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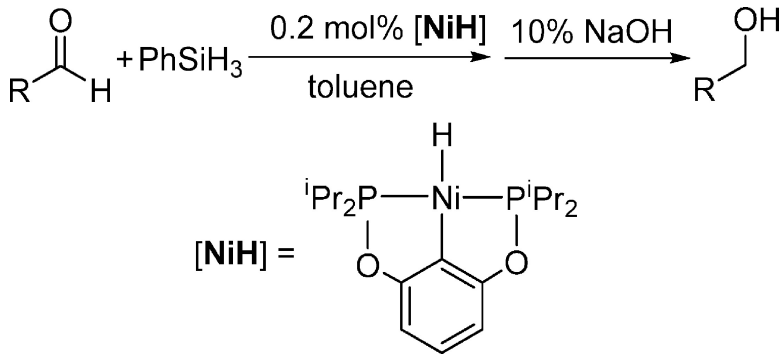

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Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes

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Nickel PCP-pincer hydride complexes catalyze chemoselective hydrosilylation of C═O bonds of aldehydes and ketones in the presence of other functional groups. The mechanism involves C═O insertion into a nickel−hydrogen bond, followed by cleavage of the newly formed Ni−O bond with a silane.

Nickel hydride complexes are of great importance in the research areas of homogeneous catalysis, coordination chemistry, and enzymatic reaction mechanisms. They are often postulated as key intermediates in a variety of nickel-catalyzed organic transformations.[1−10] These hypothesized nickel hydrides are usually too reactive to allow direct observation of reaction intermediates or thorough investigation of reaction mechanisms. Details of their existence during catalytic processes largely rely on computational studies.[4f,g,5b] In contrast, a number of discrete and stable nickel hydride complexes have been prepared and many stoichiometric transformations involving these hydrides have been reported.[4c,11−15] However, very few of these complexes are catalytically competent; of the known well-defined catalytic systems, nickel hydride complexes are solely used as catalysts for olefin isomerization and oligomerization.[15f,16] This has prompted us to study new reactivity of nickel hydride complexes and to explore their potential as relatively inexpensive metal catalysts for various organic reactions.

We have focused our initial studies on nickel hydrides supported by pincer ligands. Such a ligand set has great flexibility in terms of steric and electronic modifications. In addition, square-planar d^8 metals with pincer ligands have shown numerous applications in organic synthesis, polymerization, and

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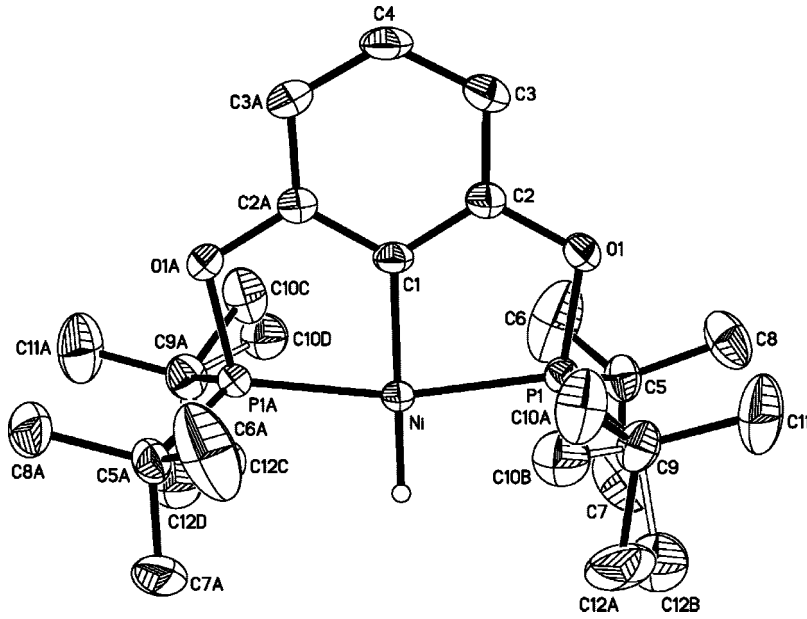

