

Piano-Stool (Pentamethylcyclopentadienyl)iron Complexes: Syntheses and Simple Coordination Chemistry

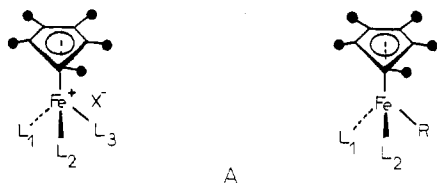
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$(Fp'CO)^+PF_6^-$, **3e** [$Fp' = (\eta^5-C_5Me_5)Fe(CO)_2$], is synthesized by reaction of $Fp'Br$ with CO (40 atm) and $AlCl_3$ or by reaction of Fp'_2 with $Cp_2Fe^+PF_6^-$ in THF under CO (1 atm). Oxidation of Fp'_2 with $Cp_2Fe^+PF_6^-$ in various coordinating solvents S (THF, acetone, acetonitrile, pyridine) gives $(Fp'S)^+PF_6^-$ (**3a-d**) in high yields. Reaction of $(Fp'/THF)^+PF_6^-$, **3a**, with various ligands L (PPh_3 , $P(OPh)_3$, CO) gives $(Fp'L)^+PF_6^-$, **3e-g**, in high yields; the reaction fails with olefins. **3a** also gives $Fp'H$, **5**, with $NaBH_4$ and $Fp'SC(S)NMe_2$, **6a**, with NaS_2CNMe_2 , but **6a** is obtained in better yield from **3e**. Bimetallic complexes $[Fp'SC(NEt_2)_2S \rightarrow Fp']^+PF_6^-$, **6c**, and $[CpFe(\eta^6-C_6Me_5CH_2)Fp']^+PF_6^-$, **7**, are also obtained by reaction of **3a** with $Fp'SC(S)NEt_2$ and $Cp(\eta^5-C_6Me_5CH_2)Fe$, respectively. Photolysis of **3e** or $(Fp'NCMe)^+PF_6^-$, **3c**, in CH_3CN gives a 80% yield of the thermally stable, air-sensitive complex $[Cp'Fe(NCMe)_3]^+PF_6^-$, **9**, as deep purple crystals. Without degassing, this photolytic reaction gives dark red $[Cp'Fe(NCMe)_2(CO)]^+PF_6^-$, **10**, also obtained from **9** under 1 atm of CO at 20 °C. **9** also reacts with PPh_3 to give $[Cp'Fe(NCMe)_2(PPh_3)]^+PF_6^-$, **11**, with dppe to give $[Cp'Fe(NCMe)(\eta^2-dppe)]^+PF_6^-$, **12**, and with cyclooctatetraene (COT) to give $[Cp'Fe(\eta^6-COT)]^+PF_6^-$, **13**. The reaction of CO with **11** and **12** gives respectively $[Cp'Fe(CO)_2(PPh_3)]^+PF_6^-$, **3f**, also obtained from **3e** and PPh_3 in refluxing acetone, and $[Cp'Fe(CO)(\eta^2-dppe)]^+PF_6^-$, **15**. Fp'^-K^+ , **16a**, obtained from Fp'_2 and K mirror, gives $Fp'CH_3$, **17**, upon alkylation with CH_3I and Fe'^-Na^+ , **16b**, obtained from Fp'_2 and Na/Hg, gives $Fp'CH_2OCH_3$, **18**, upon alkylation with $ClCH_2OCH_3$.

Whereas the cyclopentadienyliron dicarbonyl (Fp) series is one of the most widely studied organometallic families,¹ pentamethylcyclopentadienyl ($\eta^5-C_5Me_5 = Cp'$) homologues A are nearly unknown. Since this ligand has proved useful for the organometallic chemistry of many other transition metals, