# **ORGANOMETALLICS**

# Synthesis and Reactivity of Silyl Iron, Cobalt, and Nickel Complexes Bearing a [PSiP]-Pincer Ligand via Si—H Bond Activation

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**Supporting Information** 

**ABSTRACT:** The synthesis and characterization of a series of Ni, Co, and Fe complexes bearing a tridentate bis(phosphino)silyl ligand ( $\kappa^{3-}(2-Ph_2PC_6H_4)_2SiMeH$ , [PSiP]-H, 1) are reported. 1 reacted with Ni(PMe\_3)\_4 to afford the mononuclear nickel(0) complex [ $\eta^2(Si-H)-PSiP$ ]Ni(PMe\_3) (2). The halogeno nickel complexes [PSiP]Ni(X)(PMe\_3) (X = Cl (3), Br (4), I (5)) were synthesized in the reactions of 2 with Me\_3SiCl or MeHSiCl\_2, EtBr, and MeI. Complex 2 underwent ligand substitution of PMe\_3 by CO to give [ $\eta^2(Si-H)-PSiP$ ]Ni(CO) (6). Complex 3 reacted with NaOMe to deliver [PSiP]Ni(OMe)(PMe\_3) (7) through anionic ligand substitution, while the neutral ligand replacement of PMe\_3 by CO in 3 afforded the rare hexacoordinate 20-electron nickel(II) complex [PSiP]Ni(Cl)(CO)\_2 (8). Unexpectedly, reaction of 1 with



NiMe<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> produced the tetracoordinate nickel(0) complex  $[Me_2PSiP]_2Ni$  (9). The complex  $[Me_2PSiP]Ni(CO)_2$  (10) was acquired from 9 after the substitution of one [PSiP] ligand by two carbonyl ligands. 1 reacted with Co(PMe<sub>3</sub>)<sub>4</sub> or CoCl(PMe<sub>3</sub>)<sub>3</sub> to afford the hydrido cobalt(II) complex  $[PSiP]CoH(PMe_3)$  (11) or hydrido cobalt(III) complex  $[PSiP]Co(H)(Cl)(PMe_3)$  (13). Complex 12,  $[PSiP]Co(H)(I)(PMe_3)$ , could be obtained from the reaction of MeI with 11 or 13. Treatment of 13 with 1 equiv of MeLi or *n*-BuMgBr in THF resulted in the clean formation of cobalt(I) complex  $[PSiP]Co(PMe_3)_2$  (14) via reductive elimination. The simple anhydrous inorganic salt NiCl<sub>2</sub> or CoCl<sub>2</sub> could also react with 1 in the presence of PMe<sub>3</sub> to form the hexacoordinate octahedral hydrido iron(II) complex  $[PSiP]Fe(H)(PMe_3)_2$  (16). The molecular structures of complexes 2–5, 10, 12, 13, 15, and 16 were determined by X-ray single crystal diffraction. 16 has excellent catalytic reactivity for the reduction of aldehydes and ketones.

# INTRODUCTION

The preparation and reaction of silvl transition-metal (TM) complexes have attracted significant interest, since they are invoked as key intermediates in numerous TM-catalyzed reactions of silicon compounds such as hydrosilylation, dehydrogenative coupling, dehydrogenative borylation, hydrocarboxylation of allenes, and transfer hydrogenation.<sup>1</sup> The reaction of hydrosilanes with low-valent TM complexes via Si-H bond activation is one of the most important methods for preparing silyl TM complexes. Usually, oxidative addition of the Si-H bond at the metal center gives rise to silvl metal hydride complexes (Si-M-H) by the cleavage of the Si-H  $\sigma$ -bond. Occasionally, the reaction stops at the stage of Si-H  $\sigma$ -bond coordination to the metal to form a  $\eta^2(Si-H)$  metal complex, which can be considered as a "frozen intermediate".<sup>2</sup> Research on silyl metal complexes may provide deeper insight into TMcatalyzed silvlation reaction mechanisms.

A pincer ligand as the tridentate ligand could stabilize a variety of high-oxidation-state metal complexes through the bischelate effect. This has inspired widespread attention to the synthesis, reaction, and catalytic reactivity of pincer metal complexes. The silyl ligand shows strong  $\sigma$ -donating character and displays a stronger *trans* influence than common ligands in

TM chemistry.<sup>3</sup> Silyl pincer ligands have a great advantage in Si–H bond activation because they make an electron-rich metal center and coordinatively unsaturated species stable by their strong *trans*-labilizing effects and rigid framework of the multidentate ligand. Recently, the chemistry of the reactions of the pincer ligand  $\kappa^3$ -(2-R<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMeH (R = Ph, *i*-Pr, Cy, *t*-Bu) with various metal precursors (M = Ru, Rh, Ir, Pd, Pt, Ni) has been investigated by the groups of Milstein, Turculet, Iwasawa, and Li.<sup>4–7</sup> The resulting PSiP-pincer complexes exhibit remarkable reactivity in inert bond activation and TM-catalyzed transformations.

In comparison to the poisonous noble metals (Ru, Rh, Ir, Pd, Pt), Fe-, Co- and Ni-based catalysts are low cost and ecofriendly. In this paper we describe a systematic investigation of the synthesis and unique properties of silyl iron, cobalt, and nickel complexes bearing a [PSiP]-pincer ligand. These complexes were prepared by the reaction of electron-rich low-valent iron, cobalt, and nickel complexes supported by trimethylphosphine with a [PSiP]-pincer ligand. The frozen intermediate  $\eta^2$ (Si-H)Ni<sup>0</sup> complexes and silyl metal hydrides

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 $(Co^{II}-H, Co^{III}-H \text{ and } Fe^{II}-H)$  were synthesized and characterized. Their reactivity was also investigated. Furthermore, several corresponding halogenated Ni and Co complexes could be obtained directly from the reactions of simple inorganic salts NiCl<sub>2</sub> and CoCl<sub>2</sub> with ligand 1 in the presence of trimethylphosphine via Si-H bond activation.

# RESULTS AND DISCUSSION

**1. Synthesis and Reactivity of Silyl Nickel Complexes.** In the beginning, we investigated the reaction of Ni(PMe<sub>3</sub>)<sub>4</sub> with bis(*o*-(diphenylphosphino)phenyl)methylsilane (1). When a solution of 1 in THF was treated with Ni(PMe<sub>3</sub>)<sub>4</sub> at room temperature, a small amount of yellow powder deposited after 14 h. After the volatiles were removed, the residue was extracted with pentane and diethyl ether. Complex **2** was isolated at 0 °C from diethyl ether as yellow crystals in a yield of 75% (Scheme 1).





Similar to the research reported by the Iwasawa group,<sup>6</sup> we obtained a  $\eta^2$ (Si-H)Ni<sup>0</sup> complex. Unlike the traditional metal hydride complex, the resonance of the H atom of the coordinated Si-H bond linked to the Ni atom was shifted downfield ( $\delta$  -3.71 ppm), which is coupled with three phosphorus atoms (td,  $J_{\rm HP}$  = 31.4, 14.3 Hz) and with the methyl protons (q,  $J_{\rm HH}$  = 2.0 Hz), while the related resonance of  $\eta^2$ (Si-H)Ni(PPh<sub>3</sub>) reported by the Iwasawa group<sup>6f</sup> is at  $\delta$ -2.90 ppm with both  ${}^{31}P{}^{-1}H$  coupling (td,  $J_{HP}$  = 29.9, 15.8 Hz) and  ${}^{1}H-{}^{1}H$  coupling with SiCH<sub>3</sub> (q,  $J_{HH} = 1.3$  Hz). The reason for this difference may be due to the smaller steric effects and strong coordination ability of PMe<sub>3</sub>. Moreover, a strong absorption at 1721 cm<sup>-1</sup> can be observed in the IR spectrum. This can be identified as a typical vibration absorption peak of a Ni-H bond, which is close to the value for the Ni-H bond in similar [PCP]NiH complexes.8a Furthermore, the signals of the Si-H bond of 1 disappeared on monitoring by the <sup>1</sup>H NMR spectrum ( $\delta$  6.11 ppm) and IR spectrum ( $\nu$ (Si–H) 2143 cm<sup>-1</sup>). This change indicated that the Si-H bond was activated. In addition, the <sup>29</sup>Si resonance of complex 2 appears at  $\delta$  13.77 ppm (dt,  $J_{SiP}$  = 82.0 and 3.3 Hz) in C<sub>6</sub>D<sub>6</sub> at 296 K by <sup>29</sup>Si{<sup>1</sup>H} NMR. The <sup>1</sup> $J_{SiH}$  coupling constant is ca. 82.0 Hz by non-<sup>1</sup>H-decoupled <sup>29</sup>Si NMR. This is much larger than typical values found for H–M–Si complexes and implies the elongation of the Si–H bond by the  $\eta^2$ (Si–H) coordination to the nickel center. The <sup>1</sup>J<sub>SiH</sub> coupling constant of complex **2** is relatively smaller than <sup>1</sup>J<sub>SiH</sub> = 89 Hz of  $\eta^2$ (Si– H)Ni(PPh<sub>3</sub>) reported by the Iwasawa group<sup>6f</sup> and larger than those (40–70 Hz) for previously reported  $\eta^2$ (Si–H) metal complexes.<sup>9</sup>