Figure 1. Structure of [2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]NiH (**3b**) (50% probability level). Selected bond lengths (Å) and angles (deg): Ni−H = 1.37(3), Ni−C1 = 1.892(3), Ni−P1 or Ni−P1A = 2.1160(5); P1−Ni−P1A = 166.26(3), C1−Ni−H = 180.000(9), P1−Ni−C1 or P1A−Ni-C1 = 83.132(17).

molecular sensing.[17] The first synthesis of a nickel pincer hydride complex, specifically [2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$]NiH, was reported by Shaw in 1976, although it was not fully characterized.[18] Recently, the Ozerov group[15i] and the Liang group[15k,m] have independently isolated nickel hydride complexes with amido diphosphine (PNP-pincer) ligands. Liang and co-workers have also demonstrated that this class of compounds is capable of activating arene C−H bonds intermolecularly[15k] and undergoes C=C bond insertion.[15m] In any case, we are not aware of any reactions *catalyzed* by nickel pincer hydride complexes. Herein we describe our preliminary results on the reactivity of new nickel pincer hydrides that led to the discovery of efficient nickel catalysts for hydrosilylation of aldehydes and ketones. To the best of our knowledge, this catalytic system represents one of the very few examples of nickel-catalyzed hydrosilylation of carbonyl compounds.[19,20]

Results and Discussion

Encouraged by the excellent reactivity seen in Pd-catalyzed cross-coupling[21] and Ir-catalyzed alkane dehydrogenation reactions,[22] we chose diphosphinites **1a**−**c** as the pincer ligands for the synthesis of nickel hydrides. First, nickel chlorides **2a**,**c** were prepared, as reported in the literature,[23] through cyclometalation of the diphosphinites with $NiCl_2$. Nickel chloride **2b** was synthesized similarly and characterized by ^{1}H NMR, ^{31}P NMR, elemental analysis, and X-ray crystallography (see the Supporting Information). The desired nickel hydrides **3a**,**b** were isolated as yellow-orange solids in good isolated yields from treatment of nickel chlorides with $LiAlH_4$ (Scheme 1). The ^{1}H NMR spectra of **3a**,**b** in C_6D_6 revealed characteristic hydride resonances as triplets at δ −7.89 (J_{HP} = 55.2 Hz) and δ −7.96 (J_{HP} = 53.2 Hz), respectively. The hydride ligand in **3b** was also located by X-ray diffraction of its single crystal (Figure 1).[24]

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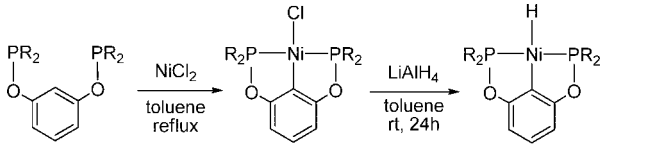
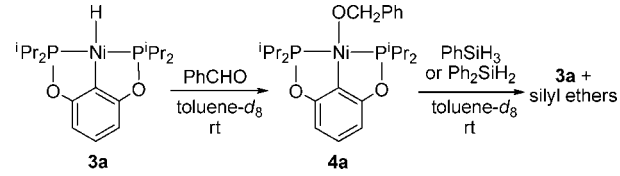
Scheme 1



1a (R = ^{i}Pr) **2a** (*known*) **3a** (88%)
1b (R = ^{t}Bu) **2b** (49%) **3b** (80%)
1c (R = Ph) **2c** (*known*) **3c** (*not isolated*)

Scheme 2

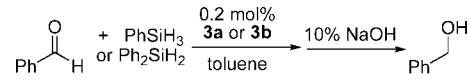


3a **4a**

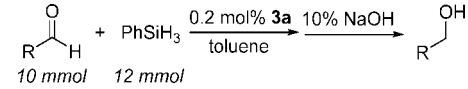
The attempted synthesis of **3c** (R = Ph) from the reduction of **2c** with $LiAlH_4$, $NaBH_4$, or $LiEt_3BH$ gave intractable products.

