Complexes with Sterically Demanding Ligands, VI[1)]

# Synthesis and Reactivity of Mono[tris(trimethylsilyl)cyclopentadienyl]iron(trimethyl phosphite) Complexes

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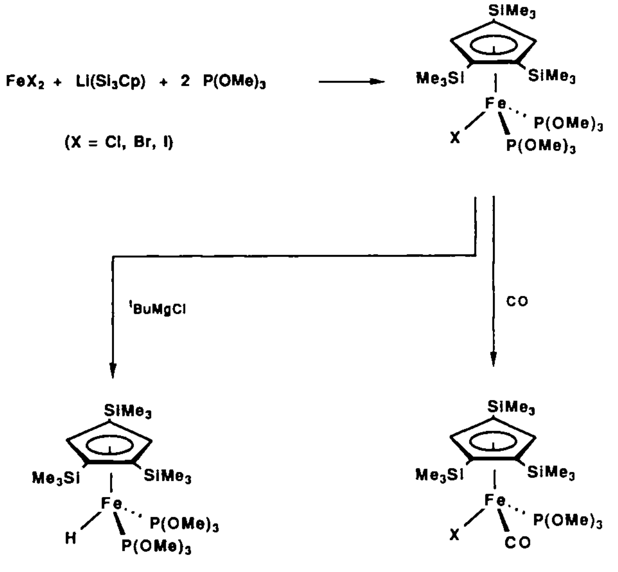
**A direct synthesis of iron(trimethyl phosphite) half-sandwich complexes $[\eta^5\text{-}C_5H_2(SiMe_3)_3]Fe[P(OMe)_3]_2X$ starting from $FeX_2$ (X = Cl, Br, I) and $Li[\eta^5\text{-}C_5H_2(SiMe_3)_3]$ is described. Their reactivity toward *t*BuMgCl and CO has been studied.**

The majoritiy of iron half-sandwich complexes is derived from the fragments $(\eta^5\text{-}C_5R_5)Fe(CO)_2$ (R = H, Me) that are easily accessible via the dicarbonyl $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]_2$[2)]. Due to the difficulty of substituting both CO ligands in these complexes[3)], only recently have extensive studies on the preparation and reactivity of carbonyl-free half-sandwich complexes of generic formula $(\eta^5\text{-}C_5R_5)FeL_2X$ (L = two-electron ligand; X = one-electron ligand) been reported[4–7)]. We have found that by reaction of ferrous halides $FeX_2$ (X = Cl, Br, I) with tris(trimethylsilyl)cyclopentadienyllithium $Li(Si_3Cp)$ [$Si_3Cp = \eta^5\text{-}1,2,4\text{-}(Me_3Si)_3C_5H_2$], a reactive species is generated that can be regarded as a functional equivalent of the 14-electron half-sandwich fragment $(Si_3Cp)FeX$[8)]. Herein we wish to describe its use for the preparation of trimethyl phosphite complexes containing the $Si_3Cp$ ligand.

When a suspension of ferrous halide $FeX_2$ as its THF or DME adduct in THF is first treated with $Li(Si_3Cp)$ at −95°C and then with two equivalents of trimethyl phosphite, a turquoise (X = Cl) or dark green (X = Br, I) solution is obtained upon warming up to room temperature. Pentane-soluble, air-sensitive blue (X = Cl) or dark green (X = Br, I) crystals of $(Si_3Cp)FeL_2X$ [$L = P(OMe)_3$] can be isolated in good yields from this solution. Elemental analysis, $^1H$-, $^{13}C\{^1H\}$-, $^{31}P$-NMR, as well as IR and EI-MS data clearly establish the required structure of a three-legged piano-stool molecule.



Reaction of $(Si_3Cp)FeL_2X$ with *t*BuMgCl in THF cleanly gives $(Si_3Cp)FeL_2H$ that can be easily isolated as analytically pure yellow crystals. The presence of an Fe−H bond can be inferred from the IR spectrum exhibiting a band of medium intensity at 1840 $cm^{-1}$ that can be assigned to $\tilde{\nu}(FeH)$ and compared to $\tilde{\nu}(FeH)$ bands of similar complexes [$(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H$: 1845 $cm^{-1}$; $(\eta^5\text{-}C_5Me_5)Fe(PMe_3)_2H$: 1820 $cm^{-1}$[5)]]. The $^1H$-NMR spectrum shows a typical high-field resonance for the hydride as a triplet with $^2J(P,H) = 89.8$ Hz at $\delta = -15.27$.