X-ray crystallography confirmed the molecular configuration of **2** (Figure 1). Two five-membered chelate rings with



**Figure 1.** ORTEP plot of complex **2** at the 50% probability level (hydrogen atoms except for Ni–H are omitted for clarity).

considerable ring bending are formed through two P atoms of the PPh<sub>2</sub> groups and a metalated Si atom. The Ni atom is centered in a distorted tetrahedron. The Ni1-H100 distance (1.26(9) Å) is obviously shorter than typical values of Ni-H bonds (1.30-1.70 Å),<sup>8</sup> while the Ni1-Si1 distance (2.235(2))Å) is relatively long among known Ni<sup>II</sup>–SiR<sub>3</sub> bonds (2.14–2.30 Å)<sup>10</sup> but shorter than that of a  $\eta^2(\text{Si}-\text{H})\text{Ni}^{\text{II}}$  complex (2.348 Å) reported by Shimada<sup>10a</sup> and a  $\eta^2(\text{Si}-\text{H})\text{Ni}^0$  complex (2.2782(4) Å) reported by Iwasawa.<sup>6f</sup> The Si1–Ni1–H100 angle is  $52(4)^{\circ}$ . The Si1-H100 distance (1.77(9) Å) is much longer than that (~1.5 Å) in the parent silane and (1.62(3) Å) in the  $\eta^2$ (Si-H)Ni<sup>0</sup> complex reported by Iwasawa.<sup>6f</sup> In addition, this distance is also among the typical values of previously reported  $\eta^2$ (Si-H) metal complexes (1.6–1.9 Å).<sup>10</sup> Ni1-P3 (2.163(2) Å) is longer than Ni1-P1 (2.147(2) Å) and Ni1-P2 (2.137(2) Å) due to the trans influence of the silyl group, while the difference between Ni1-P1 and Ni1-P2 may be caused by the packing effects in the crystal cell.

Inspired by the work on Si–H or Si–Cl bond activation via [R-PSiP]Pt complexes with hydridochlorosilanes by Turculet,<sup>5e</sup> we found that it is difficult for complex **2** to cleave the Si–H bond by reaction with  $Et_3SiH$  or  $PhMe_2SiH$  because the hydrogen atoms in both reactants are more electronegative. In fact, complex **2** did react with 1 equiv of  $Me_3SiCl$  or  $MeHSiCl_2$  to form the nickel(II) complex [PSiP]Ni(Cl)(PMe\_3) (3) in a yield of 40% (Scheme 1). In like manner, other pincer nickel halide complexes, [PSiP]Ni(Br)(PMe\_3) (4) and [PSiP]Ni(I)-(PMe\_3) (5), could be obtained bt the reactions of **2** with EtBr and MeI in THF.

Complex 4 or 5 was isolated as red blocklike crystals from diethyl ether at -30 °C. The mechanism likely begins with

cleavage of the C–X (X = Br, I) bond of EtBr or MeI and oxidative addition of the Si–H bond at the Ni(0) center to afford an intermediate Ni(IV) complex.<sup>11</sup> This Ni(IV) species is not stable and delivers complex 4 or 5 with the escape of a molecule of ethane or methane, detected by in situ <sup>1</sup>H NMR via reductive elimination. Similar reactions were reported by Tanaka.<sup>10a,b</sup>

X-ray crystallography confirmed that complexes 3-5 have a trigonal-bipyramidal coordination geometry (Figures 2-4)



**Figure 2.** ORTEP plot of complex **3** at the 50% probability level (hydrogen atoms are omitted for clarity).



Figure 3. ORTEP plot of complex 4 at the 50% probability level (hydrogen atoms are omitted for clarity).

formed by [P1P2X1] as the equatorial plane with Si1–Ni1– P3 in the axial position. Table 1 suggests that the Ni–X bond length becomes longer with an increase of the X atomic radius. The trigonal-bipyramidal structure becomes much more distorted on going from 3 to 5 because of steric effects and *trans* influence.

The carbonyl complex **6** is readily formed by placing a THF solution of **2** under an atmosphere of CO at room temperature (Scheme 1). Light yellow crystals of **6** were obtained from diethyl ether at -30 °C. The  $\eta^2$ (Si–H)Ni structural moiety remained in this transformation, as monitored by the <sup>1</sup>H NMR



**Figure 4.** ORTEP plot of complex **5** at the 50% probability level (hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) of Complexes 2-5

bond distance or angle	<b>2</b> (X = H)	3 (X = Cl)	4 (X = Br)	5 (X = I)
Ni1-X1	1.26(9)	2.379(2)	2.525(1)	2.628(1)
Ni1-Si1	2.235(2)	2.283(2)	2.298(2)	2.292(2)
Ni1-P1	2.147(2)	2.165(2)	2.229(2)	2.169(2)
Ni1-P2	2.137(2)	2.219(2)	2.180(2)	2.207(2)
Ni1-P3	2.163(2)	2.257(2)	2.264(2)	2.254(2)
P1-Ni1-P2	115.79(9)	123.29(7)	122.77(7)	123.48(6)
Si1-Ni1-P3	147.23(9)	170.26(7)	170.22(8)	172.48(7)
Si1-Ni1-X1	52(4)	84.15(6)	83.62(6)	83.87(5)
P3-Ni1-X1	95(4)	87.81(7)	88.30(7)	89.96(5)

spectrum ( $\delta$  –2.13 ppm for the H atom of Si–H group) and IR spectrum ( $\nu$  1725 cm<sup>-1</sup> for the Ni–H vibration) with a tiny shift in comparison with those of **2**. It could be concluded that the trimethylphosphine ligand was replaced by a carbonyl ligand because the characteristic absorption peak ( $\nu$  946 cm<sup>-1</sup>) of PMe<sub>3</sub> in **2** disappeared in the IR spectrum. In addition, the phosphorus resonance ( $\delta$  –15.46 ppm) of PMe<sub>3</sub> in the <sup>31</sup>P NMR spectrum was absent. Furthermore, the coupling splitting of the  $\eta^2$ (Si–H) peak in the <sup>1</sup>H NMR spectrum turned out to be tq coupling (Figure Sb for **6**) instead of tdq coupling (Figure



Figure 5. Hydrido resonances of complexes 2 (a) and 6 (b).

Sa for 2) owing to the loss of the P–H coupling with the P atom of PMe<sub>3</sub>. This shows that the couplings  ${}^{2}J(P_{methyb}H) = 14.3$ ,  ${}^{2}J(P_{phenyb}H) = 34.1$ , and  ${}^{3}J(Si_{methyb}H) = 2.0$  Hz in complex 2 shifted to  ${}^{2}J(P_{phenyb}H) = 25.1$  and  ${}^{3}J(Si_{methyb}H) = 1.9$  Hz in complex 6. In comparison to PMe<sub>3</sub>, CO has a strong coordination capability due to the smaller steric hindrance and  $\pi$ -back-bonding formation. It is considered that the weaker

electron-donating ability of CO and the decrease in the electron cloud density of the nickel center make the coupling constants smaller. The <sup>29</sup>Si{<sup>1</sup>H} NMR exhibited the Si atom resonance at  $\delta$  7.40 ppm with <sup>29</sup>Si-<sup>1</sup>H coupling (d, <sup>1</sup>J<sub>SiH</sub> = 104.8 Hz), which was shifted upfield in comparison to that of complex **2** ( $\delta$  13.71 ppm). This difference in <sup>1</sup>J<sub>SiH</sub> might be due to the strong coordination of the carbonyl ligand. The relatively larger <sup>1</sup>J<sub>SiH</sub> value suggests that back-donation from the metal center to the  $\sigma^*$  orbital of the Si-H bond in this complex is weak.

Complex 3 could also be synthesized as red crystals in over 50% yield by reaction of the simple inorganic salt NiCl<sub>2</sub> with ligand 1 in the presence of PMe<sub>3</sub> via Si–H bond activation from diethyl ether at -30 °C (Scheme 2). In addition, complex 3 was the major product of the reactions of 1 with NiCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> and NiMeCl(PMe<sub>3</sub>)<sub>2</sub> in THF.

#### Scheme 2. Preparation of Silyl Nickel Complexes 7 and 8



To explore the reactivity of complex **3**, **3** was treated with NaOMe in THF to give the methoxy complex 7. Complex 7 was isolated as red crystals in a yield of 65% from pentane. Unfortunately, no single crystals of 7 suitable for XRD were obtained. However, the NMR spectra of 7 clearly exhibited the resonance of the hydrogen of the methoxy group at 3.45 ppm and the resonance of the carbon of the methoxy group at 49.6 ppm.