Nickel hydride **3a** appeared inert toward C=C and C≡C bond insertion; no appreciable insertion product was detected when a solution of **3a** in toluene-d_8 was treated with 1-hexene, *trans*-3-hexene, styrene, 3-hexyne, 2,3-dimethyl-1,3-butadiene, or methyl methacrylate at room temperature. On the other hand, fast C=O insertion of PhCHO into the same nickel hydride was observed under similar conditions (Scheme 2). ^{1}H NMR spectroscopy showed the formation of nickel benzyloxide **4a**; the intensity of a new resonance at δ 4.88 (singlet) increased as the intensities of both hydride **3a** (δ −7.90) and PhCHO (δ 9.62) decreased. The insertion reaction was complete within 30 min and provided **4a** in >95% NMR yield. Complex **4a** was also independently generated from the metathesis between **2a** and $PhCH_2ONa$, although the isolation of compound **4a** in an analytically pure form was unsuccessful. Nevertheless, the reaction shown in Scheme 2 is the first directly observed insertion of an organic carbonyl group into a nickel−hydrogen bond.[25] The reverse step of aldehyde insertion, β-hydride elimination of a metal alkoxide, is more commonly observed for late transition metals.[26] It is possible that the insertion of PhCHO into **3a** is reversible, with an equilibrium favoring the nickel benzyloxide **4a**.[27] As expected, ketones were less reactive than PhCHO, as the resulting secondary alkoxides are more likely to undergo β-hydride elimination than primary alkoxides. When a solution of hydride **3a** in C_6D_6 was treated with an equimolar amount of $PhCOCH_3$ at room temperature for 24 h, the insertion product consisted of only 17 mol % of all nickel species. Reaction with PhCOPh under similar conditions did not yield any alkoxide species. To complete a catalytic cycle, complex **4a** was mixed with various silanes to re-form hydride **3a**. Both $PhSiH_3$ and Ph_2SiH_2 were identified as excellent silyl reagents for the nickel benzyloxide; complete regeneration of **3a** and release of the silyl ether product were seen within a few minutes (Scheme 2). Other silanes such as $(EtO)_3SiH$ and poly(methylhydrosiloxane) (PMHS) regenerated hydride **3a** after longer reaction times (>1 h), while Et_3SiH showed no reaction with complex **4a**.

Scheme 3



Scheme 4



10 mmol *12 mmol*

Having established the protocols of aldehyde insertion and hydride regeneration, we set out to investigate the catalytic activity of hydrides **3a**,**b** for the hydrosilylation of benzaldehyde (Scheme 3). With $PhSiH_3$ or Ph_2SiH_2 as the silyl reagents, hydride **3a** catalyzed the hydrosilylation reaction efficiently; the reaction was complete within 2 h at room temperature with catalyst loading as low as 0.2 mol %. Consistent with the stoichiometric experiments, catalytic reactions with $(EtO)_3SiH$, PMHS, and Et_3SiH were much slower than those with $PhSiH_3$ and Ph_2SiH_2.[28] A control experiment in the absence of the nickel hydride **3a** showed no significant hydrosilylation, even at 60 °C for 5 days. Hydride **3b** also catalyzed the hydrosilylation reaction, albeit with a slower rate.[29]

The scope of this catalytic system was studied using 0.2 mol % of **3a** in the presence of a slight excess of $PhSiH_3$, and the reduction products were isolated as alcohols following basic hydrolysis of the silyl ethers (Scheme 4). As shown in Table 1, the hydrosilylation reaction was tolerant of many functional groups, including OMe (entry 2), NMe_2 (entry 3), Cl (entry 4), NO_2 (entry 5), and CN (entry 10). It would be difficult to rationalize the electronic effect of substituents on the relative hydrosilylation rates, since both the aldehyde with an electron-donating group (entry 2) and the one with an electron-withdrawing group (entry 4) are less reactive than the unsubstituted benzaldehyde (entry 1). An explanation of these results will require more detailed kinetic studies on individual steps of the potential catalytic cycle for each substrate. These studies will be reported in due course. For α,β-unsaturated aldehydes (entries 9 and 12), only the 1,2-addition products were obtained. These results are in contrast to other Ni-catalyzed[30] or Cu-catalyzed[31] hydrosilylations of α,β-unsaturated carbonyl com-

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(24) The ^{t}Bu groups show some disorder. A disorder model is presented for C10 and C12. See the Supporting Information for details.

