Reactivity of Phosphasilametallacyclopropane toward Substrates with Polarized E−H Bonds (E = O, N, S, and P): Formation and Structures of Ring-Opening Products

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Treatment of a three-membered metallacycle Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2PPh_2$} (**1**) with substrates of the type R_nEH (ER_n = OH, OMe, O^{t}Bu, OPh, S^{p}Tol, NEt_2, NPhH, PPh_2, and PPhH) results in the instantaneous formation of the ring-opening products Cp*(CO)Fe(PPh_2H)($SiMe_2ER_n$). In these reactions, 1,2-addition of the substrates occurs exclusively across the silicon−phosphorus bond in **1**. The structures of the products have been unequivocally determined by spectroscopic data and X-ray diffraction analysis.

Introduction

Three-membered cyclic compounds with ring constituents of silicon and transition metal atoms have attracted much attention with respect to bonding modes and reactivity.[1] Although several silametallacyclopropanes have been prepared and their reactivity toward various substrates has been investigated, there have been only limited studies concerning the reactions between silametallacyclopropane and substrates with E−H single bonds (E = typical elements having nonbonding electron pairs). Berry[2] and Tilley[3] independently reported that the treatment of silene complexes, L_nM{κ^2(*C,Si*)-CH_2SiR_2} (L_nM = Cp_2W, Cp*(PMe_3)Ir), with MeOH leads to the selective cleavage of the metal−silicon bonds to give L_n(H)MCH_2Si(OMe)R_2. Similarly, the disilene platinum complex (Et_3P)$_2$Pt{κ^2(*Si,Si*)-$Mes_2SiSiMes_2$} has been shown to react with MeOH to give (Et_3P)$_2$Pt(H)$SiMes_2SiMes_2OMe$ through cleavage of the platinum−silicon bond,[4] while the disilene molybdenum complex Cp_2Mo{κ^2(*Si,Si*)-$Me_2SiSiMe_2$} reacts with MeOH to give a mixture of $Cp_2Mo(H)SiMe_2SiMe_2OMe$ and Cp_2Mo($SiMe_2OMe$)$SiMe_2H$ in a 2:8 molar ratio by 1,2-MeOH addition to the silicon−silicon bond.[5]

Recently, our research has been focused on the synthesis and properties of three-membered metallacycles of the type L_nM{κ^2(*Si,E*)-$SiMe_2ER_n$}, in which the heteroatom (E) has at least one lone pair and the κ^2(*Si,E*)-$SiMe_2ER_n$ ligand donates three electrons in total to the metal center.[6] Our previous communication described the isolation of phosphasilametallacyclopropane, Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2PPh_2$} (**1**),[6b] which exhibits unique reactivity toward molecules with a polarized unsaturated bond. For example, treatment of **1** with acetone led to insertion of the CO double bond into the silicon−phosphorus bond to produce Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2OCMe_2PPh_2$}. A heteroaromatic compound, 4-(dimethylamino)pyridine (DMAP), also reacted with **1** to give the insertion product. The present report examines the reactivity of **1** toward molecules with polarized E−H single bonds (E = O, N, S, P) such as water, alcohol, phenol, secondary amine, aniline, thiol, and primary and secondary phosphines. All reactions proceeded quickly at room temperature to give the 1,2-addition products through cleavage of the silicon−phosphorus bond.

Results and Discussion

Reactions of 1 with H_2O, MeOH, ^{t}BuOH, PhOH, ^{p}TolSH, Et_2NH, and $PhNH_2$. The reactions of **1** with R_nE−H (E = O, S, and N) are illustrated in Scheme 1. Selected infrared (IR) and nuclear magnetic resonance (NMR) data for complexes **1**−**8** are listed in Table 1. In the reactions of **1** with water, alcohols, and phenol at room temperature, the ring-opening products **2**−**5** were formed immediately and exclusively through cleavage of the silicon−phosphorus bond. The difference between the reaction mode between **1** and silene[2,3] or disilene[4,5] complexes toward MeOH is likely to reflect the highly polarized silicon−phosphorus bond. Complex **1** also reacted with ^{p}TolSH, Et_2NH, and aniline to give the corresponding products **6**−**8** under the same reaction conditions.

Pham and West reported the reaction of the disilene complex (dppe)Pt{κ^2(*Si,Si*)-$Me_2SiSiMe_2$} with ammonia to give (dppe)Pt{κ^2(*Si,Si*)-$SiMe_2N(H)SiMe_2$} in nearly

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Scheme 1. Reactions of 1 with $R_nE{-}H$ (R_nE = OH, OMe, O^tBu, OPh, S^pTol, NEt_2, NHPh)