The carbonyl complex 8 was formed by placing a THF solution of 3 under an atmosphere of CO at room temperature for 14 h. Two strong stretching absorptions at 2007 and 1938 cm<sup>-1</sup> could be observed in the IR spectrum of 8, which were identified as the signals of two terminal carbonyl ligands in asymmetric positions. The NMR spectra also confirmed the formation of complex 8. Complex 8 is a hex-coordinate nickel(II) complex with 20 valence electrons.<sup>12</sup>

The reaction of 1 with 1 equiv of  $NiMe_2(PMe_3)_3$  in THF afforded the unexpected tetracoordinate bis-chelate nickel(0) complex 9 (Scheme 3). The mechanism (Scheme 4) may begin with Si-H bond cleavage. The oxidative addition of the Si-H bond at the Ni(II) center affords a Ni(IV) intermediate. This Ni(IV) intermediate is not stable and releases a molecule of methane via reductive elimination to form intermediate 9A. The migration of the Ni-methyl of 9A from nickel to the Si atom by reductive elimination causes the reduction of nickel(II) to nickel(0) species 9B. The ligand exchange between two molecules of 9B delivers the formation of complex 9. Ni(PMe\_3)<sub>4</sub> as the second product was isolated from the









pentane extract solution and confirmed by IR.<sup>13</sup> The related reactions for Pd and Pt were discussed by Shiro and Schubert.<sup>14</sup>

To collect accurate structural information on complex 9, CO was imported into the solution of 9. The solution turned light yellow quickly. Complex 10 as pale yellow crystals was obtained from diethyl ether at -30 °C (Scheme 3).

The molecular configuration of complex 10 was confirmed by X-ray single crystal diffraction (Figure 6). The nickel(0) center is coordinated with two phosphorus atoms of the [PSiP] ligands and two carbon monoxide molecules. The nickel has a tetrahedral geometry. The C7-Ni1-C8 (106.6(3)°), C7-Ni1-P1 (114.9(2)°), C8-Ni1-P1 (108.8(2)°), C7-Ni1-P2 (115.4(2)°), C8-Ni1-P2 (101.4(2)°), and P1-Ni1-P2 angles  $(108.64(6)^{\circ})$  are typical  $(109.5^{\circ})$  for a distorted tetrahedron. Two methyl groups are linked to the Si atom. The Ni1-Si1 distance (3.82(2) Å) is much longer than those of the known Ni–Si bonds (2.14–2.30 Å).<sup>6f,10</sup> This means that there is no bond interaction between these two atoms. The result indicates that CO as a strong  $\sigma_{i}\pi$  ligand substitutes one [PSiP] ligand of complex 9 to form complex 10. This can be regarded as collateral evidence of the existence of 9B in the mechanism of formation of 9. In other words, there is an equilibrium between 9B and 9.

In order to prepare hydrido nickel complex **2A**, NaBH<sub>4</sub> was used to reduce complex **3**. However, instead of complex **2A**, complex **2** was isolated (Scheme 5). The reaction mechanism probably goes through intermediate **2A**. **2A** transforms to the  $\eta^2(Si-H)Ni^0$  complex **2** via reductive elimination, as **2A** may be thermodynamically unstable.



Figure 6. ORTEP plot of complex 10 at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni1–Si1 = 3.82(2), Ni1–C7 = 1.753(7), Ni1–C8 = 1.770(7), Ni1–P1 = 2.242(2), Ni1–P2 = 2.254(2); C7–Ni1–C8 = 106.8(3), C7–Ni1–P1 = 114.9(2), C8–Ni1–P1 = 108.8(2), C7–Ni1–P2 = 101.4(2), P1–Ni1–P2 = 108.64(6).

Scheme 5. Reduction of Complex 6 with NaBH<sub>4</sub>



Furthermore, to compare the structures and relative stability of complexes 2A and 2, theoretical calculations were carried out using DFT with the B3LYP functional. The optimized structures of 2A and 2 are shown in Table 2.  $2A_{DFT}$  exhibits a trigonal-bipyramidal configuration with P1–P2–P3 as the equatorial plane and Si1–Ni1–H in the axial direction. The H atom is almost in a *trans* position opposite the Si atom with a





Si–Ni–H angle of 172.95°. The three P atoms form a triangle with angles of 122.54, 117.98, and 119.19°. The optimized structure of  $2_{DFT}$  is almost the same as the crystal structure of 2, although the Ni–H bond distance (1.5969 Å) is longer and the Si–Ni–H angle (43.86°) is smaller. The result indicates that  $2_{DFT}$  is more stable than 2A by 5.20 kcal/mol. This is consistent with the experimental results.

2. Synthesis and Reactivity of Silyl Cobalt Complexes. Encouraged by the results of silyl nickel complexes, the reaction of  $Co(PMe_3)_4$  with 1 was studied and delivered hydrido cobalt(II) complex 11 as a yellow powder from diethyl ether at 0 °C (Scheme 6). Complex 11 was produced via Si–H





oxidative addition and has a typical  $\nu$ (Co–H) stretching band at 1916 cm<sup>-1</sup> in the IR spectrum. The <sup>1</sup>H NMR spectrum exhibits the resonance of the hydrido ligand at –14.04 ppm as a quartet with an H–P coupling constant of 61.5 Hz. Unfortunately, no single crystals of **11** suitable for X-ray crystallography could be obtained by recrystallization from pentane, diethyl ether, or toluene solution. The <sup>31</sup>P NMR data of **11** clearly show one signal ( $\delta$  68.2 ppm) for the two *trans*diphenylphosphinyl groups and a multiplet ( $\delta$  –8.5 ppm) for trimethylphosphine. Complex **11** probably has a trigonalbipyramidal geometry, and the cobalt atom is coordinated with two five-membered metallacycles, one H atom, and one trimethylphosphine ligand.

Complex 11 was treated with CH<sub>2</sub>I in THF. After workup complex 12 was isolated as orange crystals from diethyl ether at -30 °C (Scheme 6). In this transformation hydrido cobalt(II) complex 11 turns out to be the hydrido cobalt(III) complex 12, which is a very stable cobalt(III) species and does not spontaneously eliminate HI to form a cobalt(I) complex. The  $\nu$ (Co–H) stretching band of complex 12 was observed at 1927 cm<sup>-1</sup> in the IR spectra. The <sup>1</sup>H NMR spectrum of 12 in benzene- $d_6$  confirmed the presence of the hydride ligand at -14.67 ppm. The reaction mechanism from 11 to 12 probably goes through a radical reaction process. The homolytic cleavage of iodomethane produces iodine radical and methyl radical. The iodine radical addition to the cobalt(II) center of complex 11 produces complex 12 with a cobalt(III) center. Two methyl radicals combine to form one molecule of ethane. In this process the pentacoordinate 17-electron cobalt(II) complex 11 transforms to the hexacoordinate 18-electron cobalt(III) species 12. The formation of ethane was confirmed by an in situ <sup>1</sup>H NMR spectrum with a chemical shift of 0.88 ppm.<sup>15</sup>

The molecular configuration of complex 12 was confirmed by single-crystal XRD as an octahedral structure (Figure 7) with a Co center and [P1P2P3H100] in the equatorial plane and Si1-Co1-I1 in the axial direction. The cobalt atom is coordinated with two five-membered metallacycles, one trimethylphosphine, and one iodide atom as well as one H atom in a distorted-octahedral geometry. Owing to the *trans* influence the iodine atom is situated in the position *trans* to the Si atom while the PMe<sub>3</sub> ligand occupies the location opposite



**Figure 7.** ORTEP plot of complex **12** at the 50% probability level (hydrogen atoms except for Co–H are omitted for clarity).

the H atom. The Co1–H100 distance (1.40(4) Å) is very close to those of the known Co–H bonds (1.40–1.50 Å).<sup>16</sup> The Si1–H100 distance (2.406 Å) is much longer than that  $(\sim 1.5 \text{ Å})$  in the parent silane and that (1.89(1) Å) in the  $\eta^2$ (Si–H)Ni<sup>0</sup> complex **2**. This means that there is no bonding interaction between Si1 and H100. Complex **12** is a classic metal hydride complex.

