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Reduction of a CO Ligand in an Iron Phosphonate Complex with a Neutral Borane Compound. Formation of a Formyl Complex with Intramolecular Coordination to a Boron Atom

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Summary: Treatment of $Cp(CO)_2Fe\{P(O)(OMe)_2\}$ *with an electrically neutral hydroborane, 9-borabicyclo-3,3,1-nonane, yielded* $Cp(CO)\overline{Fe\{C(H)OB(C_8H_{14})OP}(OMe)_2\}$ *(**1**), with a terminal CO ligand reduced. The X-ray structure analysis revealed that **1** includes intramolecular coordination of the formyl oxygen to the boron atom to form a six-membered metallacycle, which would stabilize the complex as a whole.*

With the aim of carbon monoxide fixation, great efforts have been made in hydrogenation of CO, such as in Fischer−Tropsch reactions.[1] In relation to the CO conversion chemistry, the hydride reduction of CO in a transition metal coordination sphere has attracted considerable attention.[2,3] In general, such reduction requires highly basic hydride donors, usually borohydrides or aluminohydrides, and involves a transition metal−formyl complex as an initial product. However, in many cases, the formyl complex is generated only transiently or, in some cases, cannot even be detected, since further reduction or decomposition of the formyl ligand immediately takes place, owing to its intrinsic low stability.[4] *We report here an unprecedented reduction of a terminal CO ligand in an iron phosphonate complex, with a neutral hydroborane as a Lewis acid*. The X-ray structure analysis and the spectroscopic data of the product reveal that the formyl oxygen intramolecularly coordinates to the borane atom and forms a six-membered metallacycle. This constitutes the first structurally characterized borane adduct of a formyl complex.[3,5,6]

Treatment of $Cp(CO)_2Fe\{P(O)(OMe)_2\}$ with 9-BBN (9-borabicyclo-3,3,1-nonane) in THF gave a moisture- and/or air-sensitive pale yellow powder (Scheme 1).[7] The structure of the product was established by an X-ray diffraction analysis, and the ORTEP drawing and selected bond distances and angles are displayed in Figure 1.[8] The complex has a six-membered metallacycle structure formulated as $Cp(CO)\overline{Fe\{C(H)OB(C_8H_{14})OP}(OMe)_2\}$ (**1**). In this metallacycle, a boron atom bridges two oxygen atoms, one of which is derived from the phosphoryl group and the other from the terminal carbonyl ligand in the starting complex. The positions of all hydrogen atoms were determined experimentally, and it was found that C7 adopts sp^2 hybridization and is almost coplanar with H6, Fe1, and O2 (sum of the bond angles around C7 is 358.7°). The ^{1}H and ^{13}C NMR spectra of **1** show that two OMe groups on P1 are in different magnetic environments. Since the iron center is chiral, these observations strongly suggest that the two OMe groups should be diastereotopic, and thus the reaction in Scheme 1 is irreversible on the NMR time scale.[9]

Complex **1** can be depicted as three limiting resonance forms (Figure 2), i.e., (a) a formyl phosphite complex with intramolecular coordination of the formyl oxygen to the borane fragment, (b) a zwitterionic carbene phosphite complex, and (c) a carbene phosphonate complex with intramolecular coordination of the phos-

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(2) For a review article, see: Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.

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(4) For a review article, see: Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

