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PAPER

A terminal nickel(II) anilide complex featuring an unsymmetrically substituted amido pincer ligand: synthesis and reactivity†

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This work describes preparation and reaction chemistry of a terminal nickel(II) anilide complex supported by an unsymmetrically substituted diarylamido diphosphine ligand, $[N(o\text{-}C_6H_4PPh_2)(o\text{-}C_6H_4P^iPr_2)]^-$ ([Ph-PNP-^{i}Pr]$^-$). Treatment of $NiCl_2$(DME) with H[Ph-PNP-^{i}Pr] in THF at room temperature produced [Ph-PNP-^{i}Pr]NiCl as green crystals in 82% yield. Salt metathesis of [Ph-PNP-^{i}Pr]NiCl with LiNHPh(THF) in THF at −35 °C generated cleanly [Ph-PNP-^{i}Pr]NiNHPh as a greenish blue solid. The anilide complex deprotonates protic (*e.g.*, PhOH and PhSH) and aprotic (*e.g.*, trimethylsilylacetylene, phenylacetylene, and acetonitrile) acids in benzene at room temperature to give quantitatively [Ph-PNP-^{i}Pr]NiX (X = OPh, SPh, C≡CSiMe$_3$, C≡CPh, CH_2CN). In addition, [Ph-PNP-^{i}Pr]NiNHPh also behaves as a nucleophile to react with acetyl chloride to yield [Ph-PNP-^{i}Pr]NiCl and *N*-phenylacetamide quantitatively. Carbonylation of [Ph-PNP-^{i}Pr]NiNHPh with carbon monoxide affords cleanly the carbamoyl derivative [Ph-PNP-^{i}Pr]Ni[C(O)NHPh]. The relative bond strengths of Ni–E in [Ph-PNP-^{i}Pr]NiEPh (E = NH, O, S, C≡C) are assessed and discussed.

Introduction

Late transition metal amides are receiving increasing attention due to their important roles as intermediates in a number of biological and industrially relevant chemical transformations such as catalytic hydroamination and C–N coupling reactions, *etc*.[1–6] Understanding the nature and reactivity preferences of a non-dative metal-amide bond is essential for the rational design of catalytically active species. Due to the presence of inherent dπ–pπ repulsion,[6,7] late transition-metal amides are often relatively destabilized and thus more reactive than their organometallic analogues. Preparation and isolation of these species are therefore valuable in view of the elucidation of their reactivity preferences. Notably, the palladium catalyzed C–N bond forming reactions have evolved as a powerful tool for organic synthesis.[8–11] We are currently exploring reaction chemistry involving metal complexes containing *o*-phenylene-derived amido phosphine ligands.[12–18] In particular, the reactivity of $[N(o\text{-}C_6H_4PR_2)_2]^-$ ([R-PNP]$^-$; R = Ph, ^{i}Pr, Cy) complexes has been shown to be a function of the identity of their phosphorus substituents.[19–22] We became interested in unsymmetrically substituted pincer complexes due partly to the recent discoveries of their unusual reactivity, particularly those built on a lutidine or aryl skeleton.[23–26] We report herein the preparation and reactivity studies of a nickel anilide complex containing an unsymmetrically substituted $[N(o\text{-}C_6H_4PPh_2)(o\text{-}C_6H_4P^iPr_2)]^-$ ([Ph-PNP-^{i}Pr]$^-$) ligand, aiming to demonstrate its divergent reactivity features as both a base and a nucleophile and to assess the relative strengths of Ni–C and Ni–heteroatom bonds. The incorporation of unsymmetric substituents in the derived pincer complexes is beneficial in view of the assessment of their solution structures by the magnitude of coupling constants arisen between the two chemically inequivalent phosphorus donors involved. Insights regarding the reactivity of [Ph-PNP-^{i}Pr]NiNHPh are discussed.

Results and discussion

Synthesis of the anilide complex

The reaction of $NiCl_2$(DME)[27] with H[Ph-PNP-^{i}Pr][20] in THF at room temperature generated, after standard workup and crystallization procedures, green crystals of [Ph-PNP-^{i}Pr]NiCl in 82% yield. Interestingly, the reaction is complete in 10 min and the liberated HCl byproduct does not affect the production of the desired chloride complex. Subsequent metathetical reaction of [Ph-PNP-^{i}Pr]NiCl with LiNHPh(THF) in THF at −35 °C afforded [Ph-PNP-^{i}Pr]NiNHPh as a greenish blue solid in 90% yield. These

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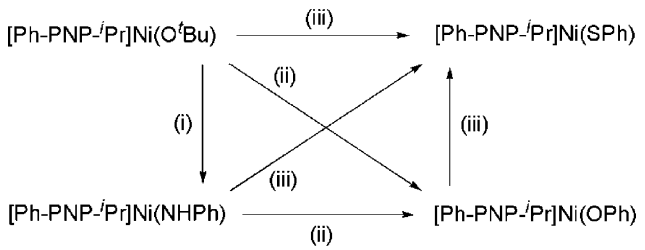
† Electronic supplementary information (ESI) available: DFT geometry optimized structures, bond distances, bond angles, and coordinates of [Ph-PNP-^{i}Pr]NiEPh (E = NH, O, S, C≡C), energy changes for protonolysis reactions involving these molecules, and contour plot of HOMO of [Ph-PNP-^{i}Pr]NiNHPh. CCDC reference number 806151. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10191a

compounds have been fully characterized by multi-nuclear NMR spectroscopy (*vide infra*), combustion analysis, and in the case of the chloride, by X-ray crystallography.

Reactivity studies of [Ph-PNP-^{i}Pr]NiNHPh

It has been documented that late transition-metal amides may, in some cases, be strongly basic due to highly polarized M–N bonds.[1] The anilide complex [Ph-PNP-^{i}Pr]NiNHPh deprotonates phenol and thiophenol readily in benzene solutions at room temperature to yield quantitatively [Ph-PNP-^{i}Pr]NiEPh (E = O, S) and aniline as evidenced by solution NMR studies. The identity of the derived phenolate and thiophenolate complexes was confirmed by independent preparation of these molecules from salt metathesis of [Ph-PNP-^{i}Pr]NiCl with NaEPh. In contrast, the anilide fails to convert to the *tert*-butoxide [Ph-PNP-^{i}Pr]NiO^{t}Bu upon reaction with *tert*-butanol under similar conditions (^{1}H and ^{31}P NMR evidence). Instead, the *tert*-butoxide complex, prepared by treating [Ph-PNP-^{i}Pr]NiCl with NaO^{t}Bu, reacts with aniline in benzene at room temperature to give [Ph-PNP-^{i}Pr]NiNHPh and *tert*-butanol quantitatively. Scheme 1 summarizes the protonolysis reactions involving [Ph-PNP-^{i}Pr]NiO^{t}Bu, [Ph-PNP-^{i}Pr]NiNHPh, [Ph-PNP-^{i}Pr]NiOPh and [Ph-PNP-^{i}Pr]NiSPh with appropriate protic sources. We note that these reactions are essentially irreversible or reversible but having an extremely large equilibrium constant, as no protonolysis was found when reverse reactions were attempted, even in the presence of an excess amount of appropriate protic sources at various temperatures. This phenomenon is notably different from what was reported for Cp*Ni(PMe$_3$)OTol,[28]

