Organometallics **2003,** *22,* 4627−4629 4627

Coordinatively and Electronically Unsaturated Zwitterionic Iron Silyl Complexes Featuring the Tripodal Phosphine Ligand $[PhB(CH_2P^iPr_2)_3]^-$

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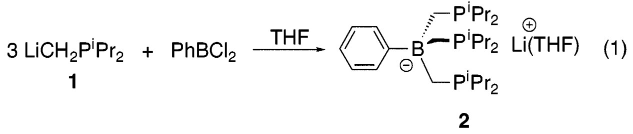
Received August 7, 2003

Summary: A series of 14-electron, coordinatively unsaturated Fe(II) silyl complexes featuring the anionic, tripodal phosphine ligand $[PhB(CH_2P^iPr_2)_3]^-$ have been prepared and characterized; preliminary reactivity studies indicate that at least one such complex can undergo redox processes to generate isolable Fe(I) species with concomitant loss of the silyl ligand.

Transition-metal complexes featuring metal−silicon bonds are key components in a number of catalytic and stoichiometric chemical transformations.[1] The majority of these silyl derivatives are coordinatively saturated and are based on “traditional” coordination spheres featuring cyclopentadienyl (Cp) or carbon monoxide ancillary ligands. With the goal of developing new reaction chemistry for metal−silicon-bonded compounds, we have explored routes to electron-deficient silyl complexes with unusual geometries and low coordination numbers.[2]

In this contribution, we report the synthesis and preliminary reactivity studies of unusual 14-electron, four-coordinate Fe(II) silyl complexes featuring the anionic, tripodal phosphine ligand $[PhB(CH_2P^iPr_2)_3]^-$ (abbreviated as $PhBP_3'$).[3,4] In previous reports we have described the synthesis and reactivity of zwitterionic iridium complexes featuring the diphenylphosphino analogue of this ligand, $[PhB(CH_2PPh_2)_3]^-$ (abbreviated as $PhBP_3$).[5] Although isoelectronic with Cp and tris(pyrazolyl)borate (Tp)[6] ligands, $PhBP_3$ differs significantly from these in that it coordinates via three soft phosphine σ-donor groups. Accordingly, the $PhBP_3$ ligand has enabled the isolation of transition-metal complexes that have no counterpart in Cp- or Tp-ligated systems, such as an Ir(III) silylene,[5] and terminal Co and Fe(III) imido complexes.[4a,c] We anticipate that replacing the phenyl substituents on the phosphorus donors with isopropyl groups will lead to significantly different steric and electronic properties for this ligand system.

Yellow, paramagnetic $[PhBP_3']FeBr$ (**3**) was obtained in high yield by the direct reaction of $[Li(THF)][[PhBP_3']$ (**2**), prepared by addition of 3 equiv of $LiCH_2P^iPr_2$ (**1**) to dichlorophenylborane (eq 1), with $FeBr_2(THF)_2$ (Scheme 1). The bromide complex **3** is readily isolated as a crystalline solid from diethyl ether solution. The crystallographically determined structure of **3** reveals a monomeric, four-coordinate complex featuring a pseudotetrahedral geometry at iron (Figure 1). The average Fe−P bond distance is 2.420 Å, which is comparable to the average Fe−P distances (2.425 Å) for $[PhBP_3]FeCl\cdot C_6H_6$ and $[PhBP_3']FeCl$.[3,4] The effective magnetic susceptibility for **3** was measured in benzene-d_6 solution according to the Evans method and was used to determine an effective magnetic moment of 4.68 μ_B (300 K), consistent with a high-spin Fe(II) center.[7]



Surprisingly, the bromide derivative **3** reacted with $KSi(SiMe_3)_3$ in benzene solvent to give an orange, diamagnetic product (**4**). An X-ray crystallographic study of **4** reveals η^5 coordination of a silylated benzene moiety to the iron center (Figure 2) to form a 6-*exo*-cyclohexadienyl complex. Complex **4** likely forms via nucleophilic addition of $(Me_3Si)_3Si^-$ to the cationic 18-electron species $\{[PhBP_3']Fe(\eta^6\text{-}C_6H_6)\}^+$, which may exist in equilibrium with **3** in benzene solution. Significant precedent exists for addition of nucleophiles to analogous $CpFe^+(\eta^6\text{-arene})$ cations to form the corresponding 6-*exo*-cyclohexadienyl complexes.[8] However, there was no indication (by ^1H NMR) for the formation of the diamagnetic $\{[PhBP_3']Fe(\eta^6\text{-}C_6H_6)\}^+$ cation upon

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[3] The syntheses of $[PhBP_3']Tl$ and of $[PhBP_3']FeCl$ have just appeared: Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074.

