L)(η^2-L-L),[9] it can be confidently assumed that compound **c** has the empirical formula $[W(CO)(NO)(ape)_2I]^{2+}$. However, the isomeric form of this species, and indeed whether it is a six-coordinate 16-electron or seven-coordinate 18-electron species, or whether the nitrosyl group is linear or bent, cannot be determined. The behavior of process VII could have its origin in a temperature-dependent distribution of bent and linear nitrosyl ligand complexes leading to a highly temperature-dependent electron-transfer rate.[25] Alternatively, a temperature-dependent distribution of isomers containing (η^1-ape)(η^2-ape) and $(\eta^2\text{-ape})_2$ could explain the behavior. In any event, $[W(CO)(NO)(ape)_2I]^{2+}$ slowly decomposes via an unknown mechanism to form the isolated 16-electron product $[W(NO)(\eta^2\text{-ape})_2I]^{2+}$ (compound **d**).

The dpm system differs only in the fact that the 17-electron intermediate $[W(CO)(NO)(dpm)_2I]^+$ (compound **b** Scheme I) is not directly observed in the voltammetric experiments, and a direct two-electron oxidation of $W(CO)(NO)(dpm)_2I$ gives compound **c** directly. Nevertheless, the oxidation probably proceeds through compound **b** which then rapidly disproportionates, a process frequently observed for 17-electron carbonyl systems.[9,27,28]

The mechanism for oxidation of $W(CO)(NO)(\eta^1\text{-dpe})(\eta^2\text{-dpe})I$ at low temperatures is similar to that of $W(CO)(NO)(ape)_2I$ at room temperature. However, an alternative pathway is available to the dpe complex to generate compound **c**, since at room temperature the first oxidation process is irreversible but the reduction response due to compound c is still observed. It is palusible that at room temperature the 17-electron W(I) species $[W(CO)(NO)(\eta^1\text{-dpe})(\eta^2\text{-dpe})I]^+$, containing the W(I)–NO$^+$ linakge, undergoes internal electronic rearrangement to give a six-coordinate W(II)–NO^0 16-electron species containing a bent NO ligand. Chelation of the second dpe ligand gives a seven-coordinate W(II) species and a further one-electron oxidation of NO to NO$^+$ would give compound **d**. Alternatively, the pendant phosphorus in the six-coordinate 1+ cation could chelate to give a 19-electron seven-coordinate species before the second electron transfer to give compound **d**. Nineteen-electron species have been observed previously in nitrosyl systems.[25,29]

Oxidation of $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ (M = Mo, W; L-L = dpm, dpe) gives species believed[9] to be $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$, as fairly stable seven-coordinate 18-electron species. In contrast, two-electron oxidation of $W(CO)(NO)(\eta^1\text{-L-L})(\eta^2\text{-L-L})I$ gives the 16-electron $[W(CO)(L\text{-}L)_2I]^{2+}$ cation as the final stable product. Thus replacing carbonyl by nitrosyl and halide has marked affects on the nature of the thermodynamically stable product.

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[27] Bagchi, R. N.; Bond, A. M.; Colton, R.; Luscombe, D. L.; Moir, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 3352.

[28] Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879.

[29] Mason, J.; Mingos, D. M. P.; Schaefer, J.; Sherman, D.; Stejskal, E. O. *J. Chem. Soc. Chem. Commun.* **1985**, 444.

Characterization of the Organometallic Lewis Acid $(\eta^5\text{-}C_5H_5)(CO)Fe(OR_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$

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Protonation of the η^3-allyl complex $Cp(CO)Fe(CH_2CHCH_2)$ (**10**) with $HBF_4{\cdot}OEt_2$ or $HBF_4{\cdot}OMe_2$ in CH_2Cl_2 (−80 °C) affords an extremely reactive organometallic Lewis acid precursor, which degrades above −65 °C. The structure assigned to this Lewis acid, on the basis of its ^{11}B and ^{19}F NMR spectral measurements and of its chemical reactivity, is $Cp(CO)Fe(OR_2)(CH_2{=}CHCH_3)^+BF_4^-$ (**8**). Similar NMR measurements are also reported for appropriate model compounds containing coordinated fluoroborate [e.g., $Cp(CO)_2FeFBF_3$ and $Cp(CO)_3MoFBF_3$] or ionic BF_4^- [e.g., $Cp(CO)_2Fe(THF)^+BF_4^-$]. Some potential ligands (e.g., THF) deprotonate **8** back to starting **10**, whereas others (e.g., acetonitrile) readily convert **8** into examples of disubstituted complexes, $Cp(CO)Fe(L_1)(L_2)^+BF_4^-$. Excess $P(OPh)_3$, for example, converts **8** first to the η^2-propene derivative $Cp(CO)Fe(CH_2{=}CHCH_3)P(OPh)_3{}^+BF_4^-$ (**13**) and then in refluxing CH_2Cl_2 to $Cp(CO)Fe[P(OPh)_3]_2{}^+BF_4^-$ (**14**). Reactions between **8** and the acetyl complexes $Cp(CO)(L)FeCOCH_3$ (L = CO, PPh_3) give the bimetallic μ-(η^1-C,O)-acetyl compounds $Cp(CO)(L)Fe{-}C(CH_3)O{-}Fe(CO)_2Cp^+BF_4^-$ (**15**) in low yields, with no evidence of forming μ-(η^2-C,O)-acetyl derivatives $Cp(CO)Fe(CH_3CO)Fe(L)Cp^+BF_4^-$. The organometallic etherate complex $Cp(CO)_2Fe(OMe_2)^+BF_4^-$ (**2a**) results through protonolysis of $Cp(CO)_2FeCH_3$ with $HBF_4{\cdot}OMe_2$ between −30 and −78 °C. This unstable salt decomposes even at −55 °C in CH_2Cl_2 or $CDCl_3$ solution, as monitored by ^1H and ^{19}F NMR spectroscopy. The ether on **2a** likewise is extremely labile; conditions are reported for replacing it by acetonitrile to give $Cp(CO)_2Fe(NCCH_3)^+BF_4^-$ (**2c**).

Introduction

The organometallic Lewis acid $Cp(CO)_2Fe^+$ or Fp^+ (**1**), which usually is associated with BF_4^- or PF_6^- counterions, serves as a useful intermediate for generating a wide variety of complexes $Fp{-}L^+$ (**2**) (L is a neutral, two-electron donor ligand).[1] This extremely reactive intermediate **1**,

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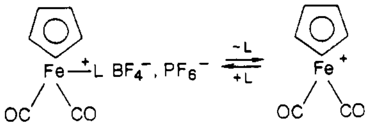
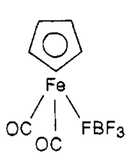
in turn, forms by dissociating a labile ligand (e.g., L = isobutylene,[1] acetone,[2] or THF[1a,2c,3]) (eq 1), by oxidizing[2,3a,4] or protonating[5] the Fe–Fe bond in Fp_2, by abstracting halide from Fp–X,[2b,3a,6] and by protonating η^1-alkyl complexes Fp–R.[7]



(1)

2 1

The putative intermediate 1 has not been detected due to its extremely high reactivity and presumed low thermodynamic stability.[7a] Even at low temperatures, 1 readily ligates a wide assortment of neutral and anionic Lewis bases. Competing side reactions include disproportionating to the coordinatively saturated $CpFe(CO)_3^+$, abstracting halide from a variety of sources, and forming solvates $Cp(CO)_2Fe\text{–}L^+$. Recent studies by Graham and Mattson[6d] demonstrate that tetrafluoroborate also coordinates 1 and gives the covalent η^1-(F)BF_3 adduct 3.



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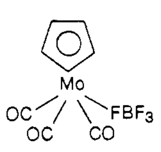
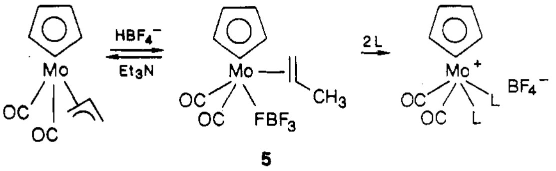


4

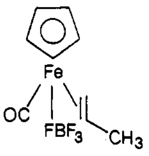
Ligating BF_4^- (or PF_6^-) to organometallic Lewis acids is well established.[8] Beck and co-workers demonstrated, for example, that BF_4^- weakly coordinates electrophilic $Cp(CO)_3Mo^+$ and that the fully characterized adduct 4 is stable in CH_2Cl_2 solution at room temperature.[9] Lewis bases (e.g., alkenes, phosphines, ethers, ketones) nevertheless rapidly displace BF_4^-, affording examples of $Cp(CO)_3MoL^+BF_4^-$. (In contrast, the less stable $Cp(CO)_3MoFPF_5$ in CH_2Cl_2 solution degrades above −40 °C via detectable $Cp(CO)_3Mo^+PF_6^-$ or its CH_2Cl_2 solvate.) In previous studies, we characterized the covalent BF_4^- compound 5 that results from protonating an η^3-allyl complex (eq 2).[10] Both latent coordination sites on 5 are available for selectively forming disubstituted derivatives although CO initially displaces BF_4^- and gives the cationic η^2-propene compound $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$.



(2)

5

This paper concerns the outcome of extending our work on 5 in an attempt to prepare the analogous organoiron Lewis acid precursor 6 and to use it in generating bimetallic μ-(η^2-C,O)-acetyl compounds $Cp(CO)Fe(\mu\text{-}CH_3CO)Fe(L)Cp^+$ (7) (L = CO, PPh_3). We now report that treating the requisite η^3-allyl iron complex with $HBF_4\cdot$etherate generates the extremely reactive Lewis acid–ether adducts $Cp(CO)Fe(OR_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$ (8) (R = Me, Et).[12] These were characterized by ^{11}B and ^{19}F NMR spectroscopy (at −80 °C) and by conversion to their disubstituted derivatives 9. Preparative and spectral data also are reported for the labile etherate $Fp\cdot OMe_2^+BF_4^-$ (**2a**).



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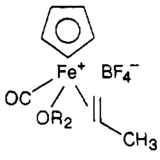

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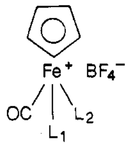

9

Experimental Section

Synthetic manipulations were performed under a nitrogen atmosphere by using standard syringe/septum and Schlenk techniques.[11] Cationic organometallic products $Cp(CO)FeL_1L_2^+BF_4^-$ (9) obtained in this study are not air-sensitive; they were precipitated (typically using CH_2Cl_2–ether) in open Erlenmeyer flasks using excess anhydrous ether.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/1.5 mL) in NaCl, lead (amalgam)-spaced (0.10-mm) solution cells and were recorded on a Perkin-elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption; they are accurate to ±2 cm^{-1} below and ±5 cm^{-1} above 2000 cm^{-1}. NMR spectral data were obtained on a Varian Model XL-200 spectrometer operating at 200 (^1H), 188.22 (^{19}F), and 64.18 (^{11}B) MHz. Solvents used for ^{19}F and ^{11}B NMR spectral data were CH_2Cl_2 and 2:1 CH_2Cl_2–$CDCl_3$, respectively. Positive chemical shifts are downfield relative to internal Me_4Si (^1H), internal $FCCl_3$ (^{19}F), or external $BF_3\cdot OEt_2$ (^{11}B). The boron data, in particular, are temperature-de-

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(1) (a) Giering, W. P.; Rosenblum, M. *J. Chem. Soc., Chem. Commun.* **1971**, 441. (b) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. Cutler, A. R.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *Ibid.* **1976**, *98*, 3495. (c) Nicholas, K. M. *J. Am. Chem. Soc.* **1975**, *97*, 3254. Boyle, P. F.; Nicholas, K. M. *J. Org. Chem.* **1975**, *40*, 2682.

(2) (a) Johnson, E. C.; Meyer, T. J.; Winterton, N. *Inorg. Chem.* **1971**, *10*, 1673. Williams, W. E.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1329. (b) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (c) Schmidt, E. K. G.; Thiel, C. H. *J. Organomet. Chem.* **1981**, *209*, 373. Haines, R. J.; du Preez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357.

(3) (a) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153. (b) Schmidt, E. K. G.; Thiel, C. H. *J. Organomet. Chem.* **1981**, *220*, 87. (c) Rosenblum, M.; Scheck, D. *Organometallics* **1982**, *1*, 397. (d) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55; **1986**, *304*, 181. Schumann, H. *Ibid.* **1986**, *299*, 169. (e) Schumann, H. *J. Organomet. Chem.* **1985**, *293*, 75.

(4) (a) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165. Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1965**, 3030. Sloan, T. E.; Wojcicki, A. *Inorg. Chem.* **1968**, *7*, 1268. (b) Ferguson, F. A.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 1025. Braddock, J. N.; Meyer, T. J. *Inorg. Chem.* **1973**, *12*, 723. (c) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307. (d) Schumann, H. *J. Organomet. Chem.* **1986**, *304*, 341.

(5) (a) Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. *Organometallics* **1983**, *2*, 1238 and references cited. (b) Callan, B.; Manning, A. R. *J. Organomet. Chem.* **1983**, *252*, C81. Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(6) (a) Triechel, P.; Shubkin, R. L.; Barnett, K. W.; Reichad, D. *Inorg. Chem.* **1966**, *5*, 1177. (b) Fischer, E. O.; Fichtel, K. *Chem. Ber.* **1961**, *94*, 1200. Fischer, E. O.; Moser, E. *Inorg. Synth.* **1970**, *12*, 35 and references cited. (c) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73. (d) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

(7) (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (b) Tso, C. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1242.

(8) Lead references on "coordinating" vs "noncoordinating" counterions: (a) Olgemöller, B.; Bauer, H.; Löbermann, H.; Nagel, U.; Beck, W. *Chem. Ber.* **1982**, *115*, 2271. Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 3412. Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. Shelly, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *Ibid.* **1986**, *108*, 3117. (b) Fernandez, J.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672.

(9) (a) Beck, W.; Schloter, K. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214. Schloter, K.; Beck, W. *Ibid.* **1980**, *35B*, 985. Sünkel, K.; Ernst, H.; Beck, W. *Ibid.* **1981**, *36B*, 474. (b) Sünkel, K.; Günter, U.; Beck, W. *J. Organomet. Chem.* **1983**, *252*, 187. (c) Sünkel, K.; Urban, G.; Beck, W. *Ibid.* **1985**, *290*, 231.

(10) Markham, J.; Menard, K.; Cutler, A. *Inorg. Chem.* **1985**, *24*, 1581.

(11) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(12) Green, M. L. H.; Nagy, P. *J. Chem. Soc.* **1963**, 189.

pendent, and accordingly solutions were kept at −80 °C when recording ^{11}B NMR spectra.

Organic reagents were procured commercially and used as received. Methylene chloride was distilled under nitrogen from P_2O_5; either anhydrous ether was taken from a freshly opened can, or it was distilled from sodium benzophenone ketyl. Organometallic starting materials $Cp(CO)Fe(\eta^3\text{-}CH_2CHCH_2)$ (**10**),[12] $CpFe(CO)_3{}^+BF_4{}^-$ and $CpFe(CO_3)^+PF_6{}^-$,[13] Cp_2WH_2,[14] $Cp(CO)_2FeCOCH_3$,[15] and $Cp(CO)(PPh_3)FeCOCH_3$[16] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. Methylene chloride solutions containing $Cp(CO)_3MoFBF_3$ (**4**),[9] $Cp(CO)_2Mo(FBF_3)(CH_2{=}CHCH_3)$ (**5**),[10] $Cp(CO)_2FeFBF_3$ (**3**),[6d] $Cp(CO)_2Fe(THF)^+BF_4{}^-$ (**2b**),[3] and $Cp(CO)_2Fe(NCCH_3)^+BF_4{}^-$ (**2c**)[6a,b,7b] were generated as previously described.

The $HBF_4{\cdot}OMe_2$ was used as received and was transferred by using a 1-mL syringe and stainless-steel needle. A 10% (by volume) stock solution of $HBF_4{\cdot}OEt_2$ in anhydrous ether was prepared, and the titer of this acid solution was established by using $Cp(CO)(PPh_3)FeCOCH_3$ (45 mg, 0.10 mmol) in 1.5 mL of CH_2Cl_2. The pale yellow solution of $Cp(CO)(PPh_3)FeCOCH_3$ immediately turned green when treated with 1 equiv of acid solution (0.1 mL) as $Cp(CO)(PPh_3)FeC(OH)CH_3{}^+BF_4{}^-$ formed.[17] This reaction was monitored by IR spectroscopy; the acetyl ν(CO) at 1600 cm^{-1} disappeared, and the starting terminal ν(CO) at 1901 cm^{-1} shifted to 1980 cm^{-1}. Quantitative IR spectral measurements were made by using a Beer's law plot.

Protonation of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (10). A yellow solution of 38 mg (0.20 mmol) of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) in 3 mL of CH_2Cl_2 was cooled to −78 °C, and 1 equiv of HBF_4·diethyl ether solution was added. The yellow solution immediately turned dark green. Attempts to record IR spectra were unsuccessful as the green solution quickly turned red in the transfer pipet or syringe. The resulting IR spectrum shows two ν(CO) peaks at 2078 and 2030 cm^{-1}. The green solution was stable below −70 °C for at least $^1/_2$ h, but it rapidly turned red above −65 °C and deposited a reddish brown precipitate. This solid was isolated at room temperature but is insoluble in CH_2Cl_2, CH_3NO_2, and acetone.

The above green solution that resulted from protonating **10** (−78 °C) was treated with 1–3 equiv of Et_3N or with THF (dropwise addition, 1 mL). A yellow solution was regenerated immediately, and IR spectral monitoring was consistent with quantitative regeneration of **10** (ν(CO) 1938 cm^{-1}). Warming the green solution to −65 °C before either the Et_3N or the THF was added left a red solution having an IR spectrum identical with that obtained from warming the green solution in the absence of Et_3N (ν(CO) 2078, 2030 cm^{-1}).

The protonation of **10** (38 mg, 0.20 mmol) in cold (−78 °C) methylene chloride solution (3 mL) was repeated by using 1 equiv of $HBF_4{\cdot}OMe_2$. A layer of ether (5 mL) was added to the resulting green solution keeping the level of the ether below that of the dry ice–acetone cooling bath. After standing 0.5 h, the mixture was stirred and a green solid immediately was precipitated. Solvent was decanted by using a double-tipped stainless-steel needle, the remaining green solid was vacuum dried briefly (1 h, −78 °C), and cold CH_2Cl_2 (3 mL) then was added. The green residue was insoluble at −78 °C and at room temperature.

Preparation of $(C_5H_5)(CO)Fe(Ph_2PCH_2CH_2PPh_2)^+BF_4{}^-$ (11). A CH_2Cl_2 solution (3 mL) containing 38 mg (0.2 mmol) of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) was cooled to −78 °C and treated with 1 equiv of HBF_4·ether solution. The resulting dark green solution was reacted with $Ph_2PCH_2CH_2PPh_2$ (86 mg, 0.22 mmol). No color change was evident after 10 min, but IR spectral monitoring indicated quantitative formation of $(C_5H_5)(CO)Fe(Ph_2PCH_2CH_2PPh_2)^+BF_4{}^-$ (**11**). The solution was warmed to room temperature, and the product was precipitated with ether (10 mL). The yellow-green solid was centrifuged and dried under vacuum affording 110 mg (87% yield) of spectroscopically pure **11**:[18] IR (CH_2Cl_2) 1980 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.40–8.22 (m, 20 H, PPh_3), 5.09 (s, 5 H, (C_5H_5)), 3.01 (m, 4 H, $-CH_2-$).

The protonation of **10** (38 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) was repeated at various temperatures, and 1.1 equiv (86 mg, 0.22 mmol) of $Ph_2PCH_2CH_2PPh_2$ was added immediately. Yields of $(C_5H_5)(CO)Fe(Ph_2PCH_2CH_2PPh_2)^+BF_4{}^-$ (**11**) were ascertained by IR spectroscopy using a Beer's law plot of the ν(CO) absorption for **11**: −78 °C (87% yield), −65 °C (22% yield), 0 °C (10%), and +22 °C (0%).

Preparation of $(C_5H_5)(CO)Fe(NCCH_3)_2{}^+BF_4{}^-$ (12). A CH_2Cl_2 solution (3 mL) containing 38 mg (0.20 mmol) of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) was cooled to −78 °C and treated with 1 equiv of HBF_4 solution. To the resulting dark green solution was added CH_3CN (3 mL). A yellow-brown solution was formed within 10 min, and IR spectral monitoring indicated that $(C_5H_5)(CO)Fe(NCCH_3)_2{}^+BF_4{}^-$ (**12**) had formed as the only organometallic species. The solution was warmed to room temperature, and the product was precipitated with ether (40 mL). A yellow-brown solid was isolated by centrifugation and dried under vacuum affording 220 mg (69% yield) of pure **12**: IR (CH_2Cl_2) 2015 cm^{-1}; NMR (CD_3NO_2) δ 4.91 (s, 5, (C_5H_5)), 2.37 (s, 6, CH_3). Anal. Calcd for $C_{10}H_{11}N_2OFeBF_4$: C, 37.79; H, 3.17; N, 8.81. Found: C, 37.13; H, 3.38; N, 8.55.