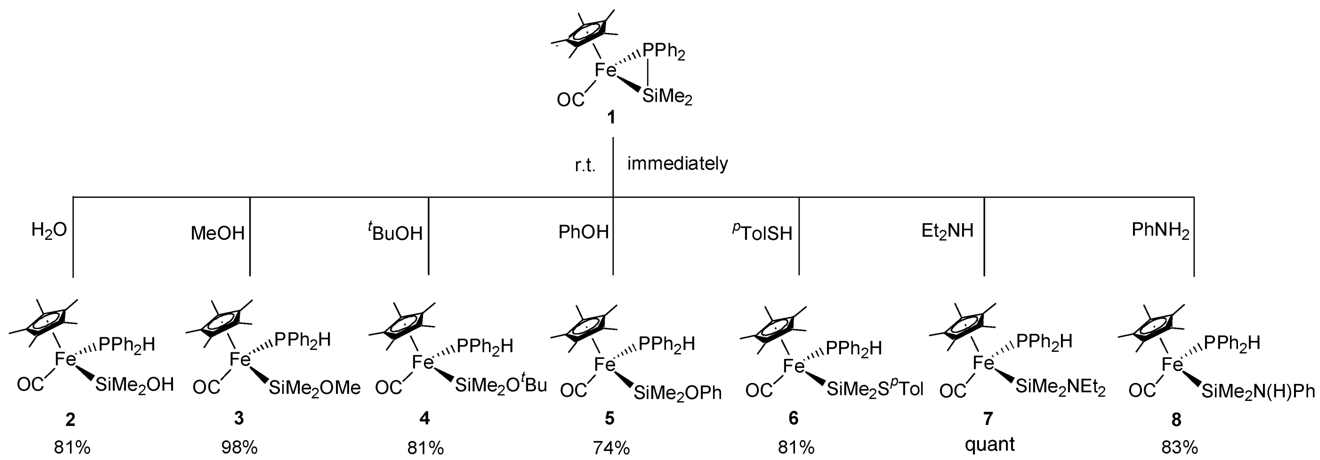

Table 1. Selected IR and NMR Data for 1−10

complex	IR (ν_{CO}), cm^{-1}	^{1}H NMR δ PH	^{29}Si NMR δ	^{31}P NMR δ
1[6b]	1894		25.4 (d, $^1J_{PSi}$ = 125.5 Hz)	−48.3
2	1897	6.62 (d, $^1J_{PH}$ = 343.5 Hz)	71.0 (d, $^2J_{PSi}$ = 40.5 Hz)	63.5
3	1896	6.67 (d, $^1J_{PH}$ = 347.0 Hz)	73.5 (d, $^2J_{PSi}$ = 42.1 Hz)	61.4
4	1894	6.87 (d, $^1J_{PH}$ = 354.3 Hz)	59.6 (d, $^2J_{PSi}$ = 45.3 Hz)	59.2
5	1900	6.67 (d, $^1J_{PH}$ = 347.1 Hz)	76.4 (d, $^2J_{PSi}$ = 42.3 Hz)	61.3
6	1901	6.89 (d, $^1J_{PH}$ = 349.2 Hz)	64.4 (d, $^2J_{PSi}$ = 42.9 Hz)	60.9
7	1890	6.68 (d, $^1J_{PH}$ = 356.7 Hz)	53.8 (d, $^2J_{PSi}$ = 39.7 Hz)	59.5
8	1898	6.73 (d, $^1J_{PH}$ = 349.8 Hz)	50.9 (d, $^2J_{PSi}$ = 42.3 Hz)	58.8
9	1898	6.67 (dd, $^1J_{PH}$ = 346.0 Hz, $^4J_{PH}$ = 1.8 Hz)	45.6 (dd, $^1J_{PSi}$ = 83.4 Hz, $^2J_{PSi}$ = 40.3 Hz)	−31.9 (d, $^3J_{PP}$ = 15.2 Hz, SiPPh$_2$) 66.1 (d, $^3J_{PP}$ = 15.2 Hz, PPh$_2$H)
10	1901	3.48 (d, $^1J_{PH}$ = 204.0, SiPH)	41.4 (dd, $^1J_{PSi}$ = 73.3 Hz, $^2J_{PSi}$ = 38.8 Hz)	−100.6 (d, $^3J_{PP}$ = 7.3 Hz, SiPPhH)
		3.83 (d, $^1J_{PH}$ = 203.7, SiPH)		−98.7 (d, $^3J_{PP}$ = 18.2 Hz, SiPPhH)
		6.69 (d, $^1J_{PH}$ = 348.6 Hz, PPh$_2$H)	42.4 (dd, $^1J_{PSi}$ = 67.3 Hz, $^2J_{PSi}$ = 39.5 Hz)	58.6 (d, $^3J_{PP}$ = 7.3 Hz, PPh$_2$H)
		6.79 (d, $^1J_{PH}$ = 350.1 Hz, PPh$_2$H)		58.7 (d, $^3J_{PP}$ = 18.2 Hz, PPh$_2$H)

quantitative yield.[4] Although the authors did not mention the reaction mechanism, it is believed that the reaction could proceed via the transient formation of (dppe)Pt($SiMe_2H$)($SiMe_2NH_2$), corresponding to complex **7**.

In accordance with the cleavage of the three-membered-ring structure, the signals in the ^{29}Si and ^{31}P NMR spectra were significantly downfield-shifted compared to those for **1**.[7] The signals of the incorporated $R_nE{-}H$ fragments were reasonably assigned in the ^{1}H NMR spectra. Typically, in complex **2**, the ^{1}H NMR signals assigned to the SiOH and PH fragments were observed at 0.88 (s) and 6.62 (d, $^1J_{PH}$ = 343.5 Hz), respectively.

The molecular structures of **2**, **3**, **5**, and **6** are shown in Figures 1, 2, 3, and 4, respectively. These complexes adopt the normal three-legged piano-stool geometry. Besides the Cp* and CO ligands, the iron center possesses the $SiMe_2ER_n$ (ER_n = OH, OMe, OPh, S^pTol) and PPh_2H ligands formed through the addition of $R_nE{-}H$ across the silicon−phosphorus bond. The iron−silicon bond is shorter than the typical iron−silicon single bonds in L_nFeSiR_3 (R = alkyl or aryl), but is comparable to those in heteroatom-substituted silyliron complexes.[1] The shortening is due to back-donation from the iron d_π orbital to the σ^* orbital of the Si−E bond.

Our previous communications demonstrated that **1** reacted with 4-(dimethylamino)pyridine (DMAP) or acetone to give the insertion product.[6b] We have proposed a mechanism involving the attack of the nucleophiles to **1** to give base-stabilized silylene complexes, followed by the nucleophilic attack of the phosphido ligand toward the α-carbon of the coordinated DMAP and acetone. The formation of **2**−**8** can also be reasonably explained by assuming the generation of the base-

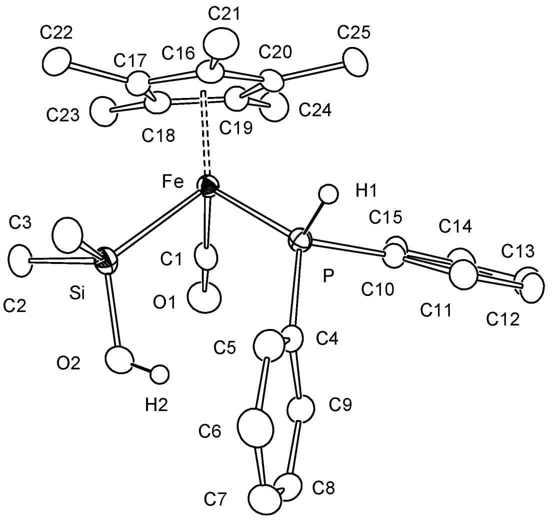

Figure 1. Molecular structure of **2** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe−P = 2.1632(11), Fe−Si = 2.3196(12), Fe−C1 = 1.738(4), C1−O1 = 1.161(5), Si−O2 = 1.685(3), P−H1 = 1.39(5), O2−H2 = 0.81(6), C1−Fe−P = 95.69(13), C1−Fe−Si = 81.80(12), P−Fe−Si = 95.15(4).