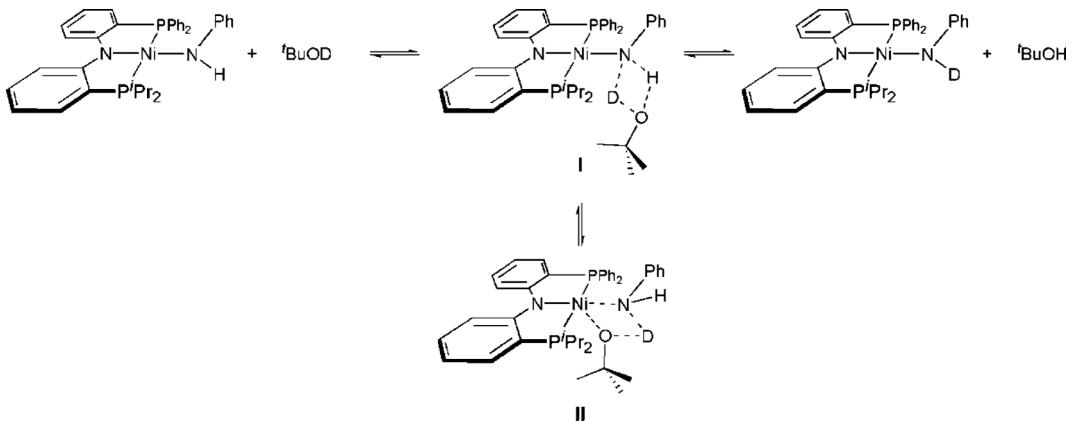


Reagents: i, $PhNH_2$; ii, PhOH; iii, PhSH

Scheme 1

which undergoes reversible exchange with *p*-toluidine. The basic strengths of these amido phosphine derived species thus follow the order of [Ph-PNP-^{i}Pr]NiO^{t}Bu > [Ph-PNP-^{i}Pr]NiNHPh > [Ph-PNP-^{i}Pr]NiOPh > [Ph-PNP-^{i}Pr]NiSPh, reminiscent of what was found for [Ph-PNP]$^{-}$ counterparts.[22] Attempts to prepare the *tert*-butyl amide [Ph-PNP-^{i}Pr]NiNH^{t}Bu by either protonolysis of [Ph-PNP-^{i}Pr]NiNHPh with ^{t}BuNH$_2$ or salt metathesis of [Ph-PNP-^{i}Pr]NiCl with LiNH^{t}Bu were not successful. It is interesting to note that both [Ph-PNP]NiNH^{t}Bu and [Ph-PNP]NiO^{t}Bu were successfully synthesized by salt metathesis reactions whereas [^{i}Pr-PNP]NiNH^{t}Bu and [^{i}Pr-PNP]NiO^{t}Bu were not.[22] The successful isolation of [Ph-PNP-^{i}Pr]NiO^{t}Bu but not [Ph-PNP-^{i}Pr]NiNH^{t}Bu clearly emphasizes that the synthetic accessibility of complexes containing these π-donor ligands is a function of the amido phosphine ligands employed. The apparently higher stability of aryl- than alkyl-derived M–OR and M–NHR complexes was also found in other systems.[1]

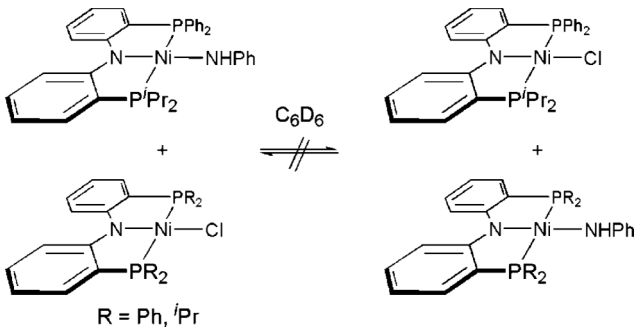
Though [Ph-PNP-^{i}Pr]NiO^{t}Bu was not produced upon protonolysis of [Ph-PNP-^{i}Pr]NiNHPh, addition of one equiv of ^{t}BuOD to a C_6D_6 solution of [Ph-PNP-^{i}Pr]NiNHPh at room temperature led to a decrease in N*H* integral by 33% in 1 h as indicated by the ^{1}H NMR spectrum. The ^{2}H NMR spectrum of the same reaction also shows the formation of [Ph-PNP-^{i}Pr]NiNDPh, indicating clearly H/D exchange occurs between nickel-bound anilide and *tert*-butanol. The exchange is reversible, as [Ph-PNP-^{i}Pr]NiNDPh re-converts to [Ph-PNP-^{i}Pr]NiNHPh in the presence of ^{t}BuOH. These results suggest the formation of a four-membered, hydrogen-bonded intermediate **I** (Scheme 2) in this exchange reaction, highlighting the strongly polarized nature of the nickel–anilide bond in [Ph-PNP-^{i}Pr]NiNHPh. The production of this hydrogen-bonded intermediate also implies that HOMO of [Ph-PNP-^{i}Pr]NiNHPh resides at the terminal anilide ligand. The formation of [Ph-PNP-^{i}Pr]NiOPh and [Ph-PNP-^{i}Pr]NiSPh instead of [Ph-PNP-^{i}Pr]NiO^{t}Bu upon protonolysis of [Ph-PNP-^{i}Pr]NiNHPh is thus apparently governed by thermodynamic reasons that involve the relative bond energies of Ni–X (X = O^{t}Bu, NHPh, OPh, SPh) and H–X. On the basis of these results, we suggest that the successful transformations of [Ph-PNP-^{i}Pr]NiNHPh to [Ph-PNP-^{i}Pr]NiEPh (E = O, S) proceed by a mechanism involving hydrogen atom transfer *via* an intermediate conceptually similar to **II** as depicted in Scheme 2. A mechanistic



Scheme 2

alternative involving proton transfer should be less likely in view of the formation of an ion pair {[Ph-PNP-^{i}Pr]Ni(NH_2Ph)}{EPh} in benzene. We note that the protonolysis solutions remain clear and homogeneous throughout the reactions.