The halide complexes rapidly and quantitatively react with carbon monoxide at room temperature to give the monocarbonyl derivatives $(Si_3Cp)FeL(CO)X$ which can be obtained as extremely pentane-soluble, fairly air-stable brown crystals. The reaction rate decreases in the series Cl−Br−I, while the crystallinity of the products increases in the same order. In accordance with the chiral structure of $C_1$ symmetry, the two vicinal trimethylsilyl groups appear as two distinct signals both in the $^1H$- and $^{13}C$-NMR spectrum and the five-membered ring gives rise to five distinct resonances for the ring carbon atoms in the $^{13}C\{^1H\}$-NMR spectrum. Most interestingly, the signals for the two ring protons of the $Si_3Cp$ ring are not only well separated in the $^1H$-NMR spectrum ($\delta = 4.55$ and 5.37), but show distinct fine structures (Figure). While the lower field signal is a barely resolved doublet, the resonance at higher

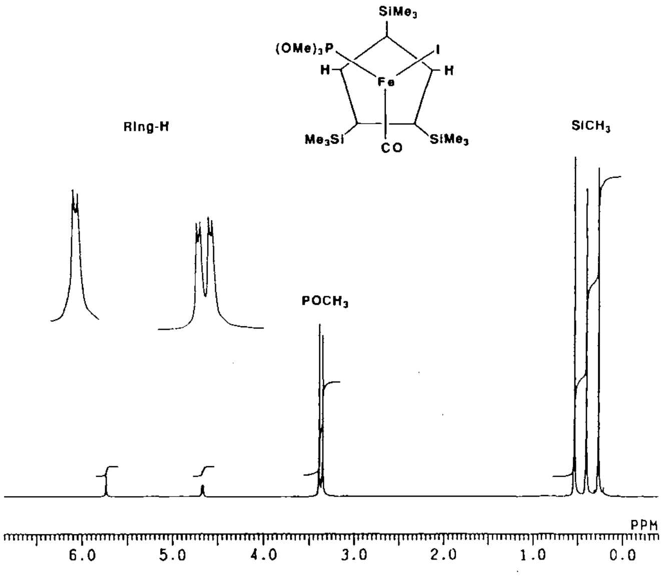


Figure. 270-MHz $^1H$-NMR spectrum of $(Si_3Cp)Fe[P(OMe)_3](CO)I$ in $C_6D_6$ at 25°C

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field is a doublet of doublets. The small splitting is due to the coupling between the inequivalent ring protons [$^4J$(H,H) = 1.5 Hz], while the large doublet arises from the coupling to the phosphorus atom of the $P(OMe)_3$ ligand. This observation can be explained by the predominant population of a conformation in which one ring proton is eclipsed with the $P(OMe)_3$ ligand, the other with the halide X or CO, depending on the enantiomer under consideration. According to the Karplus relation, the former connected with the phosphorus atom by a dihedral angle of ca. 0°, should show a $^3J$(P,H) coupling, while the latter, related by an angle of nearly 90°, should give a negligible coupling constant. This conformation is also favored considering steric repulsions between the $Si_3Cp$ ligand and the FeL(CO)X fragment, since the large phosphite ligand would avoid the side with the two vicinal trimethylsilyl groups in such an arrangement. Because of the $C_1$ point symmetry of ($Si_3Cp$)FeL(CO)X, it is not clear whether hindered rotation of the five-membered ring about the Fe−ring centroid vector has any influence on the conformation[9].

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## Experimental

*Iodobis(trimethyl phosphite)[tris(trimethylsilyl)cyclopentadienyl]iron:* To a suspension of $FeI_2$(DME) (2.00 g, 5.0 mmol) in THF (75 ml) was added a 0.1 M solution of tris(trimethylsilyl)cyclopentadienyllithium (50 ml, 5.0 mmol), and the mixture was allowed to warm up to −40°C. After recooling to −95°C a solution of trimethyl phosphite (1.24 g, 10.0 mmol) in THF (10 ml) was added dropwise. The resulting dark green mixture was allowed to warm to room temp., the solvent removed in vacuo, and the residue extracted with pentane (3 × 15 ml). The extracts were filtered through kieselguhr, the filtrate was concentrated until incipient crystallization and cooled to −40°C to afford dark green platelets; yield 2.31 g (65%), mp 129°C (dec.). − $^1$H NMR ($C_6D_6$, 25°C): δ = 0.18 (s, 9H, $SiCH_3$), 0.64 (s, 18H, $SiCH_3$), 3.50 (vt, 18H, $POCH_3$), 4.82 (vt, 2H, $C_5H_2$). − $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25°C): δ = 0.32 ($SiCH_3$), 2.40 ($SiCH_3$), 54.06 (vt, $POCH_3$), 72.35, 95.58, 95.74 (ring-C). − $^{31}$P NMR ($C_6D_6$, 25°C): δ = 174.4. − IR (KBr): $\tilde{\nu}$ = 2970 $cm^{-1}$ ms, 1244 ms, 1087 s, 1074 s, 1049 vs, 1031 s, 841 vs, 770 s, 754 s, 730 m, 555 mw. − EI MS (70 eV): *m/z* (%) = 712 (1) [$M^+$], 588 (5) [$M^+$ − $P(OMe)_3$], 464 (6) [$M^+$ − 2 $P(OMe)_3$].