Both $(C_5H_5)(CO)Fe(NCCH_3)_2{}^+BF_4{}^-$ and $(C_5H_5)(CO)Fe(NCCH_3)_2{}^+PF_6{}^-$ were prepared independently.[19] A yellow solution containing 3.00 g (10.3 mmol) of $(C_5H_5)Fe(CO)_3{}^+BF_4{}^-$ in 250 mL of $NCCH_3$ was photolyzed by using a Hanovia 450-W medium-pressure mercury vapor lamp for 1 h at 0 °C while the solution was purged with N_2. IR spectral monitoring indicated formation of $(C_5H_5)(CO)Fe(NCCH_3)_2{}^+BF_4{}^-$ (**12**). The resulting dark yellow brown solution was concentrated to about 50 mL, and the product was precipitated with ether (150 mL). A dark yellow-brown precipitate was filtered, recrystallized from CH_2Cl_2/Et_2O, and dried under vacuum affording a golden yellow solid, 2.65 g (81% yield) of spectroscopically pure **12**.

$(C_5H_5)(CO)Fe(NCCH_3)_2{}^+PF_6{}^-$ was prepared by using the same procedure to afford a yellow-gold solid, 1.00 g (74% yield) of spectroscopically pure $(C_5H_5)(CO)Fe(NCCH_3)_2{}^+PF_6{}^-$:[19] IR ($CH_2Cl_2$) 2005 cm^{-1}, ^1H NMR (CD_3NO_2) δ 4.91 (s, 5, (C_5H_5)), 2.38 (s, 6, CH_3).

Reaction of $(C_5H_5)(CO)Fe(OEt_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4{}^-$ (8) with $P(OPh)_3$. A CH_2Cl_2 solution (15 mL) containing 190 mg (1.0 mmol) of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) was cooled to −78 °C and treated with 1 equiv of $HBF_4{\cdot}Et_2O$ solution. $P(OPh)_3$ (354 mg, 1.14 mmol) was added giving a yellow-brown solution within 10 min, and IR spectral monitoring established that $(C_5H_5)(CO)Fe(\eta^2\text{-}CH_2{=}CHCH_3)P(OPh)_3{}^+BF_4{}^-$ (**13**)[20] (ν(CO) 2010 cm^{-1}) had formed. The solution was transferred to a cold (−78 °C) ether–hexane solution (50 mL–20 mL), which was stirred vigorously as a yellow-tan solid precipitated. The mixture was warmed to room temperature, and the solid was filtered and dried under N_2. The product was recrystallized from CH_2Cl_2–Et_2O at room temperature affording an air-stable yellow solid, 190 mg (32% yield), of spectroscopically pure **13**:[20] IR (CH_2Cl_2) 2010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57–7.10 (mult, 15 H, $P(OPh)_3$), 5.20 (mult, 2 H, CH=), 4.82, 4.78 [10 H, s, (C_5H_5) (both diastereomers)], 4.03 (mult, 2 H, (E)-$CH_2{=}CHCH_3$), 2.94 (mult, 2 H, (Z)-$CH_2{=}CHCH_3$), 1.95 (d, 3 H, J = 6.03 Hz, CH_3), 1.80 (d, 3 H, J = 6.03 Hz, CH_3), both diastereoisomers.

Preparation of $(C_5H_5)(CO)Fe(P(OPh)_3)_2{}^+BF_4{}^-$ (14). A CH_2Cl_2 solution (10 mL) containing 127 mg (0.67 mmol) of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) was cooled to −78 °C and converted to $(C_5H_5)(CO)Fe(OEt_2)(CH_2{=}CHCH_3)^+BF_4{}^-$. The dark green solution was treated with $P(OPh)_3$ (0.35 mL, 1.34 mmol). IR

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(13) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

(14) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 989. Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854.

(15) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918.

(16) Reger, D. L.; Fauth, D. J.; Dukes, M. D. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 151.

(17) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794.

(18) (a) Green, M. L. H.; Whiteley, R. *J. Chem. Soc. A* **1971**, 1943. Balavoine, G.; Green, M. L. H.; Sauvage, J. P. *J. Organomet. Chem.* **1977**, *128*, 247. (b) Brown, M. L.; Cramer, J. L.; Ferguson, J. A.; Meyer, T. J.; Winterton, N. *J. Am. Chem. Soc.* **1972**, *94*, 8707. (c) Haines, R. J.; du Preez, A. L. *Inorg. Chem.* **1972**, *11*, 330. (d) Sellman, D.; Kleinschmidt, E. *J. Organomet. Chem.* **1977**, *140*, 211.

(19) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417.

(20) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

spectral monitoring of the yellow-brown solution indicated formation of $(C_5H_5)(CO)Fe(\eta^2\text{-}CH_2{=}CHCH_3)P(OPh)_3{}^+BF_4{}^-$ (**13**): ν(CO) 2010. The solution was warmed to room temperature and then refluxed for 10 h, with no change in the IR spectrum. The resulting green solution was added to Et_2O (50 mL) at −78 °C, and a light green solid was formed. The mixture was warmed to room temperature, the solvent was removed by a double-ended needle, and the resulting greenish solid was dried under vacuum affording 257 mg (45% yield) of spectroscopically pure $Cp(CO)Fe[P(OPh)_3]_2{}^+BF_4{}^-$ (**14**):[3e] IR (CH_2Cl_2) 2010 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.23–7.52 (mult, 30 H, $P(OPh_3)$), 4.89 (s, 5 H, C_5H_5).

Reaction of $(C_5H_5)(CO)Fe(OEt_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$ (8) with $(C_5H_5)_2WH_2$. A CH_2Cl_2 solution (7.5 mL) containing 95 mg (0.5 mmol) of $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) was converted to $(C_5H_5)(CO)Fe(OEt_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$ (**8**) at −78 °C. Then 5% excess $(C_5H_5)(CO)Fe(\eta^3\text{-}C_3H_5)$ (**10**) was added to the solution. Treating the resulting dark green solution with $(C_5H_5)_2WH_2$, (158 mg, 0.5 mmol) did not change the color (10 min), but IR spectral monitoring indicated only the presence of **10** (ν(CO) 1938 cm^{-1}). The solution was warmed to room temperature. A blue-gray solid was precipitated with ether, centrifuged, and dried under N_2 affording 75 mg (37% yield) of spectroscopically pure $(C_5H_5)_2WH_3{}^+BF_4{}^-$:[14] ^1H NMR (acetone-d_6) δ 5.86 (s, 10 H (C_5H_5)), −6.03 (t, 1 H), −6.33 (d, 2 H).