Mechanistically, the protonolysis may also proceed *via* an initial Ni–N heterolysis to give cationic {[Ph-PNP-^{i}Pr]Ni}$^+$ and anionic [PhNH]$^-$. This possibility is rather low due to the considerably rapid reaction rates observed for these protonolysis reactions conducted in a non-polar medium. Crossover experiments involving [Ph-PNP-^{i}Pr]NiNHPh with [Ph-PNP]NiCl[22] or [^{i}Pr-PNP]NiCl[22] in benzene at room temperature showed no anilide/chloride exchange (Scheme 3). These observations certainly argue against the involvement of an initial ionization pathway.



Scheme 3

Though [Ph-PNP-^{i}Pr]NiO^{t}Bu is apparently more reactive than [Ph-PNP-^{i}Pr]NiNHPh, we found that the latter complex is much easier to be manipulated for reactivity exploration and thus chose to examine further the reactivity preferences of this derivative. Its reactions with extremely weak aprotic acids were also attempted. Addition of trimethylsilylacetylene or phenylacetylene to benzene solutions of [Ph-PNP-^{i}Pr]NiNHPh at room temperature produces quantitatively the corresponding acetylide complexes as a red solid. The anilide also deprotonates acetonitrile cleanly under similar conditions to yield the cyanomethyl complex [Ph-PNP-^{i}Pr]NiCH_2CN. On the basis of these reactions, it is also interesting to point out that these organonickel complexes appear not to react appreciably with the liberated aniline.

In addition to its inherent basic nature, the anilide complex is also a nucleophile. It reacts readily with acetyl chloride in THF at room temperature to produce [Ph-PNP-^{i}Pr]NiCl and *N*-phenylacetamide quantitatively on the basis of NMR and MS studies. Introduction of CO (1 atm) to a benzene solution of [Ph-PNP-^{i}Pr]NiNHPh at room temperature afforded the carbamoyl complex [Ph-PNP-^{i}Pr]Ni[C(O)NHPh] as a red solid in 82% yield. In [Ph-PNP-^{i}Pr]NiNHPh, the terminal Ni–N bond is thus apparently more reactive than that associated with the PNP pincer ligand. Though not unprecedented, carbon monoxide insertion into a late transition metal–amide bond is uncommon.[29,30] This carbamoyl complex is thermally stable; neither decarbonylation nor β-elimination was observed even at elevated temperatures (110 °C, 4 days, 40 mM in benzene).

Solution NMR studies

Table 1 summarizes selected NMR data for all derived complexes. In general, these compounds display solution C_s symmetry on the NMR timescale, reminiscent of what was observed for previously reported hydride and alkyl derivatives.[20] The coupling constants found for the two chemically inequivalent phosphorus donors are all consistent with a meridional coordination mode[7] for the tridentate amido diphosphine ligand. Interestingly, the $^2J_{PP}$ values of the anilide and other heteroatom-bound nickel complexes (318–358 Hz) are notably larger than those of organonickel derivatives (222–288 Hz),[20] a consequence that is likely reflective of the more electron-deficient nature of the metal due to higher electronegativity of the heteroatoms in the former. The anilide complex shows a diagnostic signal at −1.33 ppm in the ^{1}H NMR for N*H*Ph, which moves downfield to 6.89 ppm upon CO insertion. In principle, the H_α atoms in [Ph-PNP-^{i}Pr]Ni(CH_2CN) should be diastereotopic as what was found for [Ph-PNP-^{i}Pr]NiEt and [Ph-PNP-^{i}Pr]Ni(n-hexyl).[20] With the cylindrical cyano substituent at the C_α atom, rapid rotation about the Ni–C bond occurs readily and thus H_α atoms in [Ph-PNP-^{i}Pr]Ni(CH_2CN) become indistinguishable on the NMR timescale, exhibiting a doublet of doublets resonance in the ^{1}H NMR spectrum due to coupling with two inequivalent phosphorus donors.

Table 1 Selected NMR data for [Ph-PNP-^{i}Pr]NiX[a]

X	δ_{31P} (P^{i}Pr$_2$, PPh$_2$)	$^2J_{PP}$	$\delta_{H\alpha}$	$^3J_{PH\alpha}$
Cl	39.8, 16.3	331		
O^{t}Bu	24.2, 2.8	358		
NHPh	33.5, 10.0	356	−1.33	
OPh	33.7, 6.9	325		
SPh	38.2, 21.1	318		
C≡CSiMe$_3$	52.0, 28.8	281		
C≡CPh	50.1, 27.2	288		
CH_2CN	38.9, 27.5	272	0.71	9.5, 11.5
C(O)NHPh	42.8, 21.1	222		

[a] All spectra were recorded in C_6D_6 at room temperature, chemical shifts in ppm, coupling constants in hertz.

X-Ray crystal structure of [Ph-PNP-^{i}Pr]NiCl

Fig. 1 depicts the X-ray structure of [Ph-PNP-^{i}Pr]NiCl. Consistent with the solution NMR studies, the core geometry of [Ph-PNP-^{i}Pr]NiCl is best described as distorted square planar with the [Ph-PNP-^{i}Pr]$^-$ ligand being in a meridional coordination mode. The two phosphorus donors are *trans*-disposed with the P(2)–Ni(1)–P(1) angle of 167.88(7)°, which is sharper than that of [Ph-PNP-^{i}Pr]NiH (174.15(3)°)[20] but comparable to that of [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (165.65(9)°),[20] consistent with the steric repulsion arising from these formally anionic η^1-ligands. Though bearing different substituents at the phosphorus donors, the two Ni–P distances in [Ph-PNP-^{i}Pr]NiCl are virtually identical. The two *o*-phenylene rings are tilted with respect to the coordination plane so as to accommodate simultaneously two fused five-membered chelating rings and to minimize the steric repulsion between two CH moieties *ortho* to the amido nitrogen donor. The Ni–N distance of 1.888(5) Å is comparably shorter than those of [Ph-PNP-^{i}Pr]NiH (1.924(2) Å) and [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (1.961(6) Å),[20] consistent with the anticipated *trans* influence order of Cl < H < alkyl.