[4] Four-coordinate Fe and Co complexes featuring the $[PhB(CH_2PPh_2)_3]^-$ ligand (abbreviated as $PhBP_3$) have been reported by Peters and co-workers: (a) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322. (b) Jenkins, D. M.; Di Bilio, A. M.; Allen, M. J.; Betley, T. A. Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 15336. (c) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238. (d) Shapiro, I. R.; Jenkins, D. M.; Thomas, J. C.; Day, M. W.; Peters, J. C. *Chem. Commun.* **2001**, 2152.

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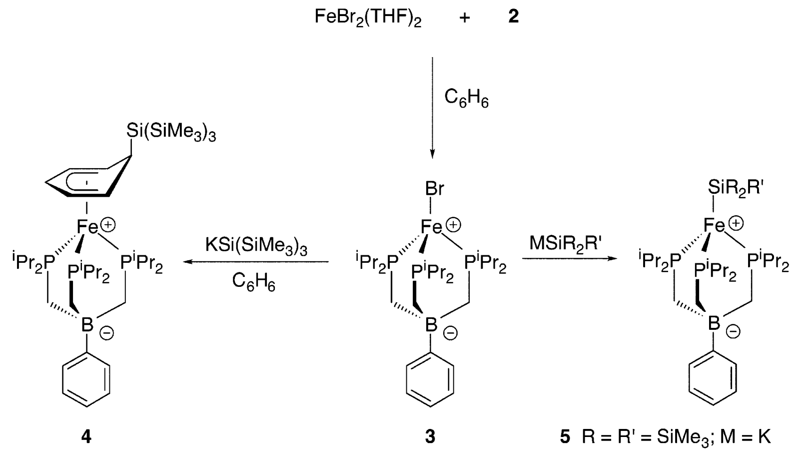
Scheme 1



5 R = R' = SiMe$_3$; M = K
6 R = R' = Ph; M = Li(THF)$_3$
7 R = 2,4,6-Me$_3$C$_6$H$_2$; R' = H; M = Li(THF)$_2$

dissolving **3** in benzene-d_6. Additionally, no reaction was observed when 1 equiv of NaBPh$_4$ was added to a benzene/THF solution of **3**.

When the reaction of **3** with KSi(SiMe$_3$)$_3$ was carried out in pentane solvent, paramagnetic [PhBP$_3'$]FeSi(SiMe$_3$)$_3$ (**5**) was isolated as purple needles in 58% yield (Scheme 1). Complex **5** has been characterized by ^{1}H NMR and IR spectroscopy, by its magnetic moment (4.85 μ_B, Evans method, 300 K), and by elemental analysis. The NMR spectrum of **5** in benzene-d_6 contains a broad resonance at 1.45 ppm that can be attributed to the methyl protons on the Si(SiMe$_3$)$_3$ ligand. The IR spectrum of **5** reveals absorptions characteristic of the Si(SiMe$_3$)$_3$ group at 831, 671, and 622 cm^{-1}. No reaction occurred over the course of 16 h upon exposure of **5** to benzene at room temperature, suggesting that **5** is not an intermediate in the formation of the cyclohexadienyl complex **4**.

Paramagnetic silyl complexes are quite rare, and to our knowledge the only previously reported examples of paramagnetic Fe silyl complexes are species of the type {[(Me$_3$Si)$_3$Si]$_2$FeX}$^-$ (X = Cl, OTf), [(Me$_3$Si)$_3$SiFeCl$_2$(pyr)]$^-$, and [(Me$_3$Si)$_3$Si]$_2$FeL (L = DME, Et$_2$O, THF).[2,9] Thus, the successful isolation of the coordinatively unsaturated silyl complex **5** prompted us to examine syntheses of additional four-coordinate iron silyl complexes. The reaction of **3** with either Ph$_3$SiLi(THF)$_3$ or Mes$_2$SiHLi(THF)$_2$ in pentane led to the formation of the corresponding silyl (**6**) and hydrosilyl (**7**) complexes (Scheme 1), indicating that silyllithium reagents can also be utilized for the preparation of [PhBP$_3'$]Fe−silyl complexes. Compounds **6** and **7** possess magnetic moments of 5.32 and 4.81 μ_B, respectively (Evans method, 300 K).

As previously reported, coordinatively unsaturated iron silyl complexes form adducts with π-acids such as CO and xylyl isocyanide.[2] Exposure of a red diethyl ether solution of **7** to an atmosphere of CO resulted in

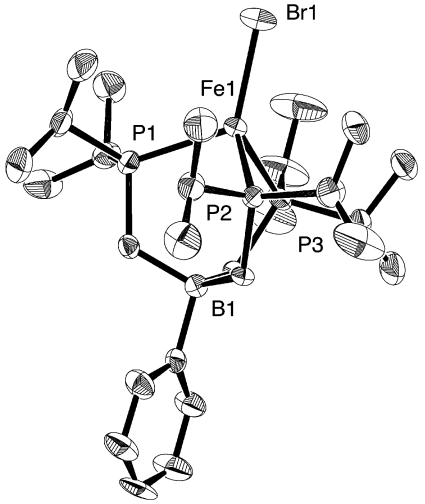


Figure 1. Crystallographically determined structure of **3**, depicted with 50% thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−Br(1), 2.375(1); Fe(1)−P(1), 2.419(2); Fe(1)−P(2), 2.411(2); Fe(1)−P(3), 2.430(2); Br(1)−Fe(1)−P(1), 120.11(6); Br(1)−Fe(1)−P(2), 123.36(7); Br(1)−Fe(1)−P(3), 123.52(7); P(1)−Fe(1)−P(2), 94.08(7); P(1)−Fe(1)−P(3), 93.84(7); P(2)−Fe(1)−P(3), 94.22(7).

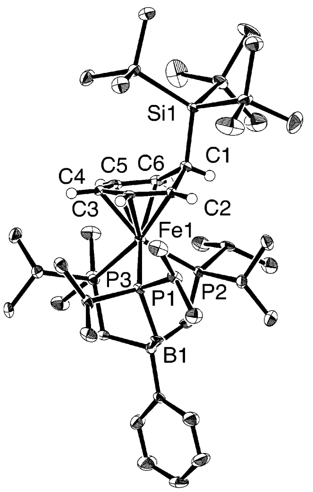
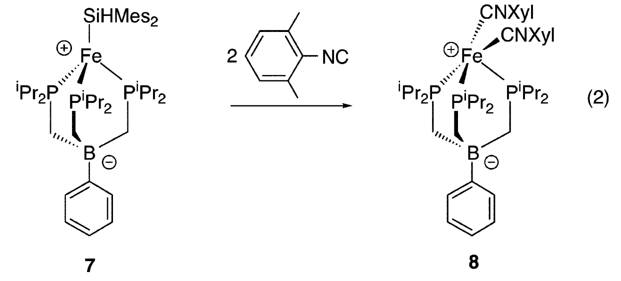


Figure 2. Crystallographically determined structure of **4**, depicted with 50% thermal ellipsoids. All hydrogen atoms have been omitted for clarity, with the exception of the hydrogen atoms on the η^5-cyclohexadienyl ring. Selected bond distances (Å) and angles (deg): Fe(1)−P(1), 2.314(1); Fe(1)−P(2), 2.323(1); Fe(1)−P(3), 2.335(1); C(1)−C(2), 1.509(6); C(1)−C(6), 1.521(7); C(2)−C(3), 1.400(6); C(3)−C(4), 1.404(7); C(4)−C(5), 1.406(7); C(5)−C(6), 1.374(7); Si(1)−C(1), 1.933(5); P(1)−Fe(1)−P(2), 88.15(5); P(1)−Fe(1)−P(3), 88.92(5); P(2)−Fe(1)−P(3), 93.53(5).

