.01 (s, $NiCH_2(CH_2)_2$-CH_3), 34.05 (t, J_{CP} = 10.4, PCH), 29.68 (s, CH_2), 28.70 (s, $NiCH_2$-$(CH_2)_2CH_3$), 28.42 (s, CH_2), 28.12 (t, J_{CP} = 5.9, CH_2), 27.73 (t, J_{CP} = 4.5, CH_2), 26.90 (s, CH_2), 14.70 (s, $NiCH_2(CH_2)_2CH_3$), −4.67 (t, J_{CP} = 22.2, $NiCH_2$). Anal. Calcd for $C_{40}H_{61}NNiP_2$: C, 71.01; H, 9.09; N, 2.07. Found: C, 71.66; H, 9.75; N, 1.54.

General Procedures for the Kumada Reactions Outlined in Table 6. A Schlenk flask was charged with aryl halide (1.0 equiv), Grignard reagent (1.1 equiv), [R-PNP]NiCl (1.0 mg for each single experiment), solvent (2 mL), and a magnetic stir bar. The flask was capped with a glass stopper and stirred at room temperature or heated in an oil bath at 60 °C with stirring for a specified period of time. After being cooled to room temperature, the reaction mixture was quenched with deionized water and the product was extracted with diethyl ether. The diethyl ether solution was separated from the aqueous layer, dried over $MgSO_4$, and subject to GC-MS analysis.

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Supporting Information Available: X-ray crystallographic data in CIF format for [Cy-PNP]Li(OEt_2), [Ph-PNP]NiCl, [^{i}Pr-PNP]NiCl, [Ph-PNP]NiMe, [^{i}Pr-PNP]NiMe, [Cy-PNP]NiMe, [Ph-PNP]Ni-(*n*-Bu), [^{i}Pr-PNP]Ni(*n*-Bu), [Ph-PNP]$NiCH_2SiMe_3$, and [Ph-PNP]-NiBr. This material is available free of charge via the Internet at http://pubs.acs.org.

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