The hydrido cobalt(III) chloride 13, a derivative of hydrido cobalt(III) iodide 12, could be obtained through the reaction of 1 with  $CoCl(PMe_3)_3$  in THF (Scheme 7). Complex 13 could



crystallize from diethyl ether at -30 °C. In the IR spectrum of 13 a typical  $\nu$ (Co-H) absorption at 1910 cm<sup>-1</sup>, less than that of 12, was found. Meanwhile, the <sup>1</sup>H NMR spectrum of 13 revealed the resonance of the hydrogen of the Co-H bond at -13.68 ppm. This signal is shifted downfield in comparison with that (-14.67 ppm) in 12. This difference is probably caused by the larger inductive effect of the Cl atom in comparison with that of the I atom. Single-crystal X-ray diffraction analysis confirmed that 13 has an octahedral coordination geometry (Figure 8). In comparison with that of 12, the Co-H bond distance is longer (Table 3). This result is consistent with inference from the data of the infrared spectra



**Figure 8.** ORTEP plot of complex **13** at the 50% probability level (hydrogen atoms except for Co–H are omitted for clarity).

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complexes 12, 13, and 15

bond distance or angle	12 (X = I)	13 (X = $Cl$ )	15 (X= Cl)
Co1-H100	1.40(4)	1.52(2)	
Co1-X1	2.6749(7)	2.410(1)	2.275(1)
Co1-Si1	2.256(1)	2.252(2)	2.259(1)
Co1-P1	2.183(1)	2.188(1)	2.160(1)
Co1-P2	2.193(1)	2.188(1)	2.200(1)
Co1-P3	2.247(1)	2.259(2)	2.230(1)
P1-Co1-P2	141.01(5)	147.09(7)	111.24(5)
Si1-Co1-P3	91.43(4)	93.76(7)	173.89(5)
Si1-Co1-X1	174.10(4)	173.38(7)	86.22(5)
P3-Co1-X1	94.47(4)	92.85(6)	89.52(5)

of complexes 12 and 13. This indicates that the Co–H bond in complex 12 is stronger than that in complex 13.

A substitution of a chlorine by an iodine ligand was observed through the reaction of complex 13 with CH<sub>3</sub>I in THF (Scheme 7). We tried to prepare alkyl pincer cobalt complexes via the reaction of complex 13 with alkylating agents. The treatments of 13 with 1 equiv of MeLi or n-BuMgBr resulted in the clean formation of the new silvl Co(I) complex 14. The expected alkyl pincer cobalt complex was not isolated. This may be caused by the instability of the expected hydrido alkyl pincer cobalt complex. The PMe<sub>3</sub> signals of complex 14 in the <sup>1</sup>H NMR ( $\delta$  0.79 and 1.19 ppm) and <sup>31</sup>P NMR spectra ( $\delta$  -17.48 and 4.00 ppm) clearly indicate that the two trimethylphosphine ligands are not in the same chemical environment. The molecular structure could be a trigonal-bipyramidal geometry, in which the two PMe<sub>3</sub> ligands are in asymmetric positions. One is in the position opposite to the Si atom (axial position), and the other is coplanar with the two P atoms of the [PSiP] ligand.

In the presence of PMe<sub>3</sub> the reaction of anhydrous  $CoCl_2$  with 1 in THF afforded complex 15 as red blocklike crystals. The IR spectrum of 15 indicated that the Si–H bond vibration absorption ( $\nu$  2143 cm<sup>-1</sup>) of 1 disappeared. A strong absorption at 934 cm<sup>-1</sup> was identified as the characteristic absorption peak of PMe<sub>3</sub>. Complex 15, as a cobalt(II) species, is paramagnetic and no reasonable spectra were available, despite the attempts made. The structure of complex 15 was

confirmed by X-ray diffraction analysis. The cobalt atom is coordinated with two five-membered metallacycles, one trimethylphosphine, and one chloride atom in a distortedtrigonal-bipyramidal geometry (Figure 9). The chelate rings are



Figure 9. ORTEP plot of complex 15 at the 50% probability level (hydrogen atoms are omitted for clarity).

almost perpendicular to each other. The axial angle of P3– Co1–Si1 is 173.89(5)°, deviating from 180°. The methyl groups of the phosphine ligand are oriented in a staggered conformation with respect to the three coordinated atoms in the triangular plane [P1P2Cl1], to decrease the repulsion among them, while the staggered conformation between the silyl group and the three coordinated atoms (P1P2Cl1) is strongly distorted because of the formation of the pincer geometry and the six crowded phenyl groups. Co1–P3 (2.230(1) Å) is longer than Co1–P1 (2.160(1) Å) and Co1–P2 (2.200(1) Å) due to the *trans* influence of the silyl group, while the difference between Co1–P1 and Co1–P2 may be caused by the packing effects in the crystal cell.

**3.** Synthesis and Reactivity of Silyl Iron Complexes. When 1 was treated with 1 equiv of  $Fe(PMe_3)_4$  in toluene, the solution turned dark red-brown after 14 h (Scheme 8).





Complex 16 was isolated as orange crystals from diethyl ether. The typical  $\nu$ (Fe–H) stretching band was found at 1870 cm<sup>-1</sup> in the IR spectrum. The characteristic hydride signal as a td peak was found at -17.09 ppm with both <sup>31</sup>P–<sup>1</sup>H coupling constants ( $J_{\rm HP}$  = 71.4, 18.1 Hz) in the <sup>1</sup>H NMR spectrum of 16. Two signals ( $\delta$  0.53 and 0.98 ppm) for the PMe<sub>3</sub> ligands in the <sup>1</sup>H NMR spectrum clearly indicate that the trimethylphosphine ligands are not chemically identical. X-ray crystallography confirmed a distorted hexacoordinate octahedral structure of 16 (Figure 10). The axial angle P1–Fe1–P2 is 148.67(6)°, greatly deviating from 180°. [Si1Fe1P3P4H1] are in the equatorial



**Figure 10.** ORTEP plot of complexes **16** at the 50% probability level (hydrogen atoms except for Fe-H are omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1-H1 = 1.55(4), Fe1-Si1 = 2.331(1), Fe1-P1 = 2.214(1), Fe1-P2 = 2.222(1), Fe1-P3 = 2.276(1), Fe1-P4 = 2.263(2); P4-Fe1-H1 = 168(1), P3-Fe1-Si1 = 169.16(5), P1-Fe1-P2 = 148.67(6), Si1-Fe1-H1 = 76(1), Si1-Fe1-P4 = 92.57(5), P1-Fe1-P3 = 95.53(5), P2-Fe1-P3 = 95.01(5), P4-Fe1-P3 = 98.26(6).

plane. The Fe1–H1 distance (1.55(4) Å) is slightly longer than a normal Fe–H bond (~1.42 Å).<sup>17</sup> The Fe–P3 distance (2.276(1) Å) is longer than the Fe–P4 distance (2.263(2) Å), presumably due to the *trans* influence of the Si atom being greater than that of the H atom, while both distances are longer than the normal Fe1–P1 (2.214(1) Å) and Fe1–P2 distances (2.222(1) Å), owing to the weaker *trans* influence of the phosphorus atom.

**4.** Catalytic Activity of the Hydrido Iron Complex 16. The metal hydride complexes are fundamentally important for their crucial roles in a wide variety of TM catalytic systems.<sup>18</sup> Recently, there has been considerable interest in developing iron-catalyzed hydrosilylation of aldehydes and ketones.<sup>17,19</sup> At the beginning of this catalytic exploration, complex 16 was used as the catalyst to reduce the five selected aldehydes and ketones (Table 4). It was found that complex 16 could catalytically reduce aldehydes and ketones efficiently with triethoxysilane as a hydrogen source under mild conditions (Scheme 9).

The catalytic result suggests that benzaldehyde and furfural exhibit good activity. With benzaldehyde as substrate benzyl alcohol could be obtained in a yield of 100% after 1h (entry 1, Table 4) while furfuryl alcohol was produced in the yield of 92% during the same time (entry 3, Table 4). 4-Methoxybenzaldehyde with an electron-donating group on the phenyl ring required a longer reaction time until complete conversion (entry 2, Table 4). Entries 4 and 5 show that complex 16 also has good catalytic activity in the reduction of substrates and reaction mechanism studies will be reported in follow-up work from our laboratory.

## CONCLUSION

A study of the reactions of the tridentate pincer-type ligand bis(o-(diphenylphosphino)phenyl)methylsilane with electronrich low-valent iron, cobalt, and nickel complexes supported bytrimethylphosphine ligands has been carried out. The synthesisand characterization of a series of nickel, cobalt, and iron $complexes bearing tridentate bis(phosphino)silyl ligands (<math>\kappa^3$ -

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n 16

Entry	Substrate	Product	Time / h	Yield <sup>a</sup> / %
1	СНО	CH <sub>2</sub> OH	1	99.9
2	МеО-СНО	MeO-CH <sub>2</sub> OH	6	93.5
3	Сно	СН2ОН	1	92.1
4	$\bigcirc \neg \checkmark$	⟨OH	6	89.0
5	< →o	ОН	6	99.3

<sup>a</sup>Reaction conditions: substrate (1.0 mmol), (EtO)<sub>3</sub>SiH (1.5 mmol), complex 16 (0.010 mmol) in 2.5 mL of THF and *n*-dodecane as internal standard.