an immediate color change to green; however, no crystalline product could be isolated from this reaction mixture. The room-temperature addition of xylyl isocyanide to a red benzene solution of **7** resulted in a similar immediate color change to green, followed by a rapid (less than 1 min) color change to red-brown. Surprisingly, the isolated product of this reaction is not an adduct of **7** but, rather, a five-coordinate Fe(I) complex, [PhBP$_3$′]Fe(CNXyl)$_2$ (**8**), which has lost the $-$SiHMes$_2$ ligand (eq 2). Monitoring the reaction at room temperature by ^{1}H NMR spectroscopy (benzene-d_6) revealed the presence of a diamagnetic product containing an SiH resonance at 5.37 ppm ($^1J_{SiH}$ = 98 Hz). However, thus far we have been unable to conclusively determine the fate of the $-$SiHMes$_2$ ligand in this reaction.



The crystallographically determined structure of **8** (Figure 3) reveals a distorted-square-pyramidal geometry at iron. The magnetic moment determined for **8** is 1.70 μ_B, which is consistent with a low-spin Fe(I) center. Although several electronically and coordinatively unsaturated monovalent iron complexes have been previously reported, few have been structurally characterized by X-ray diffraction methods.[4a,9a,10] Similar reactivity has been observed by Parkin and co-workers for a tris(pyrazolyl)borate iron methyl complex that reacted with CO at 120 °C to generate a four-coordinate Fe^I$-$CO complex with loss of the Me ligand.[9a] Additionally, four-coordinate [PhBP$_3$]FePPh$_3$ and five-coordinate [PhBP$_3$]Fe(CO)$_2$ have been recently reported.[4a] Given the suspected role of low-coordinate Fe(I) species in metalloenzyme reactivity, there has been increasing interest in the chemistry of this unusual oxidation state of iron.[11]

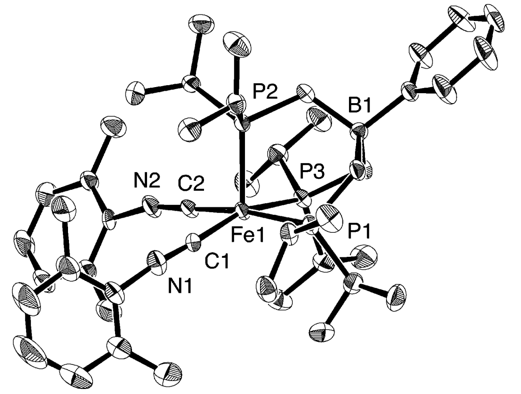


Figure 3. Crystallographically determined structure of **8**, depicted with 50% thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)$-$P(1), 2.307(1); Fe(1)$-$P(2), 2.294(1); Fe(1)$-$P(3), 2.322(1); Fe(1)$-$C(1), 1.811(4); Fe(1)$-$C(2), 1.795(4); P(1)$-$Fe(1)$-$P(2), 89.97(4); P(1)$-$Fe(1)$-$P(3), 90.34(4); P(2)$-$Fe(1)$-$P(3), 92.99(4); C(1)$-$Fe(1)$-$C(2), 82.9(2); Fe(1)$-$C(1)$-$N(1), 171.4(4); Fe(1)$-$C(2)$-$N(2), 174.5(4).

In summary, we have prepared a new class of four-coordinate, 14-electron Fe(II) silyl complexes featuring the tripodal phosphine ligand [PhB(CH$_2$P^{i}Pr$_2$)$_3$]$^-$ ([PhBP$_3$′]$^-$). These unique complexes are highly reactive, as indicated by the facile reduction of [PhBP$_3$′]FeSiHMes$_2$ in the presence of xylyl isocyanide to form an isolable five-coordinate Fe(I) complex. We are presently examining the chemistry and redox reactivity of these and related low-coordinate transition-metal silyl complexes in search of new chemical transformations.

Acknowledgment is made to the National Science Foundation for their generous support of this work. We thank Dr. Frederick J. Hollander and Dr. Allen G. Oliver for assistance with the X-ray structure determinations.

Supporting Information Available: Text giving detailed experimental procedures and characterization data and tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for complexes **3**, **4**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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