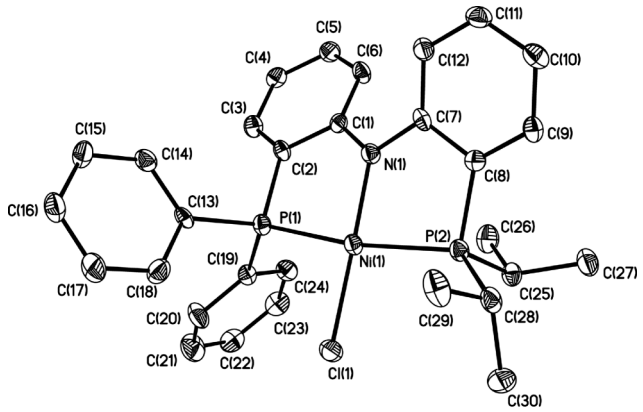


Fig. 1 Molecular structure of [Ph-PNP-^{i}Pr]NiCl with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two independent molecules and two unbound toluenes; only one [Ph-PNP-^{i}Pr]NiCl is shown for clarity. Selected bond distances (Å) and angles (°): Cl(1)–Ni(1) 2.1691(18), N(1)–Ni(1) 1.888(5), Ni(1)–P(2) 2.1871(18), Ni(1)–P(1) 2.1877(18); N(1)–Ni(1)–Cl(1) 178.33(16), N(1)–Ni(1)–P(2) 85.06(15), Cl(1)–Ni(1)–P(2) 95.50(7), N(1)–Ni(1)–P(1) 85.42(15), Cl(1)–Ni(1)–P(1) 94.23(7), P(2)–Ni(1)–P(1) 167.88(7).

Density functional theory (DFT) studies

It has been well-documented[1,28,31–33] that the relative bond dissociation energies of L_nM–X and L_nM–Y may be assessed by equilibrium constants of reversible exchange reactions of the general type:

$$L_nM\text{–}X + H\text{–}Y \rightleftharpoons L_nM\text{–}Y + H\text{–}X,$$

using the known H–X and H–Y bond energies.[34] Given the difficulty of equilibrium constant determination of the protonolysis reactions described herein, we chose to employ DFT computations to probe the bond energy differences between [Ph-PNP-^{i}Pr]NiNHPh, [Ph-PNP-^{i}Pr]NiOPh, [Ph-PNP-^{i}Pr]NiSPh and [Ph-PNP-^{i}Pr]NiC≡CPh. As summarized in Table 2, DFT studies showed that these reactions are exothermic, with extremely large computed K_{eq} values, consistent with what is observed experimentally. More importantly, the Ni–OPh, Ni–SPh, and Ni–C≡CPh bond strengths are all stronger than Ni–NHPh. These results are also consistent with the acidity of aniline *vs*. phenol, thiophenol and phenylacetylene.[35] The trend that the Ni–S bond is thermodynamically favored over Ni–O, which is in turn favored over Ni–N, is reminiscent of what was found in Cp*Ni(PMe_3)X derivatives.[28] Interestingly, the bond strength difference between M–NHPh and M–C≡CPh estimated herein is similar to that acquired in studies employing Cp*Ru(PMe_3)$_2$X.[31] DFT analysis also confirms that HOMO of [Ph-PNP-^{i}Pr]NiNHPh is primarily composed of the pπ orbitals of the terminal anilide ligand (see ESI†), consistent with what is deduced from the reversible H/D exchange reaction depicted in Scheme 2.

Conclusions

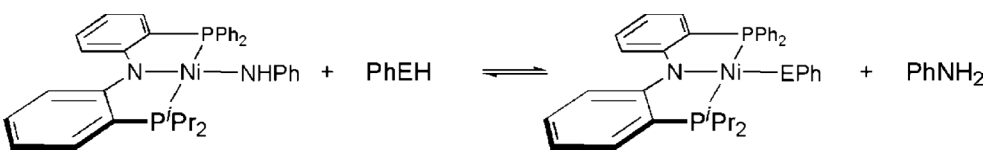
We have prepared a nickel(II) anilide complex of an unsymmetrically substituted PNP pincer ligand. Its divergent reactivity features in reactions with protic and aprotic acids and electrophiles are demonstrated. In particular, a series of π-donor ligated nickel complexes and organonickel derivatives are prepared. Of note is its highly basic strength, able to deprotonate extremely weak aprotic acids such as acetonitrile, and its high nucleophilicity to undergo CO insertion. Interestingly, a deuterium labeling study involving [Ph-PNP-^{i}Pr]NiNHPh and ^{t}BuOD revealed a reversible H/D exchange in spite of no production of [Ph-PNP-^{i}Pr]NiO^{t}Bu. The thermodynamic preferences regarding protonolysis of [Ph-PNP-^{i}Pr]NiEPh (E = NH, O, S, C≡C) were also elucidated by DFT computations. The Ni–N bond is relatively destabilized in comparison with Ni–O, Ni–S and Ni–C≡C.

Experimental

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. Compounds $NiCl_2$(DME),[27] H[Ph-PNP-^{i}Pr],[20] NaOPh,[22] and NaSPh[22] were prepared according to the procedures reported previously. LiNHPh(THF) was prepared by lithiation of aniline with one equiv. of *n*-BuLi in THF followed by evaporation of the reaction mixture. All other chemicals were obtained from commercial vendors and used as received. The NMR spectra were recorded on Varian Unity or Bruker AV 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. ^{13}C NMR spectra are referenced using the

Table 2 Relative bond energies of [Ph-PNP-^{i}Pr]NiEPh (E = NH, O, S, C≡C)



E	ΔH^a/kcal mol^{-1}	$K_{eq}{}^b$	rel D(Ni–E)/kcal mol^{-1}
NH	0	1	0
O	–10.2	3.2×10^7	7.2
S	–17.9	1.8×10^{13}	11.8
C≡C	–6.11	1.9×10^5	47.5

[a] Calculated by DFT. [b] Estimated from ΔG values (see ESI†) calculated by DFT.

residual solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms is based on the 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. With multiple attempts, we were unable to obtain satisfactory analysis for some complexes reported herein due likely to incomplete combustion of samples examined.

X-Ray crystallography

Data for [Ph-PNP-^{i}Pr]NiCl 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 SHELXL-97.[36] All full-weight non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. *Crystal data*: $C_{37}H_{40}ClNNiP_2$, M = 654.80, triclinic, space group $P\bar{1}$, a = 12.365(4), b = 15.097(5), c = 18.987(6) Å, α = 110.914(5), β = 92.567(7), γ = 91.650(6)°, V = 3303.7(18) Å^3, T = 200(2)K, Z = 4, μ(Mo-Kα) = 0.792 mm^{-1}, 33153 reflections measured, 13305 unique (R_{int} = 0.1485) which were used in all calculations. Final $R1$ [$I > 2\sigma(I)$] = 0.0616, $wR2$ [$I > 2\sigma(I)$] = 0.1268, R_1 (all data) = 0.1945, wR_2 (all data) = 0.1795, GOF (on F^2) = 0.897, CCDC 806151.

