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Communications

Formation of a Six-Membered Metallacycle Consisting of Iron, Carbon, Phosphorus, Boron, and Two Oxygens: The First Example of Precedence of Migratory Insertion of CO into an M−C Bond over OR Abstraction from Coordinating Phosphite by BF_3

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Summary: Treatment of $Cp(CO)MeFe\{P(OMe)_3\}$ *with* $BF_3{\cdot}OEt_2$ *and then* PPh_3 *gave a six-membered metallacyclic complex,* $Cp(PPh_3)\overline{FeC(Me)OBF_2OP}(OMe)_2$*, which is suggested by its NMR data and X-ray analysis to be best described as a carbene phosphite metallacycle.*

Boron trihalide, BX_3, being a typical Lewis acid, shows various reactivities toward organometallic complexes: a Fischer type carbene complex can be converted into a cationic carbyne complex[1] and a phosphite-containing complex into a cationic phosphenium complex,[2] by OR abstraction as an anion from a carbene carbon and from a phosphite phosphorus, respectively, and an alkyl carbonyl complex can be converted into an acyl complex by rapid migratory insertion of a CO ligand into an alkyl−transition-metal bond.[3] Recently, an iron complex containing CO, alkyl, and amino-substituted phosphite groups as ligands has been reported to react with $BF_3{\cdot}OEt_2$ to give a cationic phosphenium complex, and then migratory insertion of the phosphenium ligand into the iron−alkyl bond takes place to give a cationic complex, leading to an isolable complex by the addition of PPh_3 (Scheme 1).[4] The reaction sequence indicates that the OR abstraction by BF_3 and the subsequent migratory insertion of the formed phosphenium ligand have precedence over migratory insertion of CO into an Fe−C bond. Herein we describe the reaction of $Cp(CO)MeFe\{P(OMe)_3\}$ with $BF_3{\cdot}OEt_2$ and then PPh_3. We attempted the reaction in the expectation of obtaining $[Cp(CO)(PPh_3)Fe\{PMe(OMe)_2\}]^+BF_4^-$ according to the reaction sequence in Scheme 1, but the product was an unexpected complex which has a six-membered metallacycle consisting of Fe, C, P, B, and two O's (Scheme 2).

Treatment of $Cp(CO)MeFe\{P(OMe)_3\}$ with $BF_3{\cdot}OEt_2$

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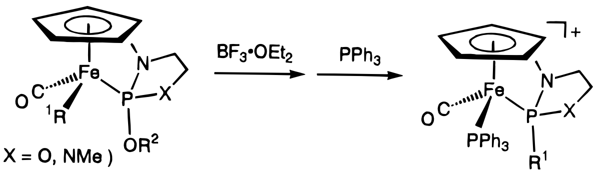
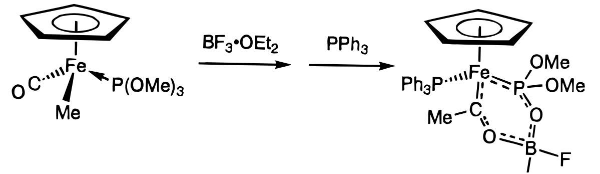
Scheme 1



Scheme 2



1

and then PPh_3 yielded yellow crystals (**1**).[5] The X-ray analysis carried out to elucidate the constitution of the compound showed that it has a six-membered metallacycle (Figure 1).[6] The ring adopts a boat-shaped structure. The NMR data and the elemental analysis data are consistent with the structure.[5] In the ^1H and ^{13}C NMR spectra, the two OMe groups were observed diastereotopically due to the Fe chiral center. The ^{19}F NMR spectrum showed two doublets. Therefore, it can be said that the six-membered ring is retained in solution at room temperature[7] and the racemization at the Fe is very slow, if it occurs at all. This M−C−O−B−O−P type metallacycle is the first of its kind, though symmetric M−C−O−B−O−C (**2**)[8] and M−P−O−B−O−P types (**3**)[9] have been reported.

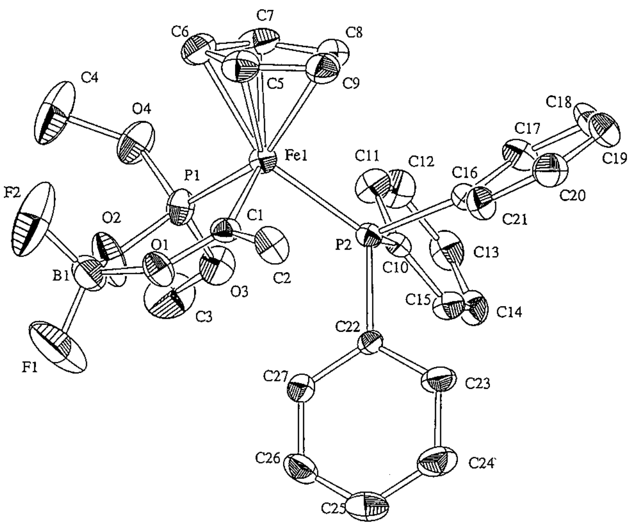
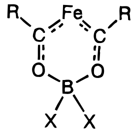
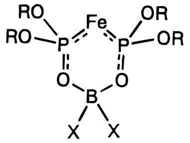


Figure 1. ORTEP view of **1** showing a numbering scheme. Selected bond distances (Å) and angles (deg): Fe1−P1 = 2.135(2), Fe1−P2 = 2.234(2), Fe1−C1 = 1.855(6), C1−C2 = 1.512(8), C1−O1 = 1.293(6), P1−O2 = 1.556(4), P1−O3 = 1.603(4), P1−O4 = 1.585(4), B1−O1 = 1.504(9), B1−O2 = 1.380(9), B1−F1 = 1.347(9), B1−F2 = 1.334(9), P1−Fe1−P2 = 98.6(1), P1−Fe1−C1 = 91.6(2), P2−Fe1−C1 = 95.2(2), Fe1−C1−O1 = 131.5(4), Fe1−C1−C2 = 121.6(4), C2−C1−O1 = 106.7(5), Fe1−P1−O2 = 116.9(2), P1−O2−B1 = 127.5(5), C1−O1−B1 = 128.4(5), O1−B1−O2 = 115.7(6).

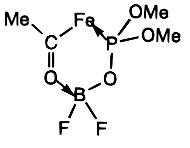


2

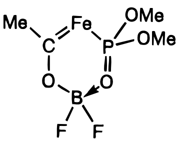


3

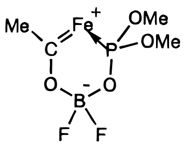
Complex **1** can be shown by three different descriptions. Type **1a** represents an acyl phosphite complex in which the acyl oxygen donates its lone-pair electrons to the OBF_2 group which is a substituent of the coordinating phosphite. Type **1b** is a carbene phosphonate complex in which the phosphonate oxygen coordinates to the OBF_2 group, which is a substituent of the carbene carbon. Type **1c** is a zwitterionic complex with a positive charge on the Fe and a negative charge on the B, corresponding to a carbene phosphite complex.



1a



1b



1c

The ^{31}P NMR spectrum of **1** showed a doublet at 168.7 ppm due to P in the ring. It has been reported that the range of ^{31}P resonances for the $-P(O)(OMe)_2$ ligand is 75−126 ppm, and it is 118−188 ppm for comparable complexes of $P(OMe)_3$.[10] Adduct formation of phosphoryl oxygen with BF_3 is reported to cause deshielding, but the shift is less than 30 ppm (103.3 ppm for $Cp(CO)_2Fe\{P(NEt_2)(OMe)(O)\}$ and 131.6 ppm for $Cp(CO)_2Fe$-

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(5) A solution of $Cp(CO)(Me)Fe\{P(OMe)_3\}$ (1.19 g, 4.12 mmol) in CH_2Cl_2 (30 mL) was cooled to −78 °C, and then $BF_3\cdot OEt_2$ (1.75 mL, 1.98 g, 13.9 mmol) was added. After it was warmed to room temperature, the solution was again cooled to −78 °C, and then PPh_3 (2.40 g, 9.15 mmol) was added. After the solution was warmed to room temperature, the solvent was removed under reduced pressure, and the residue was loaded on an alumina column. The yellow band eluted with CH_2Cl_2 was collected, and the solvent was removed under reduced pressure to give a yellow powder as a crude product (1.37 g, 2.36 mmol, 57%). The single crystals for the X-ray and elemental analyses were obtained by recrystallization from CH_2Cl_2/hexane (577 mg, 0.99 mmol, 24%). Anal. Calcd for $C_{27}H_{29}BF_2FeO_4P_2$: C, 55.52; H, 5.00. Found: C, 55.74; H, 5.04. NMR data: ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H, CCH_3), 2.69 (d, J = 10.6 Hz, 3H, OCH_3), 3.68 (d, J = 10.6 Hz, 3H, OCH_3), 4.25 (s, 5H, C_5H_5), 7.13−7.30 (m, 15H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 51.5 (s, CCH_3), 51.8 (d, J = 13.5 Hz, OCH_3), 53.0 (d, J = 11.0 Hz, OCH_3), 83.1 (s, C_5H_5), 128.1 (d, J = 9.8 Hz, o-C_6H_5), 129.6 (d, J = 2.4 Hz, p-C_6H_5), 133.3 (d, J = 9.7 Hz, m-C_6H_5), 136.7 (d, J = 41.5 Hz, ϵ-C_6H_5), 343.0 (ddd, J = 37.8, 20.8, 4.9 Hz, CCH_3); ^{31}P NMR (CH_2Cl_2) δ 76.2 (d, J = 97.7 Hz, PPh_3), 168.7 (d, J = 97.7 Hz, $P(OMe)_2(OBF_2)$); ^{19}F NMR (DMSO-d_6) δ −142.8 (d, J = 73.3 Hz, BF_2), −137.6 (d, J = 73.3 Hz, BF_2); ^{11}B NMR ($CDCl_3$) δ 2.39 (s, BF_2).