(25) For direct observation of C=O insertion into a metal−hydrogen bond, see the following examples. Ta−H: (a) Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2005**, *24*, 5759–5766. W−H: (b) van der Zeijden, A. A. H.; Berke, H. *Helv. Chim. Acta* **1992**, *75*, 513–522. (c) Furno, F.; Fox, T.; Schmalle, H. W.; Berke, H. *Organometallics* **2000**, *19*, 3620–3630. Mo−H: (d) Liang, F.; Jacobsen, H.; Schmalle, H. W.; Fox, T.; Berke, H. *Organometallics* **2000**, *19*, 1950–1962. (e) Liang, F.; Schmalle, H. W.; Fox, T.; Berke, H. *Organometallics* **2003**, *22*, 3382–3393. (f) Zhao, Y.; Schmalle, H. W.; Fox, T.; Blacque, O.; Berke, H. *Dalton Trans.* **2006**, *7*, 3–85. (g) Cugny, J.; Schmalle, H. W.; Fox, T.; Blacque, O.; Alfonso, M.; Berke, H. *Eur. J. Inorg. Chem.* **2006**, *54*, 0−552Re−H: (h) Du, G.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 5180–5187. Ru−H: (i) Baratta, W.; Ballico, M.; Esposito, G.; Rigo, P. *Chem. Eur. J.* **2008**, *14*, 5588–5595. Pt−H: (j) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Orpen, A. G. *Organometallics* **1990**, *9*, 2179–2181.

(26) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188.

(27) Experiments designed to elucidate the reversibility of aldehyde insertion will be reported later.

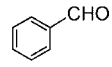
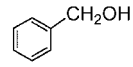
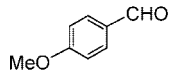
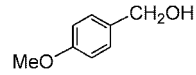
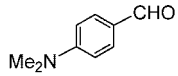
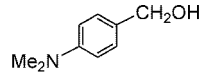
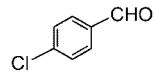
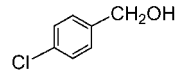
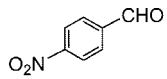
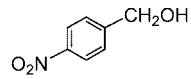
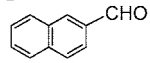
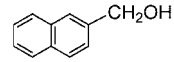
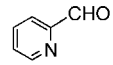
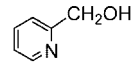
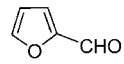
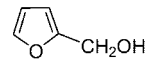
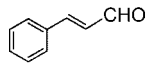
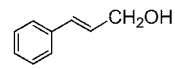
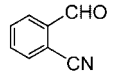
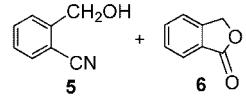
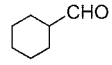
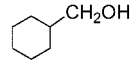
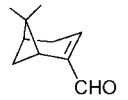
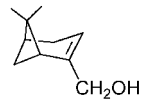
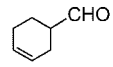
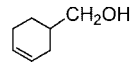
(28) Partial hydrosilylation was seen with $(EtO)_3SiH$ (80% conversion with 2.0 mol % catalyst) when the reaction was quenched after 2 h of stirring at room temperature. Reaction with Et_3SiH or PMHS under similar conditions afforded no hydrosilylation product.

(29) When 0.2 mol % of **3b** was used as the catalyst, 38 mol % of PhCHO was converted after 2 h of reaction.