#### Scheme 9. Catalytic Reduction of Aldehydes

RCHO + (EtO)<sub>3</sub>SiH  $\xrightarrow{1 \text{ mol}\% \text{ 16}}_{\text{THF}} \xrightarrow{10\% \text{ NaOH}}_{\text{MeOH, 60 °C}} \text{ RCH}_2\text{OH}$ (1.5 equiv.)

(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMeH, [PSiP]-H, 1) have been reported via the activation of Si–H bonds. The preparation and isolation of  $\eta^2$ (Si–H)M and [Si–M–H] complexes were achieved. The properties of these hydrido metal complexes were investigated. At the same time, several corresponding halogenated nickel and cobalt complexes were obtained in a survey of reactivity. Further studies showed that the metal hydride complexes could be used as catalysts in the reduction of aldehydes and ketones.

#### EXPERIMENTAL SECTION

General Procedures and Materials. Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. The compounds  $(2-Ph_2PC_6H_4)_2SiH-Me$ ,<sup>Sa</sup> Ni $(PMe_3)_{4,2}^{20a}$  Ni $(2(PMe_3)_2)^{20b}$  NiMe $Cl(PMe_3)_2$ ,<sup>OC</sup> Ni-Me<sub>2</sub>(PMe<sub>3</sub>)<sub>3,0</sub> Co $(PMe_3)_{4,2}^{20d}$  Co $Cl(PMe_3)_3$ ,<sup>20e</sup> Fe $(PMe_3)_{4,2}^{0d}$  and  $(EtO)_3SiH^{20g}$  were prepared according to literature procedures. Infrared spectra (4000–400 cm<sup>-1</sup>), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. NMR spectra were recorded using Bruker Avance 300 and 400 MHz spectrometers. GC-MS was recorded on a TRACE-DSQ instrument, and GC was recorded on a Fuli 9790 instrument. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer. Melting points were measured in capillaries sealed under N<sub>2</sub> and were uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII instrument.

*Caution*! (EtO)<sub>3</sub>SiH is flammable and highly toxic by inhalation and may cause skin irritation and blindness.

Synthesis of  $\eta^2$ (Si–H)[PSiP]Ni(PMe<sub>3</sub>) (2). (a) ( $\kappa^3$ -(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMeH (1; 1.20 g, 2.12 mmol) in 30 mL of THF was combined with Ni(PMe<sub>3</sub>)<sub>4</sub> (0.81 g, 2.23 mmol) in 20 mL of THF with stirring at room temperature for 14 h. The reaction mixture turned yellow, and a small amount of yellow powder precipitated. After removal of the volatiles under reduced pressure the residue was extracted with pentane and diethyl ether. Compound 2 (1.13 g, 1.61 mmol) was isolated as yellow crystals in 76% yield from diethyl ether at 0 °C.

(b) NaBH<sub>4</sub> (0.08 g, 2.11 mmol) was added to a solution of complex 3 (0.62 g, 0.84 mmol) in 50 mL of THF with stirring at room temperature. A few drops of methanol were added to this mixture.

Bubbles from the solution could be seen clearly, and the solution turned brown. After removal of the solvents the residue was extracted with diethyl ether. Complex 2 (0.27 g, 0.39 mmol) was isolated as yellow powder in 46% yield at -30 °C. Mp: > 177 °C dec. Anal. Calcd for C<sub>40</sub>H<sub>41</sub>NiP<sub>3</sub>Si (701.42 g/mol): C, 68.49; H, 5.84. Found: C, 68.75; H, 6.01. IR (Nujol, KBr): 3038 (ArH), 1721 ( $\eta^2$ (Ni-H)), 1583 (ArC=C), 947 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene-d<sub>6</sub>, 300 K, ppm): δ –3.71 (tdq, J = 31.4, 14.3, 2.0 Hz, NiH, 1H), 0.99 (d, J = 5.9 Hz, PMe<sub>3</sub>, 9H), 1.37 (d, J = 1.9 Hz, SiMe, 3H), 6.88 (t, J = 7.4 Hz, Ar, 4H), 6.95-7.10 (m, Ar, 10H), 7.15 (td, J = 7.2, 4.5 Hz, Ar, 6H), 7.39 (d, J = 7.6 Hz, Ar, 2H), 7.78 (dt, J = 10.6, 4.0 Hz, Ar, 4H), 8.05 (d, J = 7.3 Hz, Ar, 2H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{\kappa}$ , 300 K,  $\delta$ ): -15.5 (s, PMe<sub>3</sub>, 1P), 48.5 (s, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): 5.0 (m, SiCH<sub>3</sub>), 21.3 (m, PMe<sub>3</sub>), 126.6 (s, Ar), 127.0-127.6 (m, Ar), 128.0 (s, Ar), 130.8 (s, Ar), 131.5 (m, Ar) 131.7 (m, Ar) 131.8 (s, Ar) ppm. <sup>29</sup>Si NMR (79.5 MHz, benzene $d_{6}$  296 K,  $\delta$ ): 13.71 (dt, J = 82.0, 3.3 Hz, <sup>1</sup>H-decoupled); (tt, J = 82.0, 82.0, 3.3 Hz, non-<sup>1</sup>H-decoupled) ppm.

Synthesis of [PSiP]Ni(Cl)(PMe<sub>3</sub>) (3). (a) One equivalent of  $Me_3SiCl$  or  $MeHSiCl_2$  was added to a solution of complex 2 (0.55 g, 0.78 mmol) in 50 mL of THF at 0 °C, and the mixture was then stirred at room temperature for 6 h. After removal of the solvent under reduced pressure, the residue was extracted with pentane and diethyl ether. Compound 3 was isolated as red blocklike crystals in 40% yield from diethyl ether at -30 °C.

(b)  $(2\text{-Ph}_2\text{PC}_6\text{H}_4)_2$ SiH-Me (1; 1.20 g, 2.12 mmol) in 30 mL of THF was combined with NiMeCl(PMe<sub>3</sub>)<sub>2</sub> (0.60 g, 2.31 mmol) in 20 mL of THF with stirring at room temperature for 14 h. After workup compound 3 (1.08 g, 1.47 mmol) was isolated as red crystals in 69% yield from diethyl ether at 0 °C.

(c) Compound 1 (0.83 g, 1.45 mmol) in 30 mL of THF was combined with NiCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.41 g, 1.45 mmol) in 20 mL of THF with stirring at room temperature for 14 h. After workup complex 3 (0.66 g, 0.90 mmol) was isolated as a red powder in 62% yield from diethyl ether at 0 °C.

(d) Compound 1 (0.82 g, 1.45 mmol) in 30 mL of THF was treated with anhydrous NiCl<sub>2</sub> (0.19 g, 1.45 mmol) in 20 mL of THF. The reaction mixture turned yellow, and a yellow powder precipitated. The solution turned red after addition of PMe<sub>3</sub> (0.15 g, 2.00 mmol). Complex 3 (0.62 g, 0.84 mmol) could be obtained as a red powder in 58% yield. Mp: > 163 °C dec. Anal. Calcd for C<sub>40</sub>H<sub>40</sub>ClNiP<sub>3</sub>Si (735.88 g/mol): C, 65.28; H, 5.48. Found: C, 65.61; H, 5.61. IR (Nujol, KBr): 3046 (ArH), 1584 (ArC=C), 949 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>, 300 K,  $\delta$ ): 0.81 (d, *J* = 6.0 Hz, PCH<sub>3</sub>, 9H), 1.29 (d, *J* = 1.2 Hz, SiCH<sub>3</sub>, 3H), 6.93–7.21 (m, *Ar*, 24H), 7.61 (m, *Ar*, 2H), 8.42 (dd, *J* = 9.0 and 27.0 Hz, *Ar*, 2H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene-*d*<sub>6</sub>, 300 K,  $\delta$ ): -16.9 (t, *J* = 28.6 Hz, PMe<sub>3</sub>, 1P), 34.6 (d, *J* = 28.7 Hz,

PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6^{3}}$  300 K, δ): 3.7 (s, SiCH<sub>3</sub>), 29.9 (s, PCH<sub>3</sub>), 128.5 (m, Ar), 128.8 (m, Ar), 129.6 (m, Ar), 130.9 (s, Ar), 131.7–132.1 (m, Ar), 132.3 (dd, J = 10.6, 5.4 Hz, Ar), 132.9 (m, Ar), 133.3 (m, Ar), 134.5 (t, J = 7.2 Hz, Ar), 137.1–137.6 (m, Ar), 139.4 (s, Ar) ppm.