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(7) The ^{29}Si or ^{31}P NMR signal of a silicon or phosphorus atom in a three-membered metallacycle shows typical upfield shift: (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

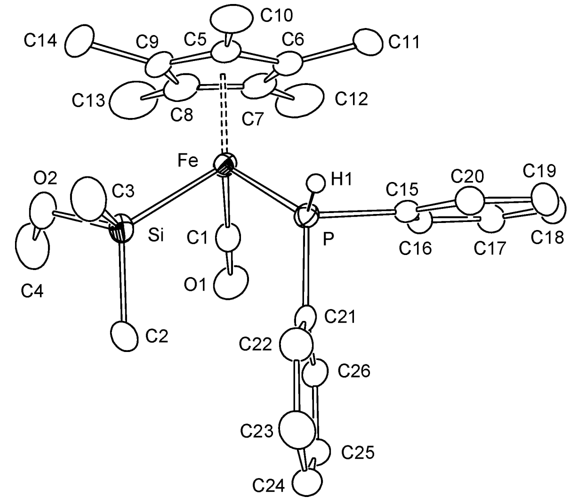


Figure 2. Molecular structure of **3** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe−P = 2.1535(9), Fe−Si = 2.3169(9), Fe−C1 = 1.722(3), C1−O1 = 1.171(4), O2−C4 = 1.397(4), Si−O2 = 1.686(2), P−H1 = 1.33(3), C1−Fe−P = 93.64(10), C1−Fe−Si = 84.77(10), P−Fe−Si = 93.08(3).

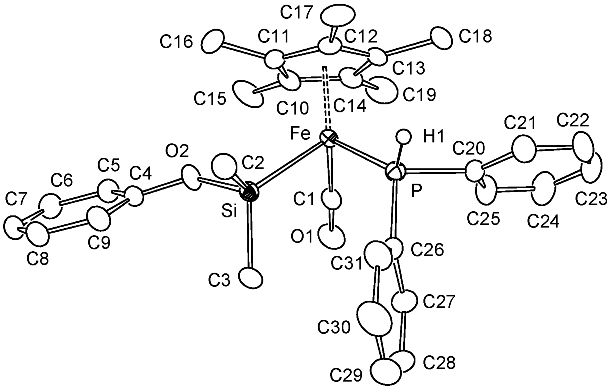


Figure 3. Molecular structure of **5** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe−P = 2.1571(5), Fe−Si = 2.2947(5), Fe−C1 = 1.7263(17), C1−O1 = 1.166(2), O2−C4 = 1.3551(19), Si−O2 = 1.7034(13), P−H1 = 1.30(2), C1−Fe−P = 96.64(6), C1−Fe−Si = 82.05(5), P−Fe−Si = 94.053(17).

stabilized silylene complexes (Scheme 2).[8] The lone pair of the phosphido ligand then attacks the proton of the coordinated molecule to give the products. An alternative concerted mechanism involving an Si−P−H−E four-membered ring transition state, however, cannot be ruled out.

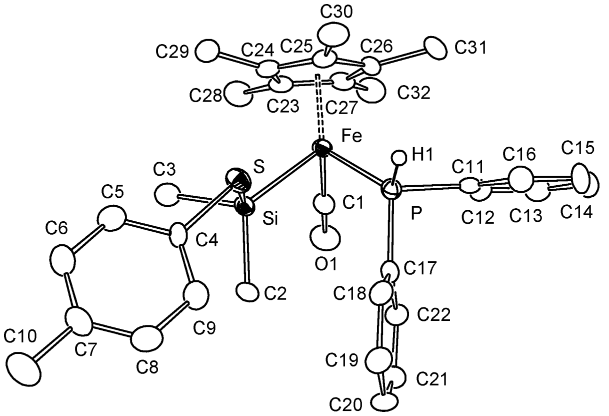
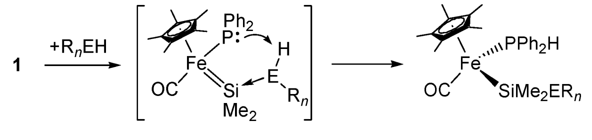
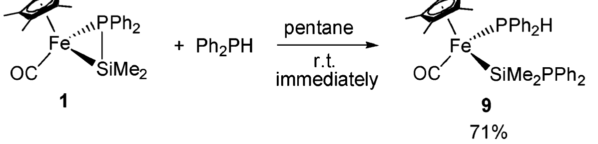


Figure 4. Molecular structure of **6** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe−P = 2.1603(16), Fe−Si = 2.2992(16), Fe−C1 = 1.721(6), C1−O1 = 1.150(7), Si−S = 2.189(2), S−C4 = 1.773(5), P−H1 = 1.44(5), C1−Fe−P = 94.92(19), C1−Fe−Si = 83.65(18), P−Fe−Si = 92.24(6), S−Si−Fe = 105.13(7).

Scheme 2 Plausible Formation Mechanism of 2−8

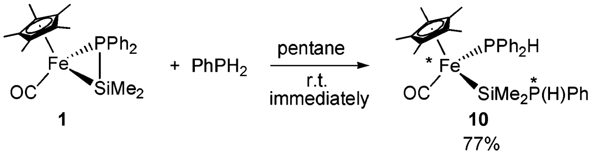


Reactions of 1 with Secondary and Primary Phosphines. Treatment of **1** with PPh$_2$H led to the formation of **9** in 71% isolated yield (eq 1). In the ^{1}H NMR spectrum, the signal of the PH fragment was observed at δ 6.67 as a doublet of doublets ($^{1}J_{PH}$ = 346.0 Hz, $^{4}J_{PH}$ = 1.8 Hz). A doublet of doublets was also observed in the ^{29}Si NMR spectrum at δ 45.6 ($^{1}J_{PSi}$ = 83.4 Hz, $^{2}J_{PSi}$ = 40.3 Hz). Furthermore, in the ^{31}P{^{1}H} NMR spectrum, two coupled doublets were observed at δ −31.9 and 66.1 with a coupling constant of J_{PP} = 15.2 Hz. As the ^{31}P NMR signal of Cp*(CO)$_2$SiMe$_2$PPh$_2$ appears at δ −44.1,[6b] these two doublet signals can be assigned to the SiPPh$_2$ and PPh$_2$H fragments, respectively.