(30) (a) Boudjouk, P.; Choi, S.-B.; Hauck, B. J.; Rajkumar, A. B. *Tetrahedron Lett.* **1998**, *39*, 3951–3952. (b) Kim, S. O.; Rhee, S.; Lee, S. H. *Bull. Korean Chem. Soc.* **1999**, *20*, 773–774.

(31) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417–2420.

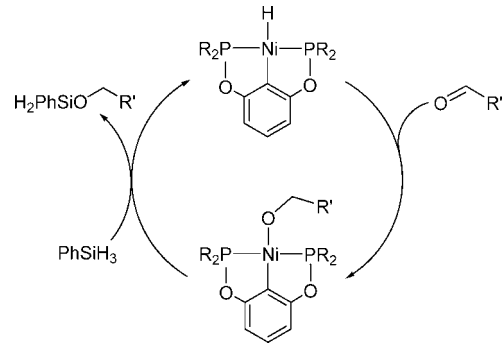
Table 1. Hydrosilylation of Aldehydes Catalyzed by Nickel Pincer Hydride

entry	substrate	product	temperature	time	isolated yield
1			rt	2 h	79%
2			rt	24 h	77%
3			rt	2 h	89%
4			70°C	24 h	92%
5			70°C	24 h	72%
6			60°C	1 h	75%
7			rt	2 h	67%
8			rt	24 h	84%
9			60°C	24 h	71%
10		 **5** **6**	rt	3 h	30%+60% (**5**) (**6**)
11			rt	24 h	85%
12			60°C	24 h	91%
13			rt	4 h	64%

pounds, where only the 1,4-addition products were isolated. The high selectivity for C═O over C═C hydrosilylation was also observed for aldehydes with isolated C═C bonds (entry 13). In addition to substituted benzaldehydes, other aromatic (entries 6−8) and aliphatic (entries 11−13) aldehydes were viable substrates for hydrosilylation. In each reaction studied, no side products such as enoxysilanes and disiloxanes were observed, making our nickel system superior to other nickel systems reported in the literature.[20a,b] An aldehyde bearing a cyano group on the ortho position (entry 10) gave a mixture of two products: the expected 2-cyanobenzyl alcohol **5** and the lactone **6**. Compound **6** resulted from cyclization of **5** under the hydrolysis conditions. Ketones were much less reactive catalytically. Only partial hydrosilylation was observed for acetophenone (18%), cyclohexanone (60%), and benzophenone (6%), even at an elevated temperature (70 °C, 24 h) using a higher catalyst loading (1 mol %).

In view of the stoichiometric experiments shown in Scheme 2, a catalytic cycle was proposed for the current hydrosilylation system (Scheme 5). A similar mechanism has also been proposed by Nolan in his Cu(I)/carbene-catalyzed hydrosilylation reactions.[32] Alternatively, nickel hydrides **3a**,**b** might activate the silanes prior to their interaction with the carbonyl groups. Such a process would resemble the well-known

Scheme 5. Catalytic Cycle for the Hydrosilylation of Aldehydes



Chalk−Harrod mechanism[33] for alkene hydrosilylation, and it has been proposed for Rh-catalyzed hydrosilylation of carbonyl substrates.[34] In addition, oxidative addition of silanes or Si−H σ-bond coordination to a nickel center has been reported.[15h,35]

(32) (a) Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157–1160. (b) Díez-González, S.; Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *J. Org. Chem.* **2005**, *70*, 4784–4796. (c) Díez-González, S.; Scott, N. M.; Nolan, S. P. *Organometallics* **2006**, *25*, 2355–2358. (d) Díez-González, S.; Stevens, E. D.; Scott, N. M.; Petersen, J. L.; Nolan, S. P. *Chem. Eur. J.* **2008**, *14*, 158–168. (e) Díez-González, S.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 349–358.

(33) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16–21.

However, the mechanism involving initial silane activation is less likely to be operating in our nickel catalytic system. We found no reaction when **3a** was treated with $PhSiH_3$ in toluene-d_8 at room temperature or 60 °C for 24 h.