Synthesis of [PSiP]Ni(Br)(PMe<sub>3</sub>) (4). EtBr (0.11 g, 1.0 mmol) was added to a solution of complex 2 (0.55 g, 0.78 mmol) in 50 mL of THF at 0 °C The mixture was stirred and refluxed for 3 h. After removal of the solvent under reduced pressure, the residue was extracted with pentane and diethyl ether. Compound 4 (0.23 g, 0.29 mmol) was isolated as red blocklike crystals in 37% yield from diethyl ether at -30 °C. Mp: > 186 °C dec. Anal. Calcd for C<sub>40</sub>H<sub>40</sub>BrNiP<sub>3</sub>Si (780.34 g/mol): C, 61.56; H, 5.17. Found: C, 61.31; H, 5.09. IR (Nujol, KBr): 3045 (ArH), 1583 (ArC=C), 948 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_6$ , 300 K,  $\delta$ ): 0.83 (d, J = 7.4 Hz, PMe<sub>3</sub>, 9H), 1.31 (d, J = 1.3 Hz, SiCH<sub>3</sub>, 3H), 6.95–7.23 (m, Ar, 22H), 7.64 (d, J = 7.2 Hz, Ar, 2H), 8.43 (dd, J = 5.1 and 12.0 Hz, Ar, 4H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): -16.9 (t, J = 28.2 Hz, PMe<sub>3</sub>, 1P), 34.6 (d, J = 28.7 Hz, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{61}$  300 K,  $\delta$ ): 5.8 (s, SiCH<sub>3</sub>), 26.6 (s, P CH<sub>3</sub>), 126.9 (s, Ar), 128.6-128.8 (m, Ar), 129.1 (s, Ar), 129.6 (s, Ar), 130.5 (s, Ar), 131.0 (s, Ar), 131.9 (s, Ar), 132.5 (s, Ar), 132.6 (t, J = 5.6 Hz, Ar), 132.7 (s, Ar), 132.6 (s, Ar), 133.2 (s, Ar), 134.3 (s, Ar), 134.4 (t, J =7.0 Hz, Ar), 134.5 (s, Ar) ppm.

Synthesis of [PSiP]Ni(I)(PMe<sub>3</sub>) (5). MeI (0.22 g, 1.51 mmol) was added to a solution of complex 2 (0.75 g, 1.06 mmol) in 50 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After removal of the solvent under reduced pressure, the residue was extracted with pentane and diethyl ether. Compound 5 (0.53 g, 0.64 mmol) was isolated as red blocklike crystals in 60% yield from diethyl ether at -30 °C. Mp: > 186 °C dec. Anal. Calcd for C40H40INiP3Si (827.33 g/mol): C, 58.07; H, 4.87. Found: C, 57.91; H, 4.61. IR (Nujol, KBr): 3050 (ArH), 1580 (ArC=C), 943 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): 0.79 (d, J = 7.2 Hz, PCH<sub>3</sub>, 9H), 1.31 (d, J = 1.2 Hz, SiCH<sub>3</sub>, 3H), 6.85-7.11 (m, Ar, 22H), 7.49 (d, J = 7.2 Hz, Ar, 2H), 8.22 (dd, J = 5.1 and 11.7 Hz, Ar, 4H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_6$ , 300 K,  $\delta$ ): -22.8 (t, J = 28.0 Hz, PMe<sub>3</sub>, 1P), 32.6 (d, J = 28.0 Hz, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6}$ , 75 K,  $\delta$ ): 9.7 (s, SiCH<sub>3</sub>), 17.0–17.4 (m, PCH<sub>3</sub>), 126.9-127.2 (m, Ar), 128.5-128.6 (m, Ar), 129.1 (s, Ar), 129.5 (s, *Ar*), 132.0 (d, *J* = 1.9 Hz, *Ar*), 133.0 (t, *J* = 5.6 Hz, *Ar*), 134.2 (t, *J* = 6.6 Hz, Ar), 136.8 (d, J = 3.9 Hz, Ar) ppm.

Synthesis of  $\eta^2$ (Si–H)[PSiP]Ni(CO) (6). A sample of 2 (0.65 g, 0.93 mmol) in 50 mL of THF was stirred under 1 bar of CO at room temperature for 14 h. All volatiles were removed in vacuo. The residue was extracted with pentane and diethyl ether. Compound 6 (0.35 g, 0.52 mmol) was isolated as pale yellow sticklike crystals in 55% yield from diethyl ether at -30 °C. Mp: > 196 °C dec. Anal. Calcd for C38H32NiOP2Si (653.39 g/mol): C, 69.85; H, 4.94. Found: C, 70.01; H, 4.81. IR (Nujol, KBr): 3034 (ArH), 1990 (CO), 1726 (η<sup>2</sup>(Ni–H)), 1585 (ArC=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_6$ , 300 K,  $\delta$ ): -2.13 (tq, J = 25.1, 1.9 Hz, NiH, 1H), 1.35 (d, J = 1.2 Hz, SiCH<sub>3</sub>, 3H), 6.63-7.15 (m, Ar, 20H), 7.34 (d, J = 7.8 Hz, Ar, 2H), 7.76 (d, J = 7.2 Hz, Ar, 2H), 7.86 (m, Ar, 4H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene-d<sub>6</sub>, 300 K, δ): 50.7 (s, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6i}$  300 K,  $\delta$ ): 3.7 (m, SiCH<sub>3</sub>), 127.6 (s, Ar), 127.6 (s, Ar), 128.0 (s, Ar), 128.0 (s, Ar), 128.2 (s, Ar), 128.3 (s, Ar), 128.3 (s, Ar), 128.3 (s, Ar), 129.1 (s, Ar), 129.3 (s, Ar), 131.8 (t, J = 6.1 Hz, Ar), 133.0 (t, J = 8.1 Hz, Ar), 136.4–137.0 (m, Ar), 139.9–140.5 (m, Ar), 144.3–145.0 (m, Ar), 152.6–154.2 (m, Ar), 204.0 (CO, s) ppm. <sup>29</sup>Si NMR (79.5 MHz, benzene- $d_{6}$ , 297 K,  $\delta$ ): 7.40 (s, <sup>1</sup>H-decoupled); (d, J = 104.8 Hz, non- $^{1}$ H-decoupled) ppm.

Synthesis of [PSiP]Ni(ÔMe)(PMe<sub>3</sub>) (7). Complex 3 (0.62 g, 0.84 mmol) was treated with NaOMe (0.05 g, 0.92 mmol) in 50 mL of THF with stirring at room temperature for 14 h. Compound 7 (0.39 g, 0.54 mmol) was isolated as red crystals by extraction with pentane and diethyl ether in 65% yield. Mp: > 158 °C dec. Anal. Calcd for C<sub>41</sub>H<sub>43</sub>NiOP<sub>3</sub>Si (731.49 g/mol): C, 67.32; H, 5.93. Found: C, 67.55; H, 5.69. IR (Nujol, KBr): 3047 (ArH), 1584 (ArC=C), 940 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_{6i}$  300 K,  $\delta$ ): 0.82 (t, J = 4.5 Hz,

SiCH<sub>3</sub>, 3H), 1.00 (d, J = 4.8 Hz, PCH<sub>3</sub>, 9H), 3.45 (s, OCH<sub>3</sub>, 3H), 6.90–7.24 (m, Ar, 22H), 7.80 (m, 4H), 8.46 (d, J = 7.2 Hz, Ar, 2H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{6'}$  300 K,  $\delta$ ): -29.8 (t, J = 23.3 Hz, PMe<sub>3</sub>, 1P), 26.3 (d, J = 23.3 Hz, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6'}$  300 K,  $\delta$ ): 14.0 (s, SiCH<sub>3</sub>), 20.1 (dt, J = 16.6, 5.0 Hz, PCH<sub>3</sub>), 49.6 (s, OCH<sub>3</sub>), 127.2 (s, Ar), 127.3–128.4 (m, Ar), 131.7 (s, Ar), 132.7 (t, J = 6.6 Hz, Ar), 133.2 (t, J = 7.8 Hz, Ar), 135.7 (t, J = 9.8 Hz, Ar), 138.3–137.7 (m, Ar), 141.7 (t, J = 18.2 Hz, Ar), 147.6–145.9 (m, Ar) ppm.

**Synthesis of [PSiP]Ni(Cl)(CO)**<sub>2</sub> (8). A sample of complex 3 (0.62 g, 0.84 mmol) in 50 mL of THF was stirred under 1 bar of CO at room temperature for 14 h. Complex 8 (0.37 g, 0.53 mmol) was isolated as a yellow powder from diethyl ether in a yield of 63%. Mp: > 215 °C dec. Anal. Calcd for C<sub>39</sub>H<sub>31</sub>ClNiO<sub>2</sub>P<sub>2</sub>Si (715.88 g/mol): C, 65.43; H, 4.36. Found: C, 65.72; H, 4.21. IR (Nujol, KBr): 3045 (ArH), 2007 (CO), 1938 (CO), 1584 (ArC=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>, 300 K,  $\delta$ ): 0.57 (s, SiCH<sub>3</sub>, 3H), 6.65 (d, *J* = 7.8 Hz, *Ar*, 2H), 6.80–7.10 (m, *Ar*, 16H), 7.29 (m, *Ar*, 4H), 7.48 (d, *J* = 7.2 Hz, *Ar*, 2H), 7.65 (m, *Ar*, 4H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene-*d*<sub>6</sub>, 300 K,  $\delta$ ): 31.8 (s, PPh<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, benzene-*d*<sub>6</sub>, 300 K,  $\delta$ ): 1.8 (s, SiCH<sub>3</sub>), 128.4–128.6 (m, *Ar*), 129.2 (s, *Ar*), 133.0 –133.6 (m, *Ar*), 136.3–136.7 (m, *Ar*), 143.2 (s, *Ar*), 188.0 (s, CO), 203.5 (s, CO) ppm.