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(7) A THF solution of 9-BBN (0.50 M, 8.4 mL, 4.2 mmol) was added to a THF solution (20 mL) of $Cp(CO)_2Fe\{P(O)(OMe)_2\}$ (0.80 g, 2.8 mmol) at room temperature. After 20 min stirring, volatile components were removed from the mixture under reduced pressure, and then pentane (25 mL) was added to the residue to form a pale yellow precipitate. After the supernatant was decanted off, the precipitate was washed with pentane repeatedly and then dried in vacuo to give a pale yellow powder of **1** (1.04 g, 2.54 mmol, 91% yield). Complex **1** is highly hygroscopic, and sufficient elemental analysis data could not be obtained, although satisfying spectroscopic data and X-ray crystal structural data had been collected. IR (ν_{CO}, in THF): 1975 cm^{-1}. ^{1}H NMR (δ, in C_6D_6): 1.04−2.66 (m, 14H, C_8H_{14}), 3.33 (d, J_{HP} = 11.6 Hz, 3H, OCH_3), 3.47 (d, J_{HP} = 11.9 Hz, 3H, OCH_3), 4.24 (s, 5H, C_5H_5), 13.74 (d, J_{HP} = 13.8 Hz, 1H, CHO). ^{13}C NMR (δ, in C_6D_6): 25.60 (s, C_8H_{14}), 25.75 (s, C_8H_{14}), 27.41 (br, C_8H_{14}), 32.29 (s, C_8H_{14}), 32.47 (s, C_8H_{14}), 32.63 (s, C_8H_{14}), 32.78 (s, C_8H_{14}), 51.07 (d, J_{CP} = 9.8 Hz, OCH_3), 51.82 (d, J_{CP} = 4.5 Hz, OCH_3), 86.83 (s, C_5H_5), 215.25 (d, J_{CP} = 43.8 Hz, CO), 294.57 (d, J_{CP} = 42.3 Hz, CHO). ^{31}P NMR (δ, in C_6D_6): 155.97 (s). ^{11}B NMR (δ, in C_6D_6): 15.16 (s).

(8) Crystal data for **1**: $C_{17}H_{26}O_5FePB$, 0.33 × 0.25 × 0.25 mm, monoclinic, $P2_1/a$, $a = 12.799(4)$ Å, $b = 16.078(4)$ Å, $c = 9.399(3)$ Å, $\beta = 105.10(2)°$, $Z = 4$, $\rho_{calcd} = 1.451$ g cm^{-3}. Data were collected on a Mac Science MXC$_\kappa$ at 298 K with $\omega-2\theta$ scans with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 5822 reflections were collected up to $2\theta = 57.3°$, of which 3627 were regarded as observed ($F_o > 3\sigma(F_o)$). The solution and refinement of the structure gave $R = 0.030$ and $R_w = 0.041$.

(9) The possibility of the rapid ring opening−closing equilibrium cannot be ruled out, in which either the PO−B bond or the CO−B bond cleaves. In both cases, the iron atom would still be chiral and two OMe groups should be in a different magnetic environment. However, the low-temperature NMR measurements of **1** suggested that there is no such equilibrium on the NMR time scale.

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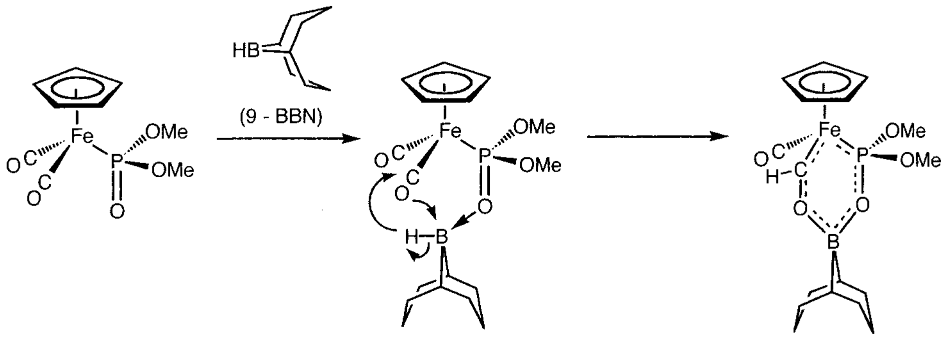
Scheme 1



phoryl oxygen to the borane fragment. According to the following NMR properties of **1**, the type (a) limiting resonance form seems to be the most dominant. That is, the chemical shift of the signal assignable to C7 (294.6 ppm, d, $J_{CP} = 42.3$ Hz) in the ^{13}C NMR spectrum, which is at a magnetic field higher than 310 ppm, is diagnostic of a formyl carbon rather than a carbene carbon.[10] In the ^{31}P NMR spectrum, **1** shows a signal at 156.9 ppm, which is at a lower magnetic field by ca. 50 ppm than that of the starting phosphonate complex, suggesting that the phosphorus fragment is described as a phosphite coordinated to a transition metal via its lone-pair electrons.

The B1−O2 bond (1.567(3) Å) is longer than the B1−O3 bond (1.515(3) Å), indicating that the interaction between B1 and O2 is weaker, as expected from the type (a) representation. The Fe1−C7 bond (1.862(2) Å) is shorter and the C7−O2 bond (1.268(3) Å) is longer than the corresponding Fe−C and C−O bonds, respectively, in a comparable acyl ligand.[11] These observations suggest the Fe1−C7 bond bears some double-bond character, and the bond order between C7 and O2 decreases correspondingly. The P1−O3 bond (1.540(1) Å) which has been derived from the phosphoryl oxygen in the starting phosphonate complex is still shorter than both P1−O4 (1.591(2) Å) and P1−O5 (1.596(2) Å) single bonds, suggesting that some double-bond character remains in the P1−O3 bond. Thus, the form (c) is also contributing to some extent to the ground state structure of the metallacycle.[12]

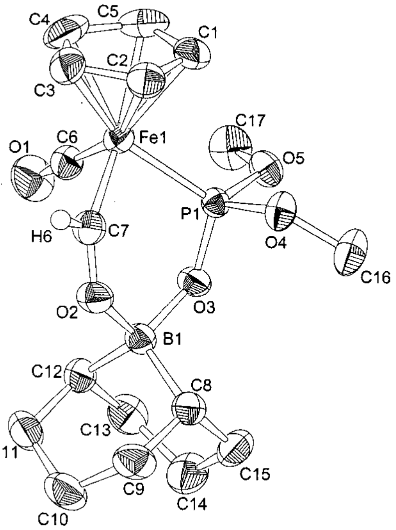


Figure 1. ORTEP drawing of **1** showing a numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)−P(1) = 2.1258(6), Fe(1)−C(7) = 1.862(2), P(1)−O(3) = 1.540(1), P(1)−O(4) = 1.591(2), P(1)−O(5) = 1.596(2), O(2)−C(7) = 1.268(3), O(2)−B(1) = 1.567(3), O(3)−B(1) = 1.515(3), P(1)−Fe(1)−C(7) = 85.74(7), Fe(1)−P(1)−O(3) = 113.63(6), C(7)−O(2)−B(1) = 130.0(2), P(1)−O(3)−B(1) = 127.7(1), Fe(1)−C(7)−O(2) = 134.7(2), O(2)−B(1)−O(3) = 108.5(2), Fe(1)−C(7)−H(6) = 114(1), O(2)−C(7)−H(6) = 110(1).

Generally, formyl complexes, especially of first-row transition metals are very unstable, and they decompose in several pathways depending on the experimental conditions.[2−4] The complex **1** is, however, stable under an N_2 atmosphere, although it is a first-row transition metal complex.[13] At least up to 60 °C in a benzene solution, no decomposition reaction was observed. Moreover, even with excess 9-BBN, there is no evidence for further reduction of **1**. The stability of **1** may be attributed to the formyl ligand interacting with the borane in an *intramolecular* fashion, to form a metallacycle structure. That is, the formyl oxygen is so strongly coordinated to the borane fragment that an-

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(10) In general, ^{13}C NMR chemical shifts of formyl carbons fall in the range of 240−310 ppm,[4] e.g., 306.5 ppm for $(\eta^5\text{-}C_5Me_5)(CO)(PBu_3)FeCHO$.[3] On the other hand, the chemical shifts for carbene carbons are generally at a lower magnetic field (i.e., downfield of 310 ppm) than that observed for formyl complexes, e.g., 325.3 ppm for $[(\eta^5\text{-}C_5Me_5)(CO)(PBu_3)FeCH(OMe)]PF_6$: Guerchais, V.; Lapinte, C.; Thépot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604.

(11) Since X-ray structures of Cp(CO)(phosphite)FeC(O)R (R = H, alkyl) have not been reported, the Fe−C and the C−O bond lengths in Cp(CO)(phosphine)FeC(O)Me and its derivative are referenced. The Fe−C and the C−O bonds in the acetyl ligand are 1.917(8) and 1.234(7) Å, respectively, in $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeC(O)CH_3$, and 1.921(9) and 1.219(8) Å, respectively, in $(\eta^5\text{-}MeC_5H_4)(CO)(PPh_3)FeC(O)CH_3$: Liu, H. Y.; Koh, L. L.; Eriks, K.; Giering W. P.; Prock, A. *Acta Crystallogr.* **1990**, *C46*, 51.