Reaction of $(C_5H_5)(CO)Fe(OEt_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$ (8) with $(C_5H_5)(CO)_2FeCOCH_3$. A cold (−78 °C) CH_2Cl_2 solution (3 mL) containing (0.20 mmol) $(C_5H_5)(CO)Fe(OEt_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$ (**8**) (0.20 mmol) was treated with $(C_5H_5)(CO)_2FeCOCH_3$ (44 mg, 0.2 mmol). The solution gradually turned dark red as it warmed to room temperature. IR spectral monitoring indicated the presence of $(C_5H_5)(CO)_2FeCOCH_3$ (ν(CO) 2019, 1910, 1645 cm^{-1}) and the bimetallic product $(C_5H_5)(CO)_2Fe{-}C(CH_3)O{-}Fe(CO)_2(C_5H_5)^+BF_4^-$ (**15a**) (ν(CO) 2063, 2042, 2019, 1989 cm^{-1}). This bimetallic product was precipitated with ether (10 mL), and the red-brown solid was centrifuged and dried under a stream of N_2 affording 28 mg (29%) of spectroscopically pure **15a**.[21]

$(C_5H_5)(CO)Fe(OEt_2)(\eta^2\text{-}CH_2CHCH_3)^+BF_4^-$ (**8**) also was treated with $(C_5H_5)(CO)(PPh_3)FeCOCH_3$. The product was isolated following the same procedure to give 37 mg (25% yield) of spectroscopically pure $(C_5H_5)(CO)(PPh_3)Fe{-}C(CH_3)O{-}Fe(CO)_2(C_5H_5)^+BF_4$ (**15b**)[21] as a red-purple solid.

Preparation of $(C_5H_5)(CO)_2Fe(OMe_2)^+BF_4^-$ (2a). A yellow CH_2Cl_2 solution (5 mL) containing $(C_5H_5)(CO)_2FeCH_3$ (576 mg, 3.0 mmol) was cooled to −30 °C and was treated with 0.3 mL (3.0 mmol) of $HBF_4{\cdot}OMe_2$. Immediate gas evolution (presumably CH_4) was evident. The burgundy solution was added quickly via double-tipped stainless-steel transfer needle to 50 mL of precooled ether (−78 °C). A dark red solid was rapidly precipitated. Solvent was decanted from the cold mixture using a transfer needle fitted with a sintered glass frit. The remaining solid was washed twice with cold ether (−78 °C), and the solvent was decanted. Solvent was removed under vacuum (10^{-2} mm, 1 h). The resulting air- and moisture-sensitive red solid corresponded to $FpOMe_2{}^+BF_4{}^-$ (**2a**) and its degradation products: IR (CH_2Cl_2) 2079, 2038 cm^{-1}; ^1H NMR ($CDCl_3$, −55 °C) δ 5.26 (s, Cp), 3.84 (s, OMe_2).

A number of other weaker singlets were evident in the Cp region (δ 5.4–5.25) as well as a singlet for free Me_2O at δ 3.25. The latter absorptions gradually increased in intensity at the expense of the absorptions assigned to **2a**. For example, the ratio of coordinated to free Me_2O increased from 1:1.6 (20 min) to 1:4 (60 min) at −55 °C. (No absorptions for diethyl ether were detected.) This degradation of **2a** was accelerated greatly at room temperature.

Protonation of FpMe using $HBF_4{\cdot}OMe_2$ at −55 °C also was monitored by ^{19}F NMR spectroscopy in CH_2Cl_2 solution. Small amounts of $Fp{-}FBF_3$ (**3**) were detected initially: δ −154.6 (d, J = 89.5 Hz), −167.7 (q, J = 91.8 Hz). Within minutes, only the singlet at δ −149, signifying ionic BF_4^-, was detected in this burgundy solution.

Preparation of $(C_5H_5)(CO)_2Fe(NCCH_3)^+BF_4^-$ (2c). A CH_2Cl_2 solution (30 mL) containing $(C_5H_5)(CO)_2FeCH_3$ (1.00 g, 5.20 mmol) was treated with $HBF_4{\cdot}OMe_2$ (0.52 mL, 5.2 mmol) at room temperature. The deep burgundy solution was treated with acetonitrile (10 mL) within 3 min. After sitting 1 h, the resulting yellow-brown solution was diluted with ether (50 mL), and the yellow-brown precipitate was filtered, washed with ether, and dried under vacuum to yield 1.27 g (72%) of spectroscopically pure $Fp(NCCH_3)^+BF_4^-$ (**2c**): IR (CH_2Cl_2) 2079, 2038 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.47 (s, Cp), 2.36 (s, CH_3CN).

A slight excess of cold 4:1 $CDCl_3{-}CH_3CN$ solution was added to a NMR tube containing a dark red $CDCl_3$ solution of $Fp{\cdot}OMe_2{}^+BF_4{}^-$ (2a), maintained at −55 °C. The solution gradually turned yellow. The virtually quantitative transformation of **2a** to $Fp(CH_3CN)^+BF_4^-$ (**2c**) was monitored by recording the ^1H NMR spectra (−55 °C) over 1 h: δ 5.26 (s, Cp) and 3.84 (s, Me_2O) for **2a** and δ 5.37 (s, Cp) and 2.35 (s, CH_3CN) for **2c**; singlets at δ 2.00 and 3.25 also were evident for noncoordinated CH_3CN and Me_2O, respectively.

Preparation of $Cp(CO)_2Fe{-}F{-}BF_3$ for ^{19}F NMR Spectral Study. $AgBF_4$ (62 mg, 0.32 mmol) and $Cp(CO)_2FeI$ (91 mg, 0.30 mmol) were transferred to a flask and dried in the dark under vacuum for $1^1/_2$ h to remove any absorbed water. Dry CH_2Cl_2 (15 mL) was added and the solution was stirred in the dark at 22 °C for 0.5 h, then cooled to −80 °C, and stirred for 0.8 h. The resulting suspension was allowed to settle. A portion (1.5 mL) of the red suspension was removed by syringe and filtered through a glass wool plug into a 5-mm NMR tube. The NMR tube had been flame-dried and cooled in a stream of nitrogen prior to use. The ^{19}F NMR was recorded at −90 °C. ^{19}F NMR (CH_2Cl_2, −90 °C): δ −149.8 (s, BF_4), −154.7 (d, ^2J = 89.5 Hz, $Fe{-}F{-}BF_3$), −167.8 (q, ^2J = 90.9 Hz, $Fe{-}F{-}BF_3$).