**Synthesis of [Me<sub>2</sub>PŠiP]<sub>2</sub>Ni (9).** Compound 1 (0.82, 1.45 mmol) in 30 mL of THF was combined with Me<sub>2</sub>Ni(PMe<sub>3</sub>)<sub>3</sub> (0.46 g, 1.45 mmol) in 20 mL of THF with stirring at room temperature for 14 h. Compound 9 (0.48 g, 0.40 mmol) was isolated as an orange powder in 55% yield from pentane. Mp: > 145 °C dec. Anal. Calcd for C<sub>76</sub>H<sub>68</sub>NiP<sub>4</sub>Si<sub>2</sub> (1219.59 g/mol): C, 74.85; H, 5.62. Found: C, 75.02; H, 5.69. IR (Nujol, KBr): 3044 (ArH), 1583 (ArC=C) cm<sup>-1.</sup> <sup>1</sup>H NMR (300 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): 0.90 (t, J = 1.5 Hz, Si(CH<sub>3</sub>)<sub>2</sub>, 12H), 6.80–7.27 (m, Ar, 48H), 7.34 (m, Ar, 4H), 7.87 (d, J = 7.2 Hz, Ar, 4H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): -10.9 (s, PPh<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): 2.8 (t, J = 10.0 Hz, Si(CH<sub>3</sub>)<sub>2</sub>), 128.8–126.9 (m, Ar), 129.2 (s, Ar), 133.5 (d, J = 13.1 Hz, Ar), 143.4 (d, J = 12.5 Hz, Ar), 148.3 (d, J = 47.5 Hz, Ar) ppm.

Synthesis of [Me<sub>2</sub>PSiP]Ni(CO)<sub>2</sub> (10). A sample of complex 9 (0.50 g, 0.41 mmol) in 50 mL of THF was stirred under 1 bar of CO at room temperature for 14 h. Complex 10 (0.33 g, 0.47 mmol) was isolated as light yellow crystals from diethyl ether at -30 °C in a yield of 58%. Mp: > 179 °C dec. Anal. Calcd for  $C_{40}H_{34}NiO_2P_2Si$  (695.41 g/mol): C, 69.08; H, 4.93. Found: C, 68.81; H, 5.01. IR (Nujol, KBr): 3058 (ArH), 2003 (CO), 1946 (CO), 1584 (ArC=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_{61}$  300 K,  $\delta$ ): 0.44 (s, SiCH<sub>3</sub>, 6H), 6.65 (t, J = 7.5 Hz, Ar, 2H), 6.71-6.81 (m, Ar, 2H), 6.87-7.06 (m, Ar, 14H), 7.40-7.47 (m, Ar, 2H), 7.47-7.59 (m, Ar, 8H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{6i}$  300 K,  $\delta$ ): 35.0 (s, PPh<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{61}$  300 K,  $\delta$ ): 5.9 (t, J = 10.0 Hz, SiCH<sub>3</sub>), 127.5–128.3 (m, Ar) 128.3 (s, Ar), 133.0 (d, J = 4.1 Hz, Ar), 133.4–133.8 (m, Ar), 137.5-137.9 (m, Ar), 138.3 (d, J = 2.8 Hz, Ar), 138.3 (d, J = 2.8 Hz, Ar), 143.4 (s, Ar), 143.8 (s, Ar), 144.1 (s, Ar), 144.4 (s, Ar), 199.4 (t, J = 4.1 Hz, CO) ppm.

**Synthesis of [PSiP]Co(H)(PMe<sub>3</sub>) (11).** Compound 1 (0.82 g, 1.45 mmol) in 30 mL of THF was combined with Co(PMe<sub>3</sub>)<sub>4</sub> (0.52 g, 1.45 mmol) in 20 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After workup, complex 11 (0.59 g, 0.84 mmol) was isolated as a yellow powder from diethyl ether in a yield of 58%. Mp: >142 °C dec. Anal. Calcd for C<sub>40</sub>H<sub>41</sub>CoP<sub>3</sub>Si (701.65 g/mol): C, 68.47; H, 5.89. Found: C, 68.41; H, 5.71. IR (Nujol, KBr): 3050 (Ar–H), 1917 (Co–H), 1558 (ArC=C), 952 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>, 300 K, δ): −14.04 (q, *J* = 61.5 Hz, Co*H*, 1H), 0.64 (d, *J* = 7.6 Hz, PCH<sub>3</sub>, 9H), 0.82 (s, SiCH<sub>3</sub>, 3H), 7.10 (dd, *J* = 14.8, 7.4 Hz, *Ar*, 14H), 7.34 (t, *J* = 7.3 Hz, *Ar*, 2H), 7.40–7.54 (m, *Ar*, 2H), 7.68–7.89 (m, *Ar*, 4H), 8.21 (t, *J* = 7.3 Hz, *Ar*, 6H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene-*d*<sub>6</sub>, 300 K, δ): −8.5 (m, PMe<sub>3</sub>, 1P), 68.2 (m, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene-*d*<sub>6</sub>, 300 K, δ): 8.2 (d, *J* = 4.6 Hz, SiCH<sub>3</sub>), 19.2 (d, *J* = 24.1 Hz, PCH<sub>3</sub>), 126.9–128.8 (m,

Ar), 129.1–129.5 (m, Ar), 132.9 (t, J = 4.5 Hz, Ar), 133.7 (t, J = 5.0 Hz, Ar) ppm.

Synthesis of [PSiP]Co(H)(I)(PMe<sub>3</sub>) (12). Complex 11 (0.52 g, 0.74 mmol) in 30 mL of THF was treated with MeI (0.12 g, 0.84 mmol) in 20 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After workup, complex 12 (0.28 g, 0.34 mmol) was obtained as orange crystals from diethyl ether in a yield of 46%. Mp: > 200 °C dec. Anal. Calcd for C40H41CoIP3Si (828.56 g/mol): C, 57.98; H, 4.99. Found: C, 58.21; H, 4.83. IR (Nujol, KBr): 3048 (Ar-H), 1927 (Co-H), 1584 (ArC=C), 950 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_{6i}$  300 K,  $\delta$ ): -14.67 (q, J = 61.8 Hz, CoH, 1H), 0.70  $(d, J = 7.5 \text{ Hz}, \text{PCH}_3, 9\text{H}), 1.45 (s, \text{SiCH}_3, 3\text{H}), 7.10 (m, Ar, 14\text{H}),$ 7.30-7.43 (m, Ar, 4H), 7.71-7.82 (m, Ar, 4H), 8.25 (t, J = 7.4 Hz, Ar, 2H), 8.29-8.38 (m, Ar, 4H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene $d_{6}$  300 K,  $\delta$ ): -14.8 (m, PMe<sub>3</sub>, 1P), 67.5 (m, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene- $d_{6i}$  300 K,  $\delta$ ): 7.6 (d, J = 3.7 Hz, SiCH<sub>3</sub>), 18.1 (m, PCH<sub>3</sub>), 127.2–128.4 (m, Ar), 129.3 (d, J = 6.8 Hz, Ar), 131.6-132.0 (m, Ar), 132.6-132.8 (m, Ar), 133.8-134.0 (m, Ar), 137.3-137.7 (m, Ar), 138.6-139.0 (m, Ar), 146.3 (m, Ar), 157.8 (m, Ar) ppm.