$C_{20}H_{47}FeIO_6P_2Si_3$ (712.5) Calcd. C 33.71 H 6.65 I 17.81
Found C 33.73 H 6.70 I 17.80

*Hydridobis(trimethyl phosphite)[tris(trimethylsilyl)cyclopentadienyl]iron:* A solution of ($Si_3Cp$)Fe[$P(OMe)_3$]$_2$I (712 mg, 1.0 mmol) in THF (15 ml) was treated with a 2.0 M solution of *t*BuMgCl in THF (0.5 ml, 1.0 mmol) at −95°C and the resulting mixture allowed to warm up to room temp. After stirring for 2 h at room temp. all volatiles were removed in vacuo and the residue extracted with pentane (3 × 10 ml). The extracts were filtered through kieselguhr and the solvent removed. The oil was taken up in pentane, filtered, concentrated and cooled to −78°C giving waxy yellow crystals; yield 550 mg (94%), mp 155°C. − $^1$H NMR ($C_6D_6$, 25°C): δ = −15.57 [t, $^3J$(P,H) = 89.8 Hz, 1H, FeH], 0.46 (s, 27H, $SiCH_3$), 3.36 (vt, 18H, $POCH_3$), 4.75 (vt, 2H, $C_5H_2$). − $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25°C): δ = 0.81 ($SiCH_3$), 2.20 ($SiCH_3$), 51.20 (vt, $POCH_3$), 83.05, 86.60, 97.77 (ring-C). − $^{31}$P NMR ($C_6D_6$, 25°C): δ = 192.3. − IR (KBr): $\tilde{\nu}$ = 2946 $cm^{-1}$ m, 1840 br. w, 1247 m, 1073 s, 1061 s, 1043 s, 1016 vs, 829 vs, 768 s, 751 s, 708 s. − EI MS (70 eV): *m/z* (%) = 586 (23) [$M^+$], 461 (44) [$M^+$ − $HP(OMe)_3$], 358 (100) [$M^+$ − $P(OMe)_3$ − $SiMe_3$ − OMe].

$C_{20}H_{48}FeO_6P_2Si_3$ (586.6) Calcd. C 40.95 H 8.25 Fe 9.52
Found C 40.89 H 8.29 Fe 9.52

*Iodocarbonyl(trimethyl phosphite)[tris(trimethylsilyl)cyclopentadienyl]iron:* A solution of ($Si_3Cp$)Fe[$P(OMe)_3$]$_2$I (600 mg, 0.84 mmol) in ether was stirred under CO for 15 min during which time the color changed from dark green to reddish brown. The solvent was removed and the remaining oil crystallized from pentane at −40°C giving brown crystals; yield 500 mg (81%), mp 85°C. − $^1$H NMR ($C_6D_6$, 25°C): δ = 0.27 (s, 9H, $SiCH_3$), 0.41 (s, 9H, $SiCH_3$), 0.54 (s, 9H, $SiCH_3$), 3.37 [d, $^3J$(P,H) = 10 Hz, 9H, $POCH_3$], 4.67 [dd, $^4J$(H,H) = 1.5, $^3J$(P,H) = 4.9 Hz, 1H, $C_5H_2$], 5.74 [d, $^4J$(H,H) = 1.5 Hz, 1H, $C_5H_2$]. − $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25°C): δ = 0.35 ($SiCH_3$), 0.93 ($SiCH_3$), 1.45 ($SiCH_3$), 54.09 [d, $^2J$(P,C) = 9 Hz, $POCH_3$], 85.84, 90.75, 92.03, 99.55, 113.44 (ring-C). − $^{31}$P NMR ($C_6D_6$, 25°C): δ = 174.5. − IR (pentane): $\tilde{\nu}$ = 1958 $cm^{-1}$; (KBr): ν = 2953 $cm^{-1}$ m, 1952 vs, 1250 s, 1056 s, 1041 s, 1018 s, 837 vs, 779 s, 758 s, 727 m. − EI MS (70 eV): *m/z* (%) = 616 (5) [$M^+$], 588 (45) [$M^+$ − CO], 464 (58) [$M^+$ − CO − $P(OMe)_3$].

$C_{18}H_{38}FeIO_4PSi_3$ (616.5) Calcd. C 35.07 H 6.21 I 20.59
Found C 35.12 H 6.23 I 20.90

CAS Registry Numbers

($Si_3Cp$)Fe[$P(OMe)_3$]$_2$I: 120788-83-2 / ($Si_3Cp$)Fe[$P(OMe)_3$]$_2$Cl: 120788-87-6 / ($Si_3Cp$)Fe[$P(OMe)_3$]$_2$Br: 120788-88-7 / ($Si_3Cp$)Fe-[$P(OMe)_3$]$_2$H: 120788-84-3 / ($Si_3Cp$)Fe[$P(OMe)_3$](CO)I: 120788-85-4 / $FeI_2$(DME): 120788-86-5 / Li($Si_3Cp$): 97535-99-4 / *t*BuMgCl: 677-22-5 / CO: 630-08-0

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