Preparation of $Cp(CO)_2Mo(\eta^2\text{-}CH_2CHCH_3)F{-}BF_3$ for ^{19}F NMR Spectral Study. A yellow solution of $Cp(CO)_2Mo(\eta^3\text{-}CH_2CHCH_2)$ (50 mg, 0.2 mmol) in 3 mL of CH_2Cl_2 was treated with 1 equiv of HBF_4·ether solution at room temperature. A dark red solution was formed immediately, and IR spectral monitoring indicated formation of $Cp(CO)_2Mo(\eta^2\text{-}CH_2CHCH_3)(F{-}BF_3)$: ν(CO) 2027, 1973 cm^{-1}. The red solution was transferred to a dry 5-mm NMR tube, and the ^{19}F NMR was recorded at −90 °C. ^{19}F NMR (CH_2Cl_2, −90 °C): minor isomer, −152.7 (d, ^2J = 88 Hz, $Mo{-}F{-}BF_3$), −284.0 (q, ^2J = 83 Hz, $Mo{-}F{-}BF_3$); major isomer, δ −153.3 (d, ^2J = 89 Hz, $Mo{-}F{-}BF_3$), −287.7 (q, ^2J = 89 Hz, $Mo{-}F{-}BF_3$).

Results and Discussion

Treating a methylene chloride solution (−75 °C) of the η^3-allyl complex $Cp(CO)Fe(CH_2CHCH_2)$ (**10**) with 1 equiv of HBF_4·etherate affords a deep green solution. Warming above −65 °C or otherwise attempting to transfer this solution inevitably affords a reddish brown suspension. Subsequent workup of these suspensions produced only insoluble, non-carbonyl-containing red solids. We assign structure **8** (eq 3) to the adduct **$10{\cdot}HBF_4{\cdot}OR_2$** present in the green solution; the presence of ligated η^2-propene and noncoordinated (ionic) fluoroborate on **8** follows from results of chemical derivatization and of ^{11}B and ^{19}F NMR spectral studies. Both acid etherates $HBF_4{\cdot}OMe_2$ and $HBF_4{\cdot}OEt_2$ were used interchangeably in this study with identical results.

A. Derivation of $(\eta^5\text{-}C_5H_5)(CO)Fe(OR_2)(\eta^2\text{-}CH_2{=}CHCH_3)^+BF_4^-$ (8). Protonation of **10** is reversible. One equivalent of triethylamine added to the green solution (−75 °C) immediately and quantitatively regenerates **10** as a pale yellow solution. The protonation of **10** is not reversed, however, if the green solution is warmed above −60 °C (resulting in a red-brown suspension) before adding the amine. Tetrahydrofuran (THF), α,α'-bipyridine, or Cp_2WH_2 also deprotonates **8** at −75 °C, with the latter base producing $Cp_2WH_3{}^+$.[14,22]

Other Lewis bases converted **8** to stable monocarbonyl, CpFe compounds $Cp(CO)FeL_1L_2{}^+BF_4{}^-$ (**9**). Treating the green solutions **8** at −75 °C with dppe produced the η^2-dppe

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[21] LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

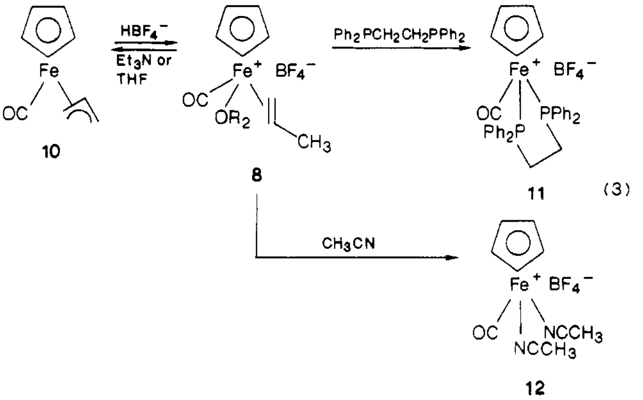
[22] Other organometallic Lewis acids react with Cp_2WH_2 and give bimetallic compounds containg double (μ-H) linkages: Albinati, A.; Togni, A.; Venanzi, L. M. *Organometallics* **1986**, *5*, 1785 and references cited.

Table I. ^{11}B NMR and ^{19}F NMR

compd in CH_2Cl_2	^{11}B,[a] ppm	^{19}F,[d] ppm
$HBF_4{\cdot}OEt_2$	0.12	−149, −153
$Cp(CO)_3Mo{-}F{-}BF_3$ (**4**)	−0.27	−154.3 (d, ^2J = 95.3 Hz)[e] −369.2 (q, ^2J = 96.4 Hz)
$Cp(CO)_2Mo(\eta^2\text{-}CH_2{=}CHCH_3)(F\text{-}BF_3)$ (**5**)	−0.32	cis product[f] −152.7 (d, ^2J = 88 Hz), −284.0 (q, ^2J = 83 Hz); trans product −153.3 (d, ^2J = 89 Hz), −287.7 (q, ^2J = 89 Hz)
$Cp(CO)_2Fe{-}F{-}BF_3$ (**3**)	−1.83[b]	−154.6 (d, ^2J = 89.5 Hz), −167.7 (q, ^2J = 91.8 Hz)
$Cp(CO)_2FeOMe_2^+BF_4^-$ (**2a**)		−149.9
$Cp(CO)_2Fe{-}THF^+BF_4^-$ (**2b**)	−1.05	−149.2
$Cp(CO)_2Fe(NCCH_3)^+BF_4^-$ (**2c**)	−0.95	
$Cp(CO)Fe(NCCH_3)_2^+BF_4^-$ (**12**)	−0.95	−149.8
$NBu_4^+BF_4^-$		−1.05
$Cp(CO)Fe(OMe_2)(\eta^2{-}CH_2{=}CHCH_3)^+BF_4^-$ (**8**)	−1.03[c]	−149.5[c]
$(C_6H_5)_3C^+BF_4^-$	−1.05	−149.0

[a] 2:1 CH_2Cl_2–$CDCl_3$ (−80 °C). [b] Mattson and Graham,[6d] $CDCl_3$ (−80 °C) δ −1.85. [c] Red solution at −55 °C: ^{11}B NMR δ −1.014; ^{19}F NMR δ −153.1. [d] CH_2Cl_2 (−80 °C). [e] Beck,[9b] CD_2Cl_2 (−80 °C), δ −156.3 (d, ^2J = 95 Hz), −371.5 (q, ^2J = 95 Hz). [f] Equilibration of cis and trans isomers is slow at −80 °C; trans is assumed to be in higher concentration.

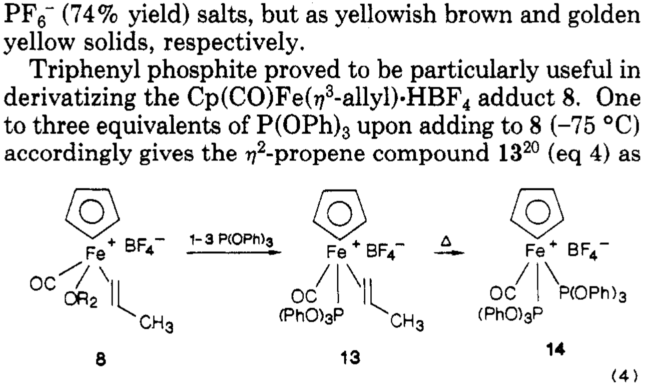
salt $Cp(CO)Fe(Ph_2PCH_2CH_2PPh_2)^+BF_4^-$[18] (**11**) in 87% yield (eq 3). This product, moreover, is not contaminated by the known η^1-dppe compound $Fp(Ph_2PCH_2CH_2PPh_2)^+$[18b,c] or its μ-dppe derivative $(Fp{-}Ph_2PCH_2CH_2PPh_2{-}Fp)^{2+}$.[6a,18c] Interestingly, 2 equiv of PPh_3 does not convert **8** to the known[6a,23] bis(phosphine) salt $Cp(CO)Fe(PPh_3)_2^+$; rather, several Cp- and PPh_3-containing organoiron compounds were detected in low concentration by ^{1}H NMR spectroscopy. Acetonitrile, when added in excess to **8**, cleanly afforded the bis(acetonitrile) adduct[19] **12** (69% yield) as a yellowish brown solid.