In conclusion, we have disclosed a nickel hydride system where the insertion of carbonyl groups into nickel−hydrogen bonds has been directly observed. The resulting nickel alkoxides react with silanes to release the silyl ether products and reform the nickel hydrides. More detailed mechanistic studies pertaining to the carbonyl insertion step, electronic influence on the turnover-limiting step of the catalytic cycle, and the development of more reactive nickel catalysts for ketone hydrosilylation are the subjects of ongoing research in our laboratory.

Experimental Section

All the air-sensitive compounds were prepared and handled under an argon atmosphere using standard Schlenk and inert-atmosphere box techniques. All aldehyde and ketone substrates were purchased from commercial sources and were used without further purification. Dry and oxygen-free solvents were collected from an Innovative Technology solvent purification system and used throughout all the experiments. Toluene-d_8 and C_6D_6 were distilled from Na and benzophenone under argon. Both ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance-400 MHz NMR spectrometer. Chemical shift values in ^1H NMR spectra were referenced internally to the residual solvent resonances (δ 7.26 for $CDCl_3$, δ 7.15 for C_6D_6, and δ 2.09 for toluene-d_8). The $^{31}P\{^1H\}$ NMR spectra were referenced to an external 85% H_3PO_4 sample (δ 0). Column chromatography was performed with silica gel and solvents of commercial grade. All isolated alcohol products were known compounds and characterized by ^1H NMR spectroscopy. The NMR data obtained for all compounds were consistent with the literature values. 1,3-(^{t}Bu$_2$PO)$_2$C$_6$H$_4$ (**1b**),[22] [2,6-(^{i}Pr$_2$PO)$_2$-C$_6$H$_3$]NiCl (**2a**),[23a] and [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiCl (**2c**)[23b] were prepared as described in the literature.

Synthesis of [2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]NiCl (2b). Under an argon atmosphere 50 mL of toluene was added to a mixture of 1,3-(^{t}Bu$_2$PO)$_2$C$_6$H$_4$ (1.20 g, 3.0 mmol) and anhydrous $NiCl_2$ (389 mg, 3.0 mmol), giving an orange suspension. While the solution was being boiled for 18 h, a brown precipitate formed, which was removed by filtration after the mixture was cooled to room temperature. The volume of the orange filtrate was reduced to 5 mL, and then Et_2O was added to cause precipitation. The product was collected by filtration, washed with Et_2O, and dried under vacuum to give an orange-green powder of **2b** (725 mg, 49% yield). X-ray-quality crystals were grown by allowing a layer of pentane to slowly diffuse into a saturated CH_2Cl_2 solution of the nickel chloride. ^1H NMR (400 MHz, $CDCl_3$): δ 1.49 (virtual triplet, PC(CH_3)$_3$, J_{P-H} = 6.8 Hz, 36H), 6.38 (d, *Ar*, J_{H-H} = 8.0 Hz, 2H), 6.92 (t, *Ar*, J_{H-H} = 8.0 Hz, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 187.20 (s). Anal. Calcd for $C_{22}H_{39}ClO_2P_2Ni$: C, 53.75; H, 8.00; Cl, 7.21. Found: C, 54.11; H, 8.09; Cl, 7.25.

Synthesis of [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiH (3a). Under an argon atmosphere the suspension of $LiAlH_4$ (872 mg, 23 mmol) and **2a** (500 mg, 1.15 mmol) in 60 mL of toluene was stirred at room temperature for 24 h. The resulting mixture was filtered through a short plug of Celite to give a yellow solution. After the solvent was evaporated under vacuum, the desired hydride **3a** was isolated as an orange-yellow crystalline solid (405 mg, 88% yield). ^1H NMR (400 MHz, toluene-d_8): δ −7.90 (t, Ni*H*, J_{P-H} = 55.2 Hz, 1H), 1.08−1.17 (m, PCH(CH_3)$_2$, 24H), 2.05−2.11 (m, PC*H*(CH$_3$)$_2$, 4H), 6.74 (d, *Ar*, J_{H-H} = 8.0 Hz, 2H), 6.97 (t, *Ar*, J_{H-H} = 8.0 Hz, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 206.56 (s). Anal. Calcd for $C_{18}H_{32}O_2P_2Ni$: C, 53.90; H, 8.04. Found: C, 53.88; H, 8.17.