(1)

The formation of **9**, in addition to the mechanism shown in Scheme 2, can be explained by considering the validity of an alternative mechanism involving the coordination of PPh$_2$H to the iron center through cleavage of the iron−phosphorus bond. To clarify the mechanism, **1** was reacted with PPhH$_2$. This reaction also proceeded quickly at room temperature to give **10** as a 1:1 mixture of two diastereomers in 77% isolated yield (eq 2). One of the diastereomers was unequivocally determined by X-ray diffraction analysis (Figure 5). Besides the Cp* and CO ligands, the iron center possesses the SiMe$_2$P(H)Ph and PPh$_2$H ligands, clearly indicating that complexes **9** and **10** were formed through 1,2-additon of the phosphorus−hydrogen bonds across the phosphorus−silicon bond. Thus, the alternative mechanism mentioned above can be ruled out.



(2)

Conclusion

The reactions of phosphasilametallacyclopropane **1** with water, MeOH, ^{t}BuOH, PhOH, ^{p}TolSH, Et$_2$NH, PhNH$_2$, Ph$_2$PH, and PhPH$_2$ were shown to proceed

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[8] (a) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (b) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493.

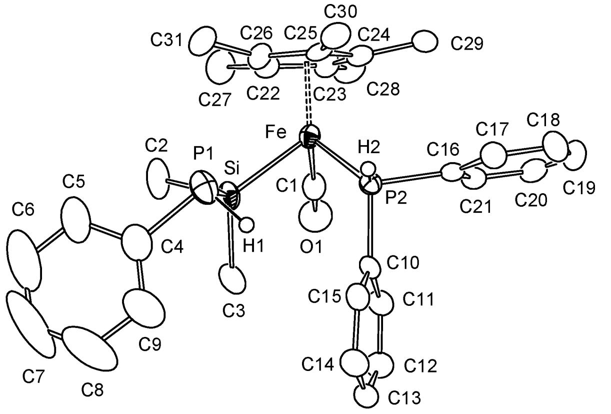

Figure 5. Molecular structure of **10** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe−P2 = 2.1673(16), Fe−Si = 2.3212(17), Fe−C1 = 1.737(6), P1−Si = 2.305(2), C1−O1 = 1.158(7), P1−H1 = 1.26(7), P2−H2 = 1.31(5), C1−Fe−P2 = 96.5(2), C1−Fe−Si = 82.86(19), P2−Fe−Si = 91.64(6), Fe−Si−P1 = 111.14(8).

immediately at room temperature to give the corresponding 1,2-additon products through cleavage of the silicon−phosphorus bond. Cleavage of the iron−silicon or iron−phosphorus bond was not observed in any of these reactions. To the best of the authors' knowledge, the carbon analogue of **1**, phosphametallacyclopropapne, does not exhibit this type of reactivity toward substrates with polarized E−H bonds.[9] Thus, the novel reactivity of phosphasilametallacyclopropane is attributable to the highly polarized silicon−phosphorus bond.

Experimental Section

General Procedures. All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade hexane and pentane were distilled from sodium-benzophenone ketyl immediately prior to use. Benzene-d_6 was dried over a potassium mirror and transferred to an NMR tube under vacuum. Dichloromethane-d_2 was distilled from CaH_2, dried over a molecular sieves (3 Å), and transferred to an NMR tube under vacuum. Methanol was distilled from $Mg(OMe)_2$ and stored in the presence of molecular sieves 3 Å. ^{t}BuOH was distilled from CaH_2 and stored in the presence of molecular sieves 4 Å. ^{p}TolSH was purified by recrystallization from pentane. NEt_2H and aniline were distilled from KOH and CaH_2, respectively, prior to use. PPh_2H[10] and $PPhH_2$[11] were prepared according to literature methods. Other chemicals were purchased and used as received. NMR data were recorded on a Bruker ARX-300 or AV-300 spectrometer. ^{29}Si NMR spectra were obtained using the DEPT pulse sequence technique. IR spectra were recorded on a Horiba FT-200 spectrometer. Mass spectral data were obtained using a JEOL JMS-HX110 or Hitachi M2500S spectrometer.

Reaction of 1 with H_2O. A Pyrex tube (20 mm o.d.) equipped with a greaseless vacuum valve and a stirrer bar was charged with **1** (19 mg, 0.041 mmol), pentane (5 mL), and an excess of H_2O (20 μL) in this order under high vacuum by the trap-to-trap transfer technique. The reaction mixture was then stirred at room temperature for 30 min. Subsequent removal of volatiles gave spectroscopically pure **2** as an orange powder. Yield: 16 mg (81%). Anal. Calcd for $C_{25}H_{33}FeO_2PSi$: C, 62.50; H, 6.92. Found: C, 62.57; H, 7.06. EI-MS (70 eV): *m/z* 480 (M^+, 6), 451 ($M^+ - CO - H$, 10), 404 ($M^+ - C_2H_8OSi$, 100). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.47, 0.63 (s, 3H × 2, $SiMe_2$), 0.88 (s, 1H, OH), 1.57 (s, 15H, Cp*), 6.62 (d, $^1J_{PH}$ = 343.5 Hz, 1H, PH), 6.95−7.09 (m, 6H, *m,p*-Ph), 7.47−7.59 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, dichloromethane-d_2): δ 9.0, 9.2 ($SiMe_2$), 9.8 (C_5Me_5), 91.8 (C_5Me_5), 128.2 (d, $^3J_{PC}$ = 9.8 Hz, *m*-Ph), 128.4 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Ph), 129.4 (d, $^4J_{PC}$ = 2.3 Hz, *p*-Ph × 2), 132.5 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Ph), 132.9 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Ph), 134.9 (d, $^1J_{PC}$ = 38.5 Hz, *ipso*-Ph), 135.9 (d, $^1J_{PC}$ = 41.5 Hz, *ipso*-Ph), 220.0 (d, $^2J_{PC}$ = 22.7 Hz, CO).