DFT computations

The three-parameter hybrid of exact exchange and Becke's exchange energy functional[37] and Lee–Yang–Parr's gradient-corrected correlation energy functional[38] (B3LYP) were used. All optimized structures were verified to be genuine minima on the potential energy surface *via* vibrational frequency analysis. The 6-31G basis sets were used for C, H, O, N and the LANL2DZ effective core potential plus basis functions for Ni, P, S.[39] The Gaussian09 suite of programs was applied in this study.[40]

Synthesis of [Ph-PNP-^{i}Pr]NiCl

THF (2 mL) was added to a solid mixture of H[Ph-PNP-^{i}Pr] (100 mg, 0.213 mmol) and $NiCl_2$(DME) (59 mg, 0.213 mmol) at room temperature. The reaction mixture was stirred at room temperature for 10 min. All volatiles were removed *in vacuo*. The solid residue was dissolved in a minimal amount of toluene (2 mL) and pentane (20 drops) was layered on top. The solution was cooled to −35 °C to afford the product as green crystals suitable for X-ray diffraction analysis; yield 98 mg (82%). ^1H NMR (C_6D_6, 500 MHz) δ 7.98 (m, 4, Ar), 7.62 (dd, 1, Ar), 7.53 (dd, 1, Ar), 7.07 (t, 1, Ar), 7.03 (m, 6, Ar), 6.95 (t, 1, Ar), 6.86 (m, 2, Ar), 6.43 (t, 1, Ar), 6.36 (t, 1, Ar), 2.20 (m, 2, C*H*Me$_2$), 1.48 (dd, 6, CH*Me*$_2$), 1.15 (dd, 6, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz) δ 39.78 (d, J_{PP} = 330.78, P^{i}Pr$_2$), 16.32 (d, J_{PP} = 330.78, PPh$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz) δ 163.94 (dd, J_{CP} = 3.77, J_{CP} = 22.46, C), 163.67 (dd, J_{CP} = 2.76, J_{CP} = 26.98, C), 135.08 (s, CH), 134.26 (d, J_{CP} = 11.04, CH), 132.39 (d, J_{CP} = 28.87, CH), 131.78 (d, J_{CP} = 1.88, CH), 130.98 (d, J_{CP} = 41.67, C), 130.86 (d, J_{CP} = 2.38, CH), 129.25 (d, J_{CP} = 10.04, CH), 128.68 (s, CH), 123.65 (d, J_{CP} = 48.95, C), 121.11 (d, J_{CP} = 38.40, C), 118.23 (d, J_{CP} = 6.40, CH), 117.86 (d, J_{CP} = 10.92, CH), 117.62 (d, J_{CP} = 6.02, CH), 117.37 (d, J_{CP} = 11.92, CH), 24.54 (d, J_{CP} = 22.46, *C*HMe$_2$), 19.01 (d, J_{CP} = 36.40, CH*Me*$_2$), 18.01 (s, CH*Me*$_2$). Anal. Calc. for $C_{30}H_{32}ClNNiP_2$: C, 64.04; H, 5.73; N, 2.49. Found: C, 63.82; H, 5.72; N, 2.46%.

Synthesis of [Ph-PNP-^{i}Pr]NiNHPh

To a solid mixture of [Ph-PNP-^{i}Pr]NiCl (100 mg, 0.178 mmol) and LiNHPh(THF) (30 mg, 0.178 mmol) was added THF (8 mL) at −35 °C. The resulting greenish blue solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*. The solid residue was dissolved in benzene (6 mL). The benzene solution was filtered through a pad of Celite, which was further washed with benzene (2 mL) until the washings became colorless. Evaporation of the combined filtrate to dryness under reduced pressure afforded the product as a greenish blue solid; yield 100 mg (90%). ^1H NMR (C_6D_6, 500 MHz) δ 7.78 (m, 4, Ar), 7.59 (m, 2, Ar), 7.08 (t, 1, Ar), 7.02 (m, 6, Ar), 6.93 (m, 5, Ar), 6.84 (m, 2, Ar), 6.46 (t, 1, Ar), 6.38 (td, 2, Ar), 1.95 (m, 2, C*H*Me$_2$), 1.22 (dd, 6, CH*Me*$_2$), 1.01 (dd, 6, CH*Me*$_2$), −1.33 (s, 1, NH). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.13 MHz) δ 33.54 (d, J_{PP} = 356.07, P^{i}Pr$_2$), 9.95 (d, J_{PP} = 356.07, PPh$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz) δ 163.77 (dd, J_{CP} = 3.77 and 24.72, C), 163.23 (dd, J_{CP} = 4.0 and 24.72, C), 159.64 (s, C), 134.43 (s, CH), 133.85 (d, J_{CP} = 11.04, CH), 132.32 (d, J_{CP} = 10.04, CH), 131.78 (s, CH), 131.68 (dd, J_{CP} = 2.76 and 40.29, C), 130.56 (d, J_{CP} = 2.76, CH), 129.14 (d, J_{CP} = 10.04, CH), 128.98 (s, CH), 128.68 (s, CH), 124.05 (d, J_{CP} = 45.75, C), 121.18 (d, J_{CP} = 40.29, C), 118.48 (s, CH), 117.67 (d, J_{CP} = 10.04, CH), 117.60 (d, J_{CP} = 12.80, CH), 117.35 (d, J_{CP} = 5.52, CH), 116.77 (d, J_{CP} = 11.92, CH), 111.26 (s, CH), 24.10 (dd, J_{CP} = 1.88 and 20.96, *C*HMe$_2$), 18.62 (d, J_{CP} = 4.64, CH*Me*$_2$), 17.74 (s, CH*Me*$_2$). Anal. Calc. for $C_{36}H_{38}N_2NiP_2$: C, 69.80; H, 6.19; N, 4.52. Found: C, 70.10; H, 6.42; N, 4.39%.

Deprotonation of phenol or thiophenol with [Ph-PNP-^{i}Pr]NiNHPh

To a C_6D_6 solution of [Ph-PNP-^{i}Pr]NiNHPh was added one equivalent of PhEH (E = O, S) at room temperature. The reaction mixture was transferred to a J. Young NMR tube and the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR which showed quantitative formation of [Ph-PNP-^{i}Pr]NiEPh and aniline in 1 h.