[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]NiH (3b). This compound was prepared in 80% yield by a procedure similar to that used for **3a**. X-ray-quality crystals were grown by layering CH_3OH on a saturated THF solution of the hydride at −35 °C and slowly allowing it to diffuse. ^1H NMR (400 MHz, C_6D_6): δ −7.96 (t, Ni*H*, J_{P-H} = 53.2 Hz, 1H), 1.30 (virtual triplet, PC(CH_3)$_3$, J_{P-H} = 6.8 Hz, 36H), 6.85 (d, *Ar*, J_{H-H} = 7.6 Hz, 2H), 7.02 (t, *Ar*, J_{H-H} = 7.6 Hz, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 219.35 (s). Anal. Calcd for $C_{22}H_{40}O_2P_2Ni$: C, 57.80; H, 8.82. Found: C, 57.65; H, 8.85.

Synthesis of [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiOCH$_2$Ph (4a). Method A. To a solution of **3a** (40 mg, 0.10 mmol) in 5 mL of toluene was added degassed benzaldehyde (10 μL, 0.10 mmol) under an argon atmosphere, and the resulting mixture was stirred at room temperature for 1 h. Evaporating the solvent under vacuum yielded an orange oil, and the NMR spectra of the crude product were recorded (see the Supporting Information). ^1H NMR (400 MHz, toluene-d_8): δ 1.18−1.29 (m, PCH(CH_3)$_2$, 12H), 1.32−1.41 (m, PCH(CH_3)$_2$, 12H), 2.09−2.15 (m, PC*H*(CH$_3$)$_2$, 4H), 4.88 (s, OCH_2Ph, 2H), 6.50 (d, *Ar*, J_{H-H} = 8.0 Hz, 2H), 6.84 (t, *Ar*, J_{H-H} = 8.0 Hz, 1H), 7.00−7.56 (m, CH$_2$*Ph*, 5H). $^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 176.59 (s). Attempts to further purify **4a** via recystallization led to decomposition of the product.

Method B. Under an argon atmosphere, a suspension of **2a** (87 mg, 0.2 mmol) and sodium benzyloxide (39 mg, 0.3 mmol) in 10 mL of toluene was stirred at room temperature for 24 h. The resulting mixture was passed through a short plug of Celite to remove NaCl, and the filtrate was concentrated under vacuum. Again, an orange oil was obtained and its NMR spectra matched the data above, although further purification of **4a** led to decomposition of the product.

General Procedures for Hydrosilylation. To a flame-dried Schlenk flask was added a solution of nickel **3a** (8.0 mg, 20 μmol) in toluene (6 mL) and an aldehyde substrate (10 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature for 5−10 min, after which $PhSiH_3$ (1.48 mL, 12 mmol) was added via a gastight syringe. The reaction mixture was stirred at room temperature or at a higher temperature until there was no aldehyde left (monitored by withdrawing aliquots and analyzing their ^1H NMR spectra). The reaction was then quenched by a 10% aqueous solution of NaOH (about 10 mL) with vigorous stirring for more than 12 h. The solution containing the alcohol product was extracted with diethyl ether three times, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The desired alcohol was further purified by flash column chromatography.

Acknowledgment. We are grateful for financial support from the University of Cincinnati. X-ray data were collected on a Bruker SMART6000 diffractometer which was funded by an NSF-MRI grant (No. CHE-0215950).

Supporting Information Available: Spectroscopic characterization data for compound **4a** and the alcohol products shown in Table 1, as well as crystallographic data (CIF and PDF) for **2b** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800948F

(34) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83–97.

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