Reaction of 1 with MeOH. Complex **3** (20 mg) was synthesized as an orange powder in 98% yield by a method similar to that for **2**, using **1** (19 mg, 0.041 mmol) and an excess of methanol (100 μL). Anal. Calcd for $C_{26}H_{35}FeO_2PSi$: C, 63.16; H, 7.13. Found: C, 63.17; H, 7.18. EI-MS (70 eV): *m/z* 494 (M^+, 4), 479 ($M^+ - Me$, 3), 451 ($M^+ - Me - CO$, 6), 435 ($M^+ - OMe - CO$, 5). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.45, 0.56 (s, 3H × 2, $SiMe_2$), 1.58 (d, $^3J_{PC}$ = 0.6 Hz, 15H, Cp*), 3.48 (s, 3H, OMe), 6.67 (d, $^1J_{PH}$ = 347.0 Hz, 1H, PH), 6.96−7.09 (m, 6H, *m,p*-Ph), 7.49−7.58 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, dichloromethane-d_2): δ 4.6, 5.4 ($SiMe_2$), 9.8 (C_5Me_5), 49.9 (OCH_3), 91.8 (C_5Me_5), 128.0 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Ph × 2), 129.10 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Ph), 129.13 (d, $^4J_{PC}$ = 2.3 Hz, *p*-Ph), 132.9 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Ph), 133.0 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Ph), 134.7 (d, $^1J_{PC}$ = 38.0 Hz, *ipso*-Ph), 135.5 (d, $^1J_{PC}$ = 40.2 Hz, *ipso*-Ph), 220.3 (d, $^2J_{PC}$ = 22.5 Hz, CO).

Reaction of 1 with ^{t}BuOH. Complex **4** (17 mg) was synthesized as an orange powder in 81% yield by a method similar to that for **2**, using **1** (18 mg, 0.039 mmol) and an excess of *tert*-butyl alcohol (200 μL). Anal. Calcd for $C_{29}H_{41}FeO_2PSi$: C, 64.92; H, 7.70. Found: C, 64.92; H, 7.67. EI-MS (70 eV): *m/z* 536 (M^+, 1), 507 ($M^+ - CO - H$, 1), 404 ($M^+ - C_6H_{16}OSi$, 51), 376 ($M^+ - C_7H_{16}O_2Si$, 100). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.63, 0.77 (s, 3H × 2, $SiMe_2$), 1.36 (s, 9H, ^{t}Bu), 1.60 (s, 15H, Cp*), 6.87 (d, $^1J_{PH}$ = 354.3 Hz, 1H, PH), 7.01−7.12 (m, 6H, *m,p*-Ph), 7.49−7.66 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, dichloromethane-d_2): δ 9.9 (C_5Me_5), 10.5, 10.6 ($SiMe_2$), 32.2 (CMe_3), 73.0 (CMe_3), 91.6 (C_5Me_5), 127.7 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Ph), 128.0 (d, $^3J_{PC}$ = 9.8 Hz, *m*-Ph), 129.0 (d, $^4J_{PC}$ = 1.5 Hz, *p*-Ph), 129.2 (d, $^4J_{PC}$ = 1.5 Hz, *p*-Ph), 133.5 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Ph), 133.7 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Ph), 134.2 (d, $^1J_{PC}$ = 36.2 Hz, *ipso*-Ph), 135.0 (d, $^1J_{PC}$ = 38.5 Hz, *ipso*-Ph), 220.1 (d, $^2J_{PC}$ = 23.4 Hz, CO).

Reaction of 1 with PhOH. Complex **5** (31 mg) was synthesized as an orange powder in 74% yield by a method similar to that for **2**, using **1** (35 mg, 0.076 mmol) and PhOH (7.0 mg, 0.074 mmol). Anal. Calcd for $C_{31}H_{37}FeO_2PSi$: C, 66.90; H, 6.70. Found: C, 66.82; H, 6.82. EI-MS (70 eV): *m/z* 556 (M^+, 1), 528 ($M^+ - CO$, 1), 404 ($M^+ - C_8H_{12}OSi$, 78), 376 ($M^+ - C_9H_{12}O_2Si$, 100). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.50 (s, 3H, $SiMe_2$), 0.63 (d, $^4J_{PH}$ = 0.6 Hz, 3H, SiMe), 1.58 (d, $^3J_{PH}$ = 0.9 Hz, 15H, Cp*), 6.67 (d, $^1J_{PH}$ = 347.1 Hz, 1H, PH), 6.85−6.91 (m, 2H, Ph), 6.96−7.11 (m, 6H, Ph), 7.18−7.24 (m, 3H, Ph), 7.46−7.59 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, dichloromethane-d_2): δ 6.5, 7.4 ($SiMe_2$), 9.8 (C_5Me_5), 92.1 (C_5Me_5), 119.6 (*p*-OPh), 120.7 (*m*-OPh), 128.15 (d, $^3J_{PC}$ = 9.1 Hz, *m*-PPh), 128.21 (d, $^3J_{PC}$ = 9.8 Hz, *m*-PPh), 128.9 (*o*-OPh), 129.3 (d, $^4J_{PC}$ = 2.3 Hz, *p*-PPh), 129.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-PPh), 133.0 (d, $^2J_{PC}$ = 10.6, *o*-PPh). 133.2 (d, $^2J_{PC}$ = 11.3 Hz, *o*-PPh), 134.3 (d, $^1J_{PC}$ = 37.8 Hz, *ipso*-PPh), 135.2 (d, $^1J_{PC}$ = 40.8 Hz, *ipso*-PPh), 157.6 (*ipso*-OPh), 220.0 (d, $^2J_{PC}$ = 22.7 Hz, CO).