Synthesis of [Ph-PNP-^{i}Pr]NiOPh

To a solid mixture of [Ph-PNP-^{i}Pr]NiCl (100 mg, 0.178 mmol) and NaOPh (21 mg, 0.178 mmol) was added THF (8 mL) at −35 °C. The resulting dark red solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*. The solid residue was dissolved in benzene (6 mL). The benzene solution was filtered through a pad of Celite, which was further washed with benzene (2 mL) until the washings became colorless. Evaporation of the combined filtrate to dryness under reduced pressure afforded the product as a red solid; yield 100 mg (90%). ^1H NMR (C_6D_6, 500 MHz) δ 7.82 (m, 4, Ar), 7.53 (dd, 1, Ar), 7.47 (dd, 1, Ar), 7.30 (d, 2, Ar), 7.13 (t, 1, Ar), 7.00 (m, 5, Ar), 6.96 (m, 2, Ar), 6.86 (m, 4, Ar), 6.51 (t, 1, Ar), 6.43 (t, 1, Ar), 6.37 (t, 1, Ar), 2.03 (m, 2, C*H*Me$_2$), 1.34 (dd, 6, CH*Me*$_2$), 1.11 (dd, 6, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.13 MHz) δ 33.70 (d, J_{PP} = 325.31, P^{i}Pr$_2$), 6.91 (d, J_{PP} = 325.31, PPh$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz) δ 168.16 (s, *ipso*-OPh), 163.79 (dd, J_{CP} = 3.76 and 21.59, C), 163.47 (dd,

J_{CP} = 2.76 and 25.60, C), 134.61 (s, CH), 134.09 (d, J_{CP} = 11.42, CH), 132.35 (d, J_{CP} = 21.96, CH), 131.73 (d, J_{CP} = 1.76, CH), 131.27 (dd, J_{CP} = 2.26 and 39.78, C), 130.66 (d, J_{CP} = 2.38, CH), 129.12 (d, J_{CP} = 10.04, CH), 128.97 (s, CH), 128.68 (s, CH), 123.18 (dd, J_{CP} = 1.38 and 48.95, C), 121.91 (s, CH), 120.60 (dd, J_{CP} = 1.38 and 40.79, C), 118.13 (d, J_{CP} = 10.17, CH), 117.93 (d, J_{CP} = 6.78, CH), 117.53 (d, J_{CP} = 6.02, CH), 117.41 (d, J_{CP} = 11.42, CH), 114.22 (s, CH), 23.89 (d, J_{CP} = 19.70, *C*HMe$_2$), 18.48 (d, J_{CP} = 4.14, CH*Me*$_2$), 17.64 (s, CH*Me*$_2$). Anal. Calc. for $C_{36}H_{37}NNiOP_2$: C, 69.70; H, 6.01; N, 2.26. Found: C, 69.59; H, 6.01; N, 2.20%.

Synthesis of [Ph-PNP-^{i}Pr]NiSPh

To a solid mixture of [Ph-PNP-^{i}Pr]NiCl (100 mg, 0.178 mmol) and NaSPh (23 mg, 0.178 mmol) was added THF (4 mL) at −35 °C. The resulting dark yellowish green solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*. The solid residue was dissolved in benzene (6 mL). The benzene solution was filtered through a pad of Celite, which was further washed with benzene (2 mL) until the washings became colorless. Evaporation of the combined filtrate to dryness under reduced pressure afforded the product as a yellowish green solid; yield 100 mg (88%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.98 (m, 1, Ar), 7.78 (m, 4, Ar), 7.66 (dd, 2, Ar), 7.63 (m, 1, Ar), 7.59 (dd, 1, Ar), 6.89–7.03 (m, 10, Ar), 6.71 (m, 1, Ar), 6.65 (t, 1, Ar), 6.46 (t, 1, Ar), 6.36 (t, 1, Ar), 2.21 (m, 2, C*H*Me$_2$), 1.43 (dd, 6, CH*Me*$_2$), 1.15 (dd, 6, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 38.24 (d, J_{PP} = 318.03, P^{i}Pr$_2$), 21.09 (d, J_{PP} = 318.03, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.54 (dd, J_{CP} = 21.08, J_{CP} = 3.64, C), 162.79 (dd, J_{CP} = 24.72, J_{CP} = 2.76, C), 145.60 (vt, J_{CP} = 5.02, C), 134.55 (s, CH), 134.16 (d, J_{CP} = 10.04, CH), 132.33 (d, J_{CP} = 12.80, CH), 131.81 (d, J_{CP} = 7.28, CH), 131.01 (dd, J_{CP} = 41.16, J_{CP} = 2.76, C), 130.83 (s, CH), 130.50 (d, J_{CP} = 1.76, CH), 129.25 (d, J_{CP} = 10.17, CH),128.86 (d, J_{CP} = 10.04, CH), 127.82 (s, CH), 126.03 (d, J_{CP} = 46.69, C), 122.99 (s, CH), 121.65 (d, J_{CP} = 38.40, C), 117.89 (d, J_{CP} = 6.40, CH), 117.40 (d, J_{CP} = 5.52, CH), 117.31 (d, J_{CP} = 4.52, CH), 116.69 (d, J_{CP} = 11.80, CH), 24.80 (d, J_{CP} = 23.85, *C*HMe$_2$), 19.02 (d, J_{CP} = 3.64, CH*Me*$_2$), 18.06 (s, *C*H*Me*$_2$). Anal. Calc. for $C_{36}H_{37}NNiP_2S$: C, 67.94; H, 5.86; N, 2.20. Found: C, 67.73; H, 5.96; N, 2.12%.