(6) Crystal data for **1**: $C_{27}H_{29}BF_2FeO_4P_2$, 0.50 × 0.10 × 0.10 mm, orthorhombic, *Pbca*, a = 9.805(1) Å, b = 18.134(2) Å, c = 30.055(5) Å, V = 5343.6(1.2) Å^3, Z = 8, ρ_{calcd} = 1.45 g cm^{-3}. Data were collected on an Enraf-Nonius CAD4 at 298 K with $\omega-2\theta$ scans with Mo Kα radiation (λ = 0.710 93 Å). A total of 6055 reflections were collected up to 2θ = 52.6°, of which 2139 were observed ($F_o > 3\sigma(F_o)$). The solution and refinement of the structure gave R = 0.045 and R_w = 0.038.

(7) The ^{13}C NMR spectrum of **1** showed a doublet of doublets of doublets at 343.02 ppm due to the carbon in the ring. This pattern results from the coupling with two different phosphorus atoms and one of the two fluorine atoms. This observation also suggests that complex **1** retains the structure in solution as depicted in the ORTEP in Figure 1, since the torsion angles of C1−O1−B1−F1 and C1−O1−B1−F2 are 98.5 and 147.9°, respectively.

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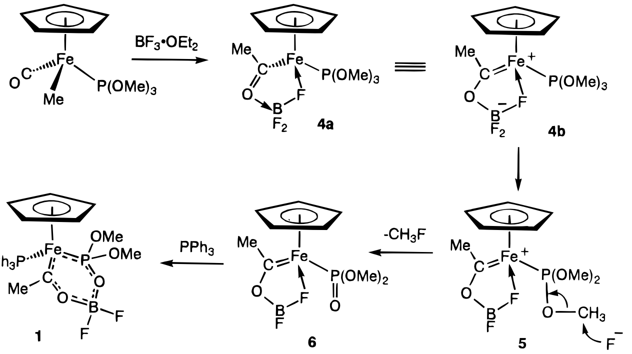
{P(NEt$_2$)(OMe)(O)···BF$_3$}).[11] The P—O bond distance in the ring is 1.556 Å, which is longer than the P═O bond distance for Cp(CO)$_2$Fe{P(O)(OEt)$_2$} (1.495 Å)[12] and also longer than that in Cp(CO)$_2$Fe{P(NEt$_2$)$_2$(O)···(FeCl$_2$)$_{1/2}$} (1.514 Å).[13] These observations suggest that **1** should be depicted as a phosphite type complex (**1a** or **1c**) rather than a phosphonate type complex (**1b**).

The ^{13}C NMR spectrum of **1** showed a doublet of doublets of doublets at 343.02 ppm due to the carbon in the ring. The chemical shift is deshielded compared with those of the acetyl carbonyl carbons in Cp(CO)-LFe{C(O)Me} (L = CO, δ 254.4; L = PPh$_3$, δ 274.1; L = CyCN, δ 268.4),[14] but it is close to those for Fischer type carbene complexes (342.0 ppm for [Cp(CO)(PPh$_3$)-Fe═CMe(OEt)]$^+$, 333.6 ppm for [Cp(CO)(PPh$_3$)Fe═CPh-(OMe)]$^+$).[15] The bond distances of Fe—C1 (1.855 Å) and C1—O1 (1.293 Å) are significantly shorter and longer, respectively, than those for Cp(CO)(PPh$_3$)FeC(O)R derivatives: average Fe—C(acyl) = 1.943 Å, average C═O(in acyl ligand) = 1.230 Å.[16] These considerations suggest that **1** should be described as a carbene complex (**1b** or **1c**) rather than an acyl complex (**1a**). Therefore, although **1** should be described as the resonance forms of **1a**—**c**, the contribution from **1c** is incomparably superior to that from **1a** or **1b**.

A plausible reaction mechanism for Scheme 2 is illustrated in Scheme 3. In the reaction, BF$_3$ induces migratory insertion of the CO ligand into an Fe—Me bond rather than OMe abstraction from the coordinating P(OMe)$_3$. The acyl complex (**4a**) thus produced, which can also be described as a cationic carbene complex (**4b**), releases F$^-$ to give **5**. Since **5** is a cationic complex containing a P(OMe)$_3$ ligand, it is reasonably expected to undergo an Arbuzov-like dealkylation with F$^-$ to give a phosphonate complex (**6**),[10,17] which is converted, by PPh$_3$ addition, into **1** with forming a bond between the phosphoryl oxygen and the boron.

Scheme 3



The interesting point is that, in the reaction of Cp-(CO)MeFe{PXY(OMe)} with BF$_3$•OEt$_2$, OMe abstraction from phosphorus takes place when X and/or Y is an amino group, whereas migratory insertion of CO into Fe—Me occurs when X = Y = OMe. The reason for the different reactivities may come from the basicity of an OMe group on the phosphorus: the OMe group in the former complex may be basic enough to attract BF$_3$ due to the electron-donating ability of an amino group to a phosphorus causing the increasing OR basicity, whereas the OMe group in the latter one would be less attractive than the carbonyl oxygen toward BF$_3$.

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Supporting Information Available: Tables giving positional and thermal parameters and bond lengths and angles for **1** (8 pages). Ordering information is given on any current masthead page.

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