Reaction of 1 with ^{p}TolSH. Complex **6** (34 mg) was synthesized as an orange powder in 81% yield by a method similar to that for **2**, using **1** (33 mg, 0.071 mmol) and ^{p}TolSH (9.0 mg, 0.072 mmol). Anal. Calcd for $C_{32}H_{39}FeOPSSi\cdot 1/2C_5H_{12}$: C, 66.54; H, 7.28. Found: C, 66.19; H, 7.34. EI-MS (70 eV): *m/z* 586 (M^+, 1), 558 ($M^+ - CO$, 1), 557 ($M^+ - CO - H$, 1), 404 ($M^+ - SiMe_2S^pTol\text{-}H$, 47), 376 ($M^+ - SiMe_2S^pTol\text{-}H - CO$, 100). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.33, 066 (s, 3H × 2, $SiMe_2$), 1.63 (s, 15H, Cp*), 2.07 (s, 3H, C_6H_4Me), 6.89 (d, $^1J_{PH}$ = 349.2

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Table 2. Crystallographic Details of 2, 3, 5, 6, and 10

	2	**3**	**5**	**6**·$1/2\mathrm{C_5H_{12}}$	**10**
cryst size, mm	0.20 × 0.15 × 0.10	0.20 × 0.15 × 0.05	0.45 × 0.40 × 0.40	0.30 × 0.20 × 0.10	0.25 × 0.15 × 0.15
formula	$\mathrm{C_{25}H_{33}FeO_2PSi}$	$\mathrm{C_{26}H_{35}FeO_2PSi}$	$\mathrm{C_{31}H_{37}FeO_2PSi}$	$\mathrm{C_{34.5}H_{39}FeOPSSi}$	$\mathrm{C_{31}H_{38}FeOP_2Si}$
fw	480.42	494.45	556.52	616.63	572.49
cryst syst	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/a$
space group	triclinic	monoclinic	monoclinic	triclinic	monoclinic
a, Å	8.9347(16)	17.8808(5)	17.2616(8)	11.564(3)	14.2343(7)
b, Å	9.4342(18)	8.6468(3)	8.8862(6)	12.333(4)	12.7285(6)
c, Å	14.924(3)	32.4251(11)	18.9897(14)	12.706(3)	16.3992(8)
α, deg	99.724(14)	90	90	73.972(12)	90
β, deg	102.811(11)	89.3244(14)	104.388(2)	80.424(8)	92.0787(10)
γ, deg	99.590(6)	90	90	68.804(9)	90
volume, Å^3	1181.4(4)	5013.0(3)	2821.5(3)	1619.4(7)	2969.3(2)
Z	2	8	4	2	4
ρ_{calc}, g cm^{-3}	1.351	1.310	1.310	1.265	1.281
μ, mm^{-1}	0.776	0.733	0.660	0.642	0.678
F(000)	508	2096	1176	650	1208
no. of reflns collected	10 010	15 055	23 123	9450	22 209
no. of indep reflns	5133 [R(int) = 0.0587]	4407 [R(int) = 0.0317]	6383 [R(int) = 0.0319]	5284 [R(int) = 0.0567]	5238 [R(int) = 0.1050]
max. and min. transmn	0.9264 and 0.8603	0.9642 and 0.8672	0.7782 and 0.7556	0.9386 and 0.8308	0.9051 and 0.8488
no. of data/restraints/ params	5133/0/286	4407/0/292	6383/0/336	5284/0/359	5238/0/477
GOF on F^2	1.160	1.213	1.091	1.168	1.278
final R indices [$I > 2\sigma(I)$]	R1 = 0.0594, wR2 = 0.1376	R1 = 0.0459, wR2 = 0.0836	R1 = 0.0354, wR2 = 0.0837	R1 = 0.0680, wR2 = 0.1496	R1 = 0.0832, wR2 = 0.1384
R indices (all data)	R1 = 0.0783, wR2 = 0.1471	R1 = 0.0567, wR2 = 0.0870	R1 = 0.0410, wR2 = 0.0872	R1 = 0.0929, wR2 = 0.1679	R1 = 0.1122, wR2 = 0.1479
largest diff peak and hole, e·Å^{-3}	0.676 and −0.405	0.303 and −0.305	0.701 and −0.263	0.680 and −0.521	0.427 and −0.495

Hz, 1H, PH), 6.90−7.11 (m, 8H, *m,p*-PPh$_2$, $\mathrm{C_6}\mathit{H_4}\mathrm{Me}$), 7.58−7.71 (m, 6H, *o*-PPh$_2$, $\mathrm{C_6}\mathit{H_4}\mathrm{Me}$). ^{13}C{^{1}H} NMR (75.5 MHz, dichloromethane-d_2): δ 5.6 (d, $^3J_{\mathrm{PC}}$ = 2.3 Hz, SiMe), 7.2 (SiMe), 10.1 ($\mathrm{C_5}\mathit{Me_5}$), 34.1 ($\mathrm{C_6H_4}\mathit{Me}$), 92.6 ($\mathit{C_5}\mathrm{Me_5}$), 128.1 (d, $^3J_{\mathrm{PC}}$ = 9.1 Hz, *m*-PPh), 128.2 (d, $^3J_{\mathrm{PC}}$ = 9.1 Hz, *m*-PPh), 128.8 (*m*-^{p}Tol), 129.3 (d, $^4J_{\mathrm{PC}}$ = 2.3 Hz, *p*-PPh), 129.3 (br s, *p*-PPh), 132.3 (*p*-^{p}Tol), 133.3 (d, $^2J_{\mathrm{PC}}$ = 9.8 Hz, *o*-PPh), 133.6 (d, $^2J_{\mathrm{PC}}$ = 9.1 Hz, *o*-PPh), 134.3 (d, $^1J_{\mathrm{PC}}$ = 37.8 Hz, *ipso*-PPh), 134.96 (d, $^1J_{\mathrm{PC}}$ = 43.8 Hz, *ipso*-PPh), 135.01 (*o*-^{p}Tol), 135.3 (*ipso*-^{p}Tol), 219.3 (d, $^2J_{\mathrm{PC}}$ = 21.1 Hz, CO).