10 8 11 12 (3)

Compound **12**, in our hands, always resulted as a yellowish-brown solid, whereas Catheline and Astruc report[19] that photolysis of $CpFe(CO)_3^+PF_6^-$ in acetonitrile produces **12** (PF_6^-) as a red solid. We repeated their photolytic procedure and obtained **12** as its BF_4^- (81% yield) and PF_6^- (74% yield) salts, but as yellowish brown and golden yellow solids, respectively.

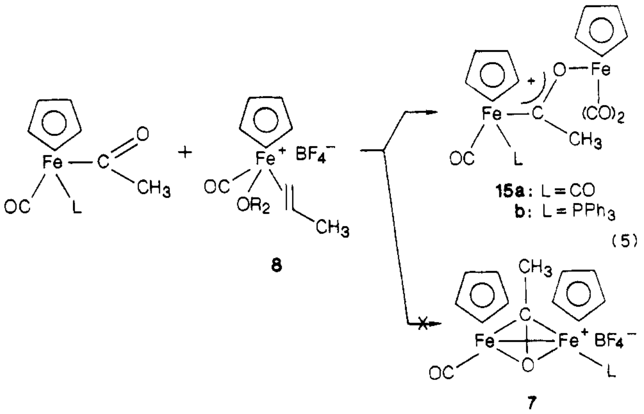
Triphenyl phosphite proved to be particularly useful in derivatizing the $Cp(CO)Fe(\eta^3\text{-allyl}){\cdot}HBF_4$ adduct **8**. One to three equivalents of $P(OPh)_3$ upon adding to **8** (−75 °C) accordingly gives the η^2-propene compound **13**[20] (eq 4) as a yellow solid in 32% yield. Excess phosphite does not react further with **13** at room temperature (12 h), although refluxing the CH_2Cl_2 solution for 10 h affords the bis(phosphite) complex **14**[3e] (45% yield).



8 13 14 (4)

Spectral data for the phosphite derivatives **13** and **14** match with that previously reported. Reger and Coleman[20] had prepared **13** as a similar mixture of diastereomers by binding propene to the in situ generated $Cp(CO)Fe[P(OPh)_3]^+BF_4^-$. Schuman[3e] had demonstrated that **14** results from treating $Cp(CO)Fe(SMe_2)_2^+BF_4^-$ with excess phosphite in refluxing 1,2-dichloroethane.

Attempts were made to use the two accessible coordination sites on the Lewis acid **8** in forming bimetallic μ-(η^2-C,O)-acetyl compounds **7** (eq 5). This approach parallels our successful preparation of the analogous molybdenum μ-(η^2-C,O)-acetyl $[Cp(CO)_2Mo]_2(CH_3CO)^+BF_4^-$ from **5**.[10] We found, however, that **8** reacts with either acetyl compound $Cp(CO)(L)FeCOCH_3$ (L = CO, PPh_3) to give only the known[21] bimetallic μ-(η^1-C,O)-acetyl complexes **15a**,**b** in low yields. No reaction occurred between methyl complexes $Cp(CO)_2Fe{-}CH_3$ or $Cp(CO)_3MoCH_3$ and **8**: only the red-brown insoluble decomposition residue from **8** and starting methyl complexes were recovered.



8 15a: L = CO b: L = PPh3 (5) 7

B. Structural Assignment of (η^5-C_5H_5)(CO)Fe(OR_2)(η^2-CH_2CHCH_3)$^+BF_4^-$ (8) and of (η^5-C_5H_5)$(CO)_2Fe[O(CH_3)_2]^+BF_4^-$ (2a). Plausible structures for the Lewis acid that results from protonation of the (η^3-allyl) iron complex **10** must, due to our derivatization results, retain both ligated η^2-propene and tetrafluoroborate. The tetrafluoroborate in principle can occur as covalently attached (η^1-F)-F–BF_3^- (e.g., on **6**) or as noncoordinated BF_4^-. Existence of ionic BF_4^-, in turn, is satisfied by having either coordinately unsaturated (16-electron) $Cp(CO)Fe(CH_2CHCH_3)^+BF_4^-$ or solvates involving ether (**8**) or methylene chloride (**9**, L_1 = η^2-propene, L_2 = CH_2Cl_2).

Results of our ^{11}B and ^{19}F NMR spectral studies on **8** and on related Lewis acids appear in Table I; ^{19}F NMR data, in particular, permit distinction between covalent and

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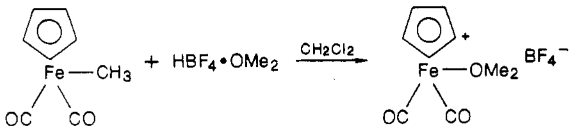
[23] Johnson, B. V.; Ouseph, P. J.; Hsieh, J. S.; Steinmetz, A. L.; Shade, J. E. *Inorg. Chem.* **1979**, *18*, 1796. Davies, S. G. *J. Organomet. Chem.* **1979**, *179*, C5.

ionic tetrafluoroborate. A double-quartet appearance for the M–F–BF_3 unit on **3**, **4**, and **5** signals the presence of coordinated (covalent) fluoroborate, whereas a singlet absorption near δ –150 for the remaining salts (including **8**) indicates noncoordinated BF_4^-. Our ^{19}F NMR spectral data for $Cp(CO)_3MoFBF_3$ (**4**) are in excellent agreement with similar data reported by Beck and co-workers.[9b]

The ^{11}B NMR chemical shifts for BF_4^- also indicate the extent of its coordination with a metal center. Values for ionic BF_4^-, including **8**, occur between δ –0.95 and δ –1.05, whereas the ^{11}B chemical shift for $FpFBF_3$ (**3**) is at δ –1.8. (This latter value is in excellent agreement with that reported by Graham.[6d]) We cannot account for either the magnitude or the direction of the ^{11}B NMR chemical shift for **3** vs noncoordinated BF_4^-. The covalent molybdenum fluoroborates **4** and **5**, for example, exhibit downfield shifts from that of ionic fluoroborate.

We favor structure **8** (with ligated propene and ionic BF_4^-), even though no direct evidence exists for coordinated ether. Attempts at getting definitive ^1H NMR spectra of (–78 °C) proved unsuccessful due to excessive line broadening. Certainly, ligating ether to this organometallic Lewis acid would be preferred over CH_2Cl_2. The related etherate $Cp(CO)_3W(OEt_2)^+PF_6^-$, for example, has been prepared in CH_2Cl_2 solution and fully characterized, although it also is very labile in solution.[9c] In order to further examine the high liability of CpFe(ether) complexes, we have prepared and studied $Cp(CO)_2Fe\cdot OMe_2^+BF_4^-$ (**2a**).