(12) A complex having a similar six-membered metallacycle structure, $Cp(PPh_3)Fe\{C(Me)OB(F)_2OP(OMe)_2\}$, has been reported: Nakazawa, H.; Yamaguch, Y.; Miyoshi, K. *Organometallics* **1996**, *15*, 4661. For this complex, the twitterionic form (b) has been proposed as the most dominant resonance form, probably because of two highly electronegative F atoms present on the boron atom and an electron-donating PPh_3 ligand present on the metal center, which would in turn promote back-donation from the iron to the carbenoid carbon atom.

(13) A neutral formyl complex of iron with a piano-stool configuration, $(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)FeCHO$, was reported so far, which is stable even at room temperature. In this complex, the bulky and electron-withdrawing phenyl groups in the C_5Ph_5 ligand may stabilize the formyl ligand both kinetically and thermodynamically: (a) Brégaint, P.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1417. (b) Li, L.; Decken, A.; Sayer, B. G.; McGlinchey, M. J.; Brégaint, P.; Thépot, J.-Y.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1994**, *13*, 682.

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(15) (a) Nakazawa, H.; Morimasa, K.; Kushi, Y.; Yoneda, H. *Organometallics* **1988**, *7*, 458. (b) Nakazawa, H.; Fujita, T.; Kubo, K.; Miyoshi, K. *J. Organomet. Chem.* **1994**, *473*, 243.

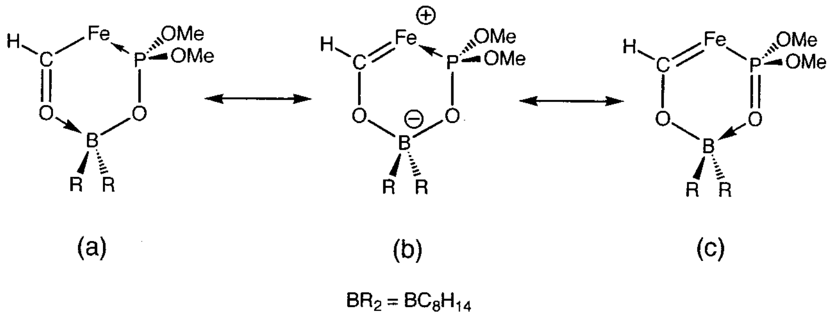

Figure 2. Canonical structures of **1**.

other free hydroborane might no longer interact with the formyl oxygen, to prevent the further reduction of the formyl ligand.

The reaction presented here proceeds readily and quantitatively at room temperature. In this reaction, 9-BBN may first attack electrophilically not the carbonyl oxygen but the phosphoryl oxygen,[14] because of the greater polarization of the phosphoryl group as $P^{\delta+}-O^{\delta-}$ (Scheme 1).[15] That is, the phosphonate ligand seems to play two important roles: (1) activation of the B−H bond in 9-BBN through the electron donation from the phosphoryl oxygen to the boron atom; (2) anchoring the borane fragment to induce the strong coordination of the formyl oxygen. To exemplify the role of the phosphonate ligand, we attempted the reaction of the corresponding methyl complex, $Cp(CO)_2FeMe$, with 9-BBN under similar conditions and found that no CO reduction product was detected at all.[16] This result shows that the phosphonate ligand is essential to the present unusual reduction of the terminal CO with a neutral hydroborane and also to stabilizing the resulting formyl complex.

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Supporting Information Available: Details of synthetic procedures and X-ray crystal structure determination of **1**, including tables of intensity collection and refinement details, atomic coordinates and thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Under an atmosphere of CO and in the presence of a catalyst such as BF_3 or $AgBF_4$, Cp(CO)LFeMe (L = CO, PMe_3) reacts with boranes to produce C2 and higher molecular weight hydrocarbons via several cycles of CO insertion into the transition metal−alkyl bond and borane reduction: (a) Stimson, R. E.; Shriver, D. F. *Organometallics* **1982**, *1*, 787. (b) Brown, S. L.; Davies S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 84. In these chain-growth reactions, catalysts may induce CO insertion into a metal−alkyl bond: Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.