Reaction of 1 with $\mathbf{Et_2NH}$. Complex **7** (34 mg) was synthesized as an orange powder in 100% yield by a method similar to that for **2**, using **1** (29 mg, 0.063 mmol) and an excess of $\mathrm{NEt_2H}$ (100 μL). Anal. Calcd for $\mathrm{C_{29}H_{42}FeNOPSi}$: C, 65.04; H, 7.90; N, 2.62. Found: C, 64.30; H, 7.86; N, 1.90. EI-MS (70 eV): *m/z* 535 (M$^+$, 0.1), 462 (M$^+$ − $\mathrm{HNEt_2}$, 2), 404 (M$^+$ − $\mathrm{SiMe_2NEt_2}$ − H, 47), 376 (M$^+$ − $\mathrm{SiMe_2NEt_2}$ − H − CO, 100). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.56, 0.63 (s, 3H × 2, SiMe$_2$), 1.10 (t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 6H, $\mathrm{CH_2}\mathit{CH_3}$), 1.56 (d, 15H, Cp*), 3.02 (q, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 4H, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 6.68 (d, $^1J_{\mathrm{PH}}$ = 356.7 Hz, 1H, PH), 6.94−7.10 (m, 6H, *m,p*-Ph), 7.40−7.58 (m, 4H, *o*-Ph). ^{13}C{^{1}H} NMR (75.5 MHz, cyclohexane-d_{12}): δ 7.8 (d, $^3J_{\mathrm{PC}}$ = 1.1 Hz, SiMe), 7.9 (SiMe$_2$), 10.6 ($\mathrm{C_5}\mathit{Me_5}$), 15.8 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 42.2 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 92.0 ($\mathit{C_5}\mathrm{Me_5}$), 128.3 (d, $^3J_{\mathrm{PC}}$ = 7.6 Hz, *m*-Ph), 128.4 (d, $^3J_{\mathrm{PC}}$ = 6.8 Hz, *m*-Ph), 129.2 (d, $^4J_{\mathrm{PC}}$ = 2.2 Hz, *p*-Ph), 129.6 (*p*-Ph), 133.4 (d, $^2J_{\mathrm{PC}}$ = 9.8 Hz, *o*-Ph), 134.6 (d, $^2J_{\mathrm{PC}}$ = 10.6 Hz, *o*-Ph), 135.4 (d, $^1J_{\mathrm{PC}}$ = 33.3 Hz, *ipso*-Ph), 137.8 (d, $^1J_{\mathrm{PC}}$ = 39.3 Hz, *ipso*-Ph), 220.1 (d, $^2J_{\mathrm{PC}}$ = 25.3 Hz, CO).

Reaction of 1 with $\mathbf{PhNH_2}$. Complex **8** (30 mg) was synthesized as an orange powder in 83% yield by a method similar to that for **2**, using **1** (30 mg, 0.065 mmol) and excess $\mathrm{PhNH_2}$ (50 μL). Anal. Calcd for $\mathrm{C_{31}H_{38}FeNOPSi}$: C, 67.02; H, 6.89; N, 2.52. Found: C, 67.53; H, 7.34; N, 2.36. EI-MS (70 eV): *m/z* 553 (M$^+$ − 2H, 2), 525 (M$^+$ − CO − 2H, 2), 462 (M$^+$ − $\mathrm{C_6H_7N}$, 12), 404 (M$^+$ − $\mathrm{C_8H_{13}SiN}$, 42), 376 (M$^+$ − $\mathrm{C_9H_{13}SiON}$, 58). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.74 (d, $^4J_{\mathrm{PH}}$ = 1.1 Hz, SiMe), 0.76 (s, 3H, SiMe), 1.49 (s, 15H, Cp*), 3.50 (s, 1H, NH), 6.73 (d, $^1J_{\mathrm{PH}}$ = 349.8 Hz, 1H, PH), 6.78 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 1H, *p*-NPh), 6.85 (d, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2H, *o*-NPh), 6.95−7.07 (m, 6H, *m,p*-PPh), 7.24 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2H, *m*-NPh), 7.38−7.57 (m, 4H, *o*-PPh). ^{13}C{^{1}H} NMR (75.5 MHz, dichloromethane-d_2): δ 5.9, 6.5 (SiMe$_2$), 9.9 ($\mathrm{C_5}\mathit{Me_5}$), 92.0 ($\mathit{C_5}\mathrm{Me_5}$), 115.6 (*p*-NPh), 116.0 (*m*-NPh), 128.2 (d, $^3J_{\mathrm{PC}}$ = 9.1 Hz, *m*-PPh), 128.3 (d, $^3J_{\mathrm{PC}}$ = 8.3 Hz, *m*-PPh), 128.8 (*o*-NPh), 129.4 (d, $^4J_{\mathrm{PC}}$ = 2.3 Hz, *p*-PPh), 129.5 (d, $^4J_{\mathrm{PC}}$ = 2.3 Hz, *p*-PPh), 132.9 (d, $^2J_{\mathrm{PC}}$ = 9.1 Hz, *o*-PPh), 133.3 (d, $^2J_{\mathrm{PC}}$ = 9.8 Hz, *o*-PPh), 134.2 (d, $^1J_{\mathrm{PC}}$ = 38.5 Hz, *ipso*-PPh), 134.3 (d, $^1J_{\mathrm{PC}}$= 40.2, *ipso*-PPh), 149.4 (*ipso*-NPh), 219.9 (d, $^2J_{\mathrm{PC}}$ = 21.9 Hz, CO).