Synthesis of [PSiP]Co(H)(Cl)(PMe<sub>3</sub>) (13). Complex 1 (0.82 g, 1.45 mmol) in 30 mL of THF was combined with  $CoCl(PMe_3)_3$  (0.47 g, 1.45 mmol) in 20 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After workup, complex 13 (0.82 g, 1.12 mmol) was obtained as yellow crystals at -30 °C from diethyl ether in a yield of 77%. Mp: > 156 °C dec. Anal. Calcd for C<sub>40</sub>H<sub>41</sub>ClCoP<sub>3</sub>Si (737.11 g/mol): C, 65.18; H, 5.61. Found: C, 65.31; H, 5.79. IR (Nujol, KBr): 3047 (Ar-H), 1910 (Co-H), 1592 (ArC=C), 952 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): -13.68 (q, J = 61.2 Hz, CoH, 1H), 0.63 (d, J = 7.30 Hz, PCH<sub>3</sub>, 9H), 0.78 (s, SiCH<sub>3</sub>, 3H), 6.99–7.18 (m, Ar, 14H), 7.34 (t, J = 7.20 Hz, Ar, 2H), 7.41-7.52 (m, Ar, 2H), 7.83 (m, Ar, 4H), 8.10-8.27 (m, Ar, 6H) ppm.  ${}^{31}P{}^{1}H$  NMR (121 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): -3.7 (m, PMe<sub>3</sub>, 1P), 68.9 (m, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene-d<sub>6</sub>, 300 K,  $\delta$ ): 7.6 (d, J = 4.4 Hz, SiCH<sub>3</sub>), 20.0 (d, J = 24.1 Hz, PCH<sub>3</sub>), 125.4 (s, Ar), 127.1-128.4 (m, Ar), 129.3 (d, J = 6.6 Hz, Ar), 130.5 (s, *Ar*), 131.8 (t, *J* = 10.2 Hz, *Ar*), 132.7 (t, *J* = 4.7 Hz, *Ar*), 133.0 (s, *Ar*), 133.9 (t, J = 5.1 Hz, Ar), 135.1 (s, Ar) ppm.

Synthesis of [PSiP]Co(PMe<sub>3</sub>)<sub>2</sub> (14). One equivalent of MeLi (0.65 mL, 1.6 M) or n-BuMgBr (1.0 mL, 1.02 M) was added to a solution of complex 13 (0.75 g, 1.02 mmol) in 50 mL of THF at 0  $^\circ\text{C}.$ After the mixture was stirred for 14 h at room temperature, the volatiles were removed under reduced pressure and the residue was extracted with pentane and diethyl ether. Compound 14 (0.51 g, 0.66 mmol) was isolated as a red powder in 65% yield. Mp: > 174 °C dec. Anal. Calcd for C43H49CoP4Si (776.73 g/mol): C, 66.49; H, 6.36. Found: C, 66.76; H, 6.11. IR (Nujol, KBr): 3045 (Ar–H), 1579 (ArC=C), 938 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene-d<sub>6</sub>, 300 K,  $\delta$ ): 0.58 (s, SiCH<sub>3</sub>, 3H), 0.79 (d, J = 6.30 Hz, PCH<sub>3</sub>, 9H), 1.19 (d, J= 5.30 Hz, PCH<sub>3</sub>, 9H), 6.93 (t, I = 7.10 Hz, Ar, 8H), 6.99-7.14 (m, Ar, 14H), 7.72 (dd, J = 9.30, 5.90 Hz, Ar, 6H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): -17.5 (m, PMe<sub>3</sub>, 1P), 4.0 (m, PMe<sub>3</sub>, 1P), 56.5 (PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene-d<sub>6</sub>, 300 K,  $\delta$ ): 4.4 (s, SiCH<sub>3</sub>), 24.2 (d, J = 5.8 Hz, PCH<sub>3</sub>), 24.4 (d, J = 5.5 Hz, PCH<sub>3</sub>), 126.8 (s, Ar),127.0 (s, Ar), 127.3 (s, Ar), 127.5 (s, Ar), 127.7 (s, Ar), 127.8 (s, Ar), 128.1 (s, Ar), 130.5 (s, Ar), 130.9 (t, J = 11.1 Hz, Ar), 132.8 (t, J = 5.3 Hz, Ar), 133.2 (t, J = 6.8 Hz, Ar), 142.6 (s, Ar) ppm.

**Synthesis of [PSiP]Co(Cl)(PMe<sub>3</sub>) (15).** Compound 1 (0.82 g, 1.45 mmol) was treated with anhydrous CoCl<sub>2</sub> (0.19 g, 1.45 mmol) in THF. The reaction mixture turned purple. The solution turned reddish brown after PMe<sub>3</sub> (0.15 g, 2.00 mmol) was added. After workup compound **15** (0.43 g, 0.58 mmol) was isolated as red crystals in 40% yield. Mp: > 183 °C dec. Anal. Calcd for C<sub>40</sub>H<sub>40</sub>ClCoP<sub>3</sub>Si (736.10 g/mol): C, 65.27; H, 5.48. Found: C, 65.57; H, 5.39. IR (Nujol, KBr): 3045 (Ar–H), 1582 (ArC=C), 934 (PMe<sub>3</sub>) cm<sup>-1</sup>. Complex **15** is paramagnetic, and its <sup>1</sup>H NMR spectrum is given in the Supporting Information.

Synthesis of [PSiP]Fe(H)(PMe<sub>3</sub>)<sub>2</sub> (16). Compound 1 (0.82 g, 1.45 mmol) in 30 mL of toluene was treated with  $Fe(PMe_3)_4$  (0.55 g, 1.53

mmol) in 20 mL of toluene with stirring at room temperature for 24 h. After workup, complex 16 (0.72 g, 0.93 mmol) was isolated as orange crystals from diethyl ether in a yield of 64%. Mp: > 141 °C dec. Anal. Calcd for C43H50FeP4Si (774.65 g/mol): C, 66.67; H, 6.50. Found: C, 66.91; H, 6.62. IR (Nujol, KBr): 3047 (Ar-H), 1870 (Fe-H), 1584 (ArC=C), 939 (PMe<sub>3</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, benzene-d<sub>6</sub>, 300 K,  $\delta$ ): -17.09 (td, J = 71.4, 18.1 Hz, FeH, 1H), 0.53 (d, J = 5.1 Hz,  $PCH_{3}$ , 9H), 0.98 (d, J = 5.4 Hz,  $PCH_{3}$ , 9H), 1.06 (s, SiCH<sub>3</sub>, 3H), 7.07-6.82 (m, Ar, 16H), 7.34 (t, J = 7.1 Hz, Ar, 2H), 7.55 (m, Ar, 4H), 7.76 (t, J = 3.9 Hz, Ar, 4H), 8.50 (d, J = 7.3 Hz, Ar, 2H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_{6}$ , 300 K,  $\delta$ ): 5.6 (t, J = 21.8 Hz, PMe<sub>3</sub>, 2P), 88.9 (t, J = 19.7 Hz, PPh<sub>2</sub>, 2P) ppm. <sup>13</sup>C NMR (75 MHz, benzene-d<sub>6</sub>, 300 K, δ): 15.3 (s, SiCH<sub>3</sub>), 29.9 (s, PCH<sub>3</sub>), 126.5-126.7 (m, Ar), 126.9-127.0 (m, Ar), 128.5-128.6 (m, Ar), 130.8 (s, Ar), 131.5–131.6 (m, Ar), 133.6 (dt, J = 4.9, 6.9 Hz, Ar), 144.1–144.2 (m, Ar) ppm.

General Procedure for Catalytic Reduction. In a 25 mL Schlenk tube containing a solution of 16 (7.7 mg, 0.01 mmol) in 2.5 mL of THF were added the substrates (1.0 mmol) and  $(EtO)_3SiH$  (1.5 mmol). The reaction mixture was stirred at 60 °C until there were no substrates left (monitored by GC). The reaction was then quenched by MeOH (1 mL) and a 10% aqueous solution of NaOH (3 mL) with vigorous stirring at 60 °C for about 1 day. The organic product was extracted with Et<sub>2</sub>O. All products were confirmed by GC-MS, and the yields were determined by GC with *n*-dodecane (1.0 mmol) as internal standard.

X-ray Structure Determinations. Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Crystallographic data for complexes 2– 5, 10, 12, 13, 15, and 16 are summarized in the Supporting Information. The structures were solved by direct methods and refined with full-matrix least squares on all  $F^2$  (SHELXL-97) with nonhydrogen atoms anisotropic. Each hydride was located directly from the difference map and the position refined. The remaining H atoms were either located or calculated and subsequently treated with a riding model. CCDC-914016 (2), CCDC-914017 (3), CCDC-914018 (4), CCDC-914019 (5), CCDC-914011 (10), CCDC-914012 (12), CCDC-914013 (13), CCDC-914014 (15), and CCDC-914015 (16) contain supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (+44)1223-336--033; e-mail, deposit@ccdc.cam.ac.uk).

**Computational Methods.** All calculations were performed with the Gaussian03 package with the hybrid B3LYP functional.<sup>21</sup> The basis set was LANL2DZ for Ni and  $6-31g(d)/6-31g^*$  for all other atoms. The LANL2DZ pseudopotential was used for Ni. Full optimization of geometry was performed without any symmetry constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima. The zero-point, thermal, and entropy corrections were evaluated to compute enthalpies and Gibbs free energies.

#### ASSOCIATED CONTENT

#### S Supporting Information

CIF files and a table giving crystallographic data for 2-5, 10, 12, 13, 15, and 16 and a figure giving the <sup>1</sup>H NMR spectrum of 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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# The authors declare no competing financial interest.

Notes

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