The synthesis of $Fp\cdot OMe_2^+BF_4^-$ (2a) (eq 6) is patterned after that for the stable tetrahydrofuran adduct $Fp\cdot THF^+BF_4^-$ (**2b**), except that excess dimethyl ether is not present. Treating a methylene chloride solution of FpMe between –30 and –78 °C with 1 equiv of $HBF\cdot OMe_2$ forms a deep burgundy solution within 5 min. Adding cold ether then precipitates a red salt to which we assign the structure **2a**. This salt is both extremely air- and moisture-sensitive and is much less stable thermally than the fully characterized THF adduct. Compound **2a** as a solid significantly degrades within a few hours when stored under vacuum at –20 °C: ^1H NMR spectra ($CDCl_3$, –55 °C) then showed five to six new singlets (30% relative intensity) in the Cp region δ 5.4–5.25.



(6)

2a

The high lability of $Fp\cdot OMe_2^+BF_4^-$ (**2a**) is especially evident in solution, with the results of ^1H NMR spectral monitoring of in situ generated **2a** proving instructive. Treating a yellow $CDCl_3$ solution of FpMe, maintained at –55 °C, with between 0.50 and 0.95 equiv of $HBF\cdot OMe_2$ affords a dark red solution. In addition to the ^1H NMR spectral absorptions (–55 °C) for residual FpMe (δ 4.67 and 0.14), singlets also appear for **2a** (δ 5.26 and 3.84 for the Cp and coordinated Me_2O, respectively) as well as for free Me_2O (δ 3.25). Over 90 min, absorptions for **2a** transform into a broad envelope of singlets in the Cp region (those at δ 5.40, 5.39, 5.38, and 5.36 being especially prominent) and the sharp singlet for free Me_2O. (The ratio of bound to unbound Me_2O changes from 1:1.6 after 20 min to 1:3 after 90 min.) Adding acetonitrile and warming to room temperature afford less than 10% $Fp\cdot NCCH_3^+BF_4^-$ (**2c**) as ascertained by ^1H NMR spectroscopy.

Similar protonation of FpMe at room temperature followed by immediate cooling of the red solution to –55 °C produces NMR spectra analogous to those obtained after protonating and then sitting at –55 °C for 90 min.

Protonation of $FpCH_3$ at –55 °C followed by rapidly recording of the ^1H NMR spectrum at room temperature gives prominent absorptions at δ 5.26 and 3.59. These are assigned to the Cp and exchanged averaged Me_2O groups, respectively, of **2a**. Recooling of this solution to –55 °C leaves the Cp resonance unchanged, but the δ 3.59 absorption transforms into two singlets for ligated and free Me_2O at δ 3.84 and 3.25, respectively. Temperature dependence of these NMR spectra is reversible limited, of course, by the continuing degradation of **2a**.

Thermal sensitivity of **2a** in solution does not preclude its usefulness in organometallic synthesis as a source of Fp^+ (**1**). Having the displacing ligand present during protonation of FpMe or adding it shortly thereafter efficiently traps this organometallic Lewis acid. We accordingly found it convenient to prepare the useful organoiron reagents $Fp(THF)^+BF_4^-$ (**2b**) and FpOC(O)R (R = H, CH_3) using this procedure.[7b] In the present study, we report preparing $Fp(NCCH_3)^+BF_4^-$ (**2c**)[6a,b,7b] in moderate yield by displacing dimethyl ether from **2a**: adding the acetonitrile immediately after forming **2a**, minimizes its decomposition.

Conclusions

Protonation of the η^3-allyl complex $Cp(CO)Fe(CH_2CHCH_2)$ (**10**) with $HBF_4\cdot OR_2$ (R = Me, Et) affords the etherate compound $Cp(CO)Fe(OR_2)(CH_2{=}CHCH_3)^+BF_4^-$ (**8**) retaining η^2-propene and ionic BF_4^-. The presence of BF_4^- and ligated ether contrasts the established structure of the more stable $Cp(CO)_2Mo(CH{=}CHCH_3)(FBF_3)$ (**5**), which results from protonation under the same conditions of the η^3-allyl complex $Cp(CO)_2Mo(CH_2CHCH_2)$. Lewis acid precursor **8**, however, is quite unstable in CH_2Cl_2 solution above –65 °C, although a variety of disubstituted complexes $Cp(CO)Fe(L_1)(L_2)^+BF_4^-$ (**9**) are prepared readily by adding the appropriate Lewis base at lower temperatures. The synthetic utility of this reaction, however, is limited by the tendency of some Lewis bases (e.g., THF) to deprotonate **8** back to the starting η^3-allyl compound **10**.

Another labile etherate compound $Cp(CO)_2Fe(OMe_2)^+BF_4^-$ (**2a**) results from protonation of $Cp(CO)_2FeCH_3$ with $HBF_4\cdot OMe_2$ in CH_2Cl_2 solution. This Lewis acid precursor degrades slowly even at –55 °C, although adding acetonitrile efficiently intercepts $Cp(CO)_2Fe^+$ (**1**) and gives the adduct $Cp(CO)_2Fe(NCCH_3)^+BF_4^-$ (**2c**).

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Registry No. **2a**, 115162-07-7; **2b**, 63313-71-3; **2c**, 32824-71-8; **3**, 76391-69-0; **4**, 68868-78-0; *cis*-**5**, 95739-92-7; *trans*-**5**, 95839-27-3; **8** (R = Me), 115162-05-5; **8** (R = Et), 115162-09-9; **10**, 52326-25-7; **11**, 35004-56-9; **12**, 115162-02-2; **13** (isomer 1), 71425-14-4; **13** (isomer 2), 71359-43-8; **14**, 103473-75-2; **15a**, 87794-75-0; **15b**, 115162-06-6; $(C_5H_5)Fe(CO)_3^+BF_4^-$, 12244-69-8; $(C_5H_5)Fe(CO)_3^+PF_6^-$, 38834-26-3; $(C_5H_5)(CO)Fe(NCCH_3)_2^+PF_6^-$, 86991-78-8; $(C_5H_5)_2WH_2$, 1271-33-6; $(C_5H_5)_2WH_3^+BF_4^-$, 115162-03-3; $(C_5H_5)(CO)_2FeCOCH_3$, 12108-22-4; $(C_5H_5)(CO)(PPh_3)FeCOCH_3$, 12101-02-9; $(C_5H_5)(CO)_2FeCH_3$, 12080-06-7; $(C_5H_5)(CO)_2FeI$, 12078-28-3; $(C_5H_5)(CO)_2Mo(\eta^3\text{-}CH_2CHCH_2)$, 12128-87-9; $HBF_4\cdot OEt_2$, 67969-82-8; $NBu_4^+BF_4^-$, 429-42-5; $(C_6H_5)_3C^+BF_4^-$, 341-02-6.