Reaction of 1 with $\mathbf{Ph_2PH}$. Complex **9** was synthesized by a method similar to that for **2**, using **1** (28 mg, 0.061 mmol) and $\mathrm{Ph_2PH}$ (12 mg, 0.064 mmol). Recrystallization from pentane at −30 °C gave yellow crystals of **9**. Yield: 28 mg (71%). Anal. Calcd for $\mathrm{C_{37}H_{42}FeOP_2Si}$: C, 68.52; H, 6.53. Found: C, 68.60; H, 6.49. EI-MS (70 eV): *m/z* 462 (M$^+$ − $\mathrm{Ph_2PH}$, 9), 404 (M$^+$ − $\mathrm{Ph_2PH}$ − SiMe$_2$, 34), 376 (M$^+$ − $\mathrm{Ph_2PH}$ − SiMe$_2$ − CO, 100). ^{1}H NMR (300 MHz, cyclohexane-d_{12}): δ 0.03 (d, $^3J_{\mathrm{PH}}$ = 3.2 Hz, SiMe), 0.10 (d, $^3J_{\mathrm{PH}}$ = 4.6 Hz, SiMe), 1.63 (s, 15H, Cp*), 6.67 (dd, $^1J_{\mathrm{PH}}$ = 346.0 Hz, $^4J_{\mathrm{PH}}$ = 1.8 Hz, 1H, PH), 6.98−7.12 (m, 6H, *m,p*-Ph), 7.12−7.22 (m, 6H, *m,p*-Ph), 7.28−7.42 (m, 4H, *o*-Ph), 7.43−7.55 (m, 4H, *o*-Ph). ^{13}C{^{1}H} NMR (75.5 MHz, cyclohexane-d_{12}): δ 4.5 (m, SiMe), 4.8 (dd, $^2J_{\mathrm{PC}}$ = 8.7 Hz, $^3J_{\mathrm{PC}}$ = 3.3 Hz, SiMe), 10.8 (d, $^3J_{\mathrm{PC}}$ = 5.9 Hz, $\mathrm{C_5}\mathit{Me_5}$), 92.8 ($\mathit{C_5}\mathrm{Me_5}$), 126.8 (Ph), 127.9 (d, J_{PC} = 6.7 Hz, Ph), 128.5 (d, J_{PC} = 9.8 Hz, Ph), 128.6 (d, J_{PC} = 10.0 Hz, Ph), 129.6 (d, J_{PC} = 3.3 Hz, Ph), 133.8 (d, J_{PC} = 9.6 Hz, Ph), 134.0 (d, J_{PC} = 9.7 Hz, Ph), 134.6 (d, J_{PC} = 17.2 Hz, Ph), 135.7 (d, J_{PC} = 35.1 Hz, Ph), 136.7 (d, J_{PC} = 41.6 Hz, Ph), 140.1 (m, Ph), 220.9 (d, $^2J_{\mathrm{PC}}$ = 23.6 Hz, CO).

Reaction of 1 with $\mathbf{PhPH_2}$. Complex **10** was synthesized by a method similar to that for **2**, using **1** (58 mg, 0.13 mmol) and $\mathrm{PhPH_2}$ (50 μL). Recrystallization from pentane at −30 °C gave yellow crystals of **10**. Yield: 55 mg (77%). Complex **10** consists of two diastereomers in a 1:1 molar ratio. Anal. Calcd for $\mathrm{C_{31}H_{38}FeOP_2Si}$: C, 65.03; H, 6.69. Found: C, 65.25; H, 6.91. EI-MS (70 eV): *m/z* 571 (M$^+$ − H, 1), 462 (M$^+$ − $\mathrm{PhPH_2}$, 12), 404 (M$^+$ − $\mathrm{PhPH_2}$ − SiMe$_2$, 17), 376 (M$^+$ − $\mathrm{PhPH_2}$ − SiMe$_2$ − CO, 33). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.19 (s, 3H, SiMe), 0.37 (d, $^3J_{\mathrm{PH}}$ = 7.2 Hz, 3H, SiMe), 0.40 (s, 3H, SiMe), 0.61 (d, $^3J_{\mathrm{PH}}$ = 6.3 Hz, 3H, SiMe), 1.57 (s, 15H, Cp*), 1.60 (s, 15H, Cp*), 3.48 (d, $^1J_{\mathrm{PH}}$ = 204.0 Hz, 1H, SiPH), 3.83 (d, $^1J_{\mathrm{PH}}$ = 203.7 Hz, 1H, SiPH), 6.69 (d, $^1J_{\mathrm{PH}}$ = 348.6 Hz, 1H, $\mathrm{PPh_2}\mathit{H}$), 6.79 (d, $^1J_{\mathrm{PH}}$ = 350.1 Hz, 1H, $\mathrm{PPh_2}\mathit{H}$), 6.95−7.13 (m, 18H, Ph), 7.38−

7.59 (m, 12H, Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, cyclohexane-d_{12}): δ 1.3 (SiMe), 3.2 (d, J_{PC} = 15.1 Hz, SiMe), 4.5 (d, J_{PC} = 15.9 Hz, SiMe), 5.6 (dt, J_{PC} = 17.4 Hz, J_{PC} = 3.4 Hz, SiMe), 10.80 (C_5Me_5), 10.84 (d, J_{PC} = 5.3 Hz, C_5Me_5), 92.5 (C_5Me_5), 92.6 (C_5Me_5), 125.56 (Ph), 125.61 (Ph), 127.88 (d, $^3J_{CP}$ = 6.0 Hz, Ph), 127.96 (d, $^3J_{CP}$ = 5.3 Hz, Ph), 128.4 (d, $^3J_{CP}$ = 8.3 Hz, Ph), 128.5 (d, $^3J_{PC}$ = 7.6 Hz, Ph), 128.6 (d, $^3J_{CP}$ = 8.3 Hz, Ph), 129.6 (d, $^2J_{CP}$ = 1.7 Hz, Ph), 129.7 (Ph), 129.8 (d, $^2J_{CP}$ = 2.3 Hz, Ph), 129.9 (Ph), 133.7 (d, $^2J_{CP}$ = 9.1 Hz, Ph), 134.1 (d, $^2J_{CP}$ = 10.6 Hz, Ph), 134.29 (d, $^2J_{CP}$ = 14.3 Hz, Ph), 134.33 (d, $^2J_{CP}$ = 10.4 Hz, Ph), 134.4 (d, $^2J_{CP}$ = 15.9 Hz, Ph), 134.9 (d, $^1J_{CP}$ = 18.4 Hz, Ph), 135.4 (d, $^1J_{CP}$ = 34.5 Hz, Ph), 135.7 (d, $^1J_{CP}$ = 18.4 Hz, Ph), 136.4 (d, $^1J_{PC}$ = 37.8 Hz, Ph), 138.3 (d, $^1J_{CP}$ = 25.7 Hz, Ph), 138.4 (d, $^1J_{CP}$ = 26.0 Hz, Ph), 219.5 (d, $^2J_{CP}$ = 22.3 Hz, CO), 219.6 (d, $^2J_{CP}$ = 23.1 Hz, CO).

X-ray Diffraction Analysis. Single crystals of **2**, **3**, **5**, **6**·1/2C_5H_{12}, and **10** were obtained by cooling the solutions at −30 °C. Intensity data were collected on a RIGAKU RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation at 150 K. The data were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied. The crystallographic data are listed in Table 2. The structure was solved by Patterson and Fourier transform methods using SHELXS-97[12] and refined by full matrix least-squares techniques on all F^2 data (SHELXL-97).[13] In each complex, the hydrogen atom on the phosphorus and nitrogen atoms were located by the differential Fourier map and refined isotropically.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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