Synthesis of [Ph-PNP-^{i}Pr]NiO^{t}Bu

To a solid mixture of [Ph-PNP-^{i}Pr]NiCl (50 mg, 0.0889 mmol) and NaO^{t}Bu (8.5 mg, 0.0889 mmol) was added THF (4 mL) at −35 °C. The resulting dark greenish blue solution was stirred at room temperature for 10 min. All volatiles were removed *in vacuo*. The solid residue was dissolved in benzene (6 mL). The benzene solution was filtered through a pad of Celite, which was further washed with benzene (2 mL) until the washings became colorless. Evaporation of the combined filtrate to dryness under reduced pressure afforded the product as a dark greenish blue solid; yield 50 mg (94%). ^{1}H NMR (C_6D_6, 500 MHz) δ 8.01 (td, 4, Ar), 7.48 (dd, 1, Ar), 7.32 (dd, 1, Ar), 7.09 (m, 6, Ar), 7.00 (td, 2, Ar), 6.82 (t, 1, Ar), 6.73 (t, 1, Ar), 6.37 (m, 2, Ar), 2.25 (m, 2, C*H*Me$_2$), 1.65 (dd, 6, CH*Me*$_2$), 1.32 (dd, 6, CH*Me*$_2$), 1.15 (s, 9, OC*Me*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.13 MHz) δ 24.15 (d, J_{PP} = 358.49, P^{i}Pr$_2$), 2.83 (d, J_{PP} = 358.49, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 164.32 (dd, J_{CP} = 4.14 and 21.46, C), 162.74 (dd, J_{CP} = 2.64 and 24.22, C), 134.80 (d, J_{CP} = 10.92, CH), 134.54 (s, CH), 133.08 (dd, J_{CP} = 3.14 and 33.38, C), 132.14 (s, CH), 131.35 (dd, J_{CP} = 1.76 and 10.92, CH), 130.52 (d, J_{CP} = 2.26, CH), 129.02 (d, J_{CP} = 9.54, CH), 128.68 (s, CH), 125.83 (dd, J_{CP} = 2.26 and 47.56, C), 121.41 (d, J_{CP} = 37.90, C), 118.06 (d, J_{CP} = 10.17, CH), 117.77 (d, J_{CP} = 5.90, CH), 117.71 (d, J_{CP} = 1.88, CH), 116.60 (d, J_{CP} = 5.90, CH), 68.20 (d, J_{CP} = 2.76, O*C*Me$_3$), 35.50 (s, OC*Me*$_3$), 24.27 (d, J_{CP} = 21.46, *C*HMe$_2$), 19.32 (d, J_{CP} = 4.02, CH*Me*$_2$), 17.93 (s, CH*Me*$_2$). Anal. Calc. for $C_{34}H_{41}NNiOP_2$: C, 68.00; H, 6.88; N, 2.33. Found: C, 67.77; H, 6.27; N, 2.27%.

Synthesis of [Ph-PNP-^{i}Pr]NiC≡CSiMe$_3$

Trimethylsilylacetylene (6 mg, 0.057 mmol) was added to a solution of [Ph-PNP-^{i}Pr]NiNHPh (35 mg, 0.057 mmol) in benzene (2 mL) at room temperature. The red reaction solution was stirred at room temperature for 20 h and evaporated to dryness under reduced pressure, affording the product as a red solid; yield 30 mg (84%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.99 (ddd, 4, Ar), 7.76 (dd, 1, Ar), 7.68 (dd, 1, Ar), 7.15 (m, 2, Ar), 7.07 (m, 6, Ar), 6.95 (m, 2, Ar), 6.50 (t, 1, Ar), 6.42 (t, 1, Ar), 2.30 (m, 2, C*H*Me$_2$), 1.45 (dd, 6, CH*Me*$_2$), 1.08 (dd, 6, CH*Me*$_2$), 0.16 (s, 9, SiMe$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 52.04 (d, J_{PP} = 281.21, P^{i}Pr$_2$), 28.77 (d, J_{PP} = 281.21, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.58 (dd, J_{CP} = 16.94, J_{CP} = 3.64, C), 163.38 (dd, J_{CP} = 21.46, J_{CP} = 3.64, C), 135.40 (s, CH), 134.52 (d, J_{CP} = 11.04, CH), 132.78 (s, NiC≡*C*SiMe$_3$), 132.70 (s, CH), 132.47 (d, J_{CP} = 1.76, CH), 131.96 (d, J_{CP} = 1.76, CH), 131.92 (dd, J_{CP} = 47.57, J_{CP} = 1.38, C), 130.71 (d, J_{CP} = 2.39, CH), 128.96 (d, J_{CP} = 10.54, CH), 123.84 (d, J_{CP} = 44.36, C), 121.61 (d, J_{CP} = 36.14, C), 120.38 (vt, J_{CP} = 40.47, Ni*C*≡CSiMe$_3$), 117.70 (d, J_{CP} = 6.40, CH), 117.21 (d, J_{CP} = 5.90, CH), 116.79 (d, J_{CP} = 11.04, CH), 116.33 (d, J_{CP} = 12.30, CH), 24.98 (dd, J_{CP} = 25.23, J_{CP} = 1.88, *C*HMe$_2$), 19.20 (d, J_{CP} = 3.77, CH*Me*$_2$), 18.27 (d, J_{CP} = 1.26, CH*Me*$_2$), 1.71 (s, SiMe$_3$). Anal. Calc. for $(C_{35}H_{41}NNiP_2Si)(C_6H_6)_{0.8}$: C, 69.58; H, 6.72; N, 2.04. Found: C, 69.53; H, 6.83; N, 2.06%.

Synthesis of [Ph-PNP-^{i}Pr]NiC≡CPh

Phenylacetylene (18 mg, 0.176 mmol) was added to a solution of [Ph-PNP-^{i}Pr]NiNHPh (109 mg, 0.176 mmol) in benzene (4 mL) at room temperature. The red reaction solution was stirred at room temperature for 20 h and evaporated to dryness under reduced pressure, affording the product as a red solid; yield 100 mg (90%). ^{1}H NMR (C_6D_6, 500 MHz) δ 8.02 (m, 4, Ar), 7.80 (dd, 1, Ar), 7.72 (dd, 1, Ar), 7.25 (d, 2, Ar), 7.19 (t, 1, Ar), 7.03 (m, 9, Ar), 6.98 (m, 2, Ar), 6.92 (t, 2, Ar), 6.53 (t, 1, Ar), 6.44 (t, 1, Ar), 2.32 (m, 2, C*H*Me$_2$), 1.48 (dd, 6, CH*Me*$_2$), 1.11 (dd, 6, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 50.11 (d, J_{PP} = 287.88, P^{i}Pr$_2$), 27.16 (d, J_{PP} = 287.88, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.65 (dd, J_{CP} = 22.47, J_{CP} = 3.77, C), 163.46 (dd, J_{CP} = 26.48, J_{CP} = 2.76, C), 135.33 (s, CH), 134.43 (d, J_{CP} = 10.54, CH), 132.76 (s, CH), 132.51 (s, CH), 132.00 (d, J_{CP} = 1.26, CH), 131.96 (d, J_{CP} = 47.57, C), 131.29 (s, CH), 130.76 (d, J_{CP} = 1.76, CH), 129.78 (s, C), 129.12 (d, J_{CP} = 10.04, CH), 128.92 (s, CH), 126.09 (d, J_{CP} = 1.76, C), 125.66 (s, CH), 123.95 (d, J_{CP} = 44.93, C), 121.65 (d, J_{CP} = 36.14, C), 117.76 (d, J_{CP} = 6.40, CH), 117.33 (d, J_{CP} = 5.90, CH), 116.90 (d, J_{CP} = 11.42, CH), 116.30 (d, J_{CP} = 11.80, CH), 96.80 (vt, J_{CP} = 42.98, Ni*C*≡CPh), 24.99 (d, J_{CP} = 24.72, *C*HMe$_2$), 19.23 (d, J_{CP} = 3.64, CH*Me*$_2$), 18.32 (s, CH*Me*$_2$).

Synthesis of [Ph-PNP-^{i}Pr]NiCH$_2$CN

Acetonitrile (4 mg, 0.097 mmol) was added to a solution of [Ph-PNP-^{i}Pr]NiNHPh (60 mg, 0.097 mmol) in benzene (5 mL) at room temperature. The reaction solution was heated to 80 °C for 21 h and evaporated to dryness under reduced pressure, affording the product as a red solid; yield 50 mg (90%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.76 (m, 4, Ar), 7.61 (dd, 1, Ar), 7.54 (dd, 1, Ar), 7.05 (m, 6, Ar), 6.91 (m, 4, Ar), 6.47 (t, 1, Ar), 6.36 (t, 1, Ar), 2.25 (m, 2, C*H*Me$_2$), 1.34 (dd, 6, CH*Me*$_2$), 0.98 (dd, 6, CH*Me*$_2$), 0.71 (dd, 2, $^{3}J_{HP}$ = 9.5 and 11.5, NiCH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 38.92 (d, J_{PP} = 272.11, P^{i}Pr$_2$), 27.52 (d, J_{PP} = 272.11, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.25 (dd, J_{CP} = 20.83, J_{CP} = 3.39, C), 163.07 (dd, J_{CP} = 25.23, J_{CP} = 2.89, C), 134.31 (s, CH), 133.86 (d, J_{CP} = 10.79, CH), 132.74 (d, J_{CP} = 1.88, CH), 132.56 (s, CH), 131.87 (d, J_{CP} = 2.01, CH), 131.10 (d, J_{CP} = 2.51, CH), 130.76 (dd, J_{CP} = 42.67, J_{CP} = 2.01, C), 129.57 (d, J_{CP} = 9.92, CH), 126.57 (vt, J_{CP} = 2.51, NiCH$_2$*C*N), 124.34 (d, J_{CP} = 49.10, C), 120.80 (d, J_{CP} = 40.04, C), 117.46 (d, J_{CP} = 6.90, CH), 117.21 (d, J_{CP} = 7.28, CH), 117.16 (d, J_{CP} = 11.04, CH), 116.10 (d, J_{CP} = 11.42, CH), 23.90 (dd, J_{CP} = 20.83, J_{CP} = 2.01, *C*HMe$_2$), 19.12 (d, J_{CP} = 4.39, CH*Me*$_2$), 17.69 (s, CH*Me*$_2$), –27.33 (vt, J_{CP} = 20.33, NiCH$_2$).

Reaction of [Ph-PNP-^{i}Pr]Ni(NHPh) with acetyl chloride

To a THF solution (2 mL) of [Ph-PNP-^{i}Pr]NiNHPh (26.1 mg, 0.042 mmol) in an NMR tube was added acetyl chloride (3 μL, 0.042 mmol) at room temperature. The reaction was monitored by ^{31}P{^{1}H} NMR which showed quantitative formation of [Ph-PNP-^{i}Pr]NiCl in 10 min. The presence of *N*-phenylacetamide was confirmed by analyzing a reaction aliquot by ESI-MS: found 136.1, calc. 135.07.

Synthesis of [Ph-PNP-^{i}Pr]Ni[C(O)NHPh]

A reaction vessel was charged with a solution of [Ph-PNP-^{i}Pr]Ni(NHPh) (60 mg, 0.097 mmol) in benzene (4 mL). The solution was degassed with three times of freeze-pump-thaw cycles and CO (1 atm) was introduced. The reaction solution was stirred at room temperature for 1 d. The resulting solution was evaporated to dryness under reduced pressure to afford the product as a red solid; yield 52 mg (82%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.82 (m, 5, Ar), 7.72 (dd, 1, *J* = 4.5 and 8.5, Ar), 7.32 (d, 2, *J* = 8.0, Ar), 7.18 (m, 2, *J* = 8.5, Ar), 7.05 (m, 5, Ar), 6.98 (m, 6, Ar), 6.89 (s, 1, NH), 6.78 (t, 1, *J* = 7.5, Ar), 6.54 (t, 1, *J* = 7.5, Ar), 6.43 (t, 1, *J* = 7.5, Ar), 2.25 (m, 2, C*H*Me$_2$), 1.28 (dd, 6, *J* = 7.0 and 16.5, CH*Me*$_2$), 1.01 (dd, 6, *J* = 7.5 and 15.0, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 42.84 (d, $^{2}J_{PP}$ = 222.34, P^{i}Pr$_2$), 21.13 (d, $^{2}J_{PP}$ = 222.34, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 195.70 (t, $^{2}J_{CP}$ = 26.98, C═O), 163.00 (dd, J_{CP} = 3.77 and 20.206, C), 162.78 (dd, J_{CP} = 3.26 and 24.22, C), 139.78 (s, C), 135.09 (s, CH), 134.05 (d, J_{CP} = 11.42, CH), 132.68 (s, CH), 132.38 (d, J_{CP} = 44.80, C), 131.91 (d, J_{CP} = 1.38, CH), 130.67 (d, J_{CP} = 1.76, CH), 129.43 (s, CH), 129.34 (d, J_{CP} = 1.38, CH), 128.68 (s, CH), 123.49 (d, J_{CP} = 48.07, C), 122.57 (s, CH), 120.99 (d, J_{CP} = 38.40, C), 118.38 (s, CH), 117.27 (d, J_{CP} = 9.66, CH), 117.08 (d, J_{CP} = 10.04, CH), 117.03 (d, J_{CP} = 10.92, CH), 115.45 (d, J_{CP} = 10.92, CH), 23.65 (d, J_{CP} = 24.22, *C*HMe$_2$), 18.94 (d, J_{CP} = 4.14, CH*Me*$_2$), 17.60 (s, CH*Me*$_2$). Anal. Calc. for $C_{37}H_{38}N_2NiOP_2$: C, 68.65; H, 5.92; N, 4.33. Found: C, 68.31; H, 5.89; N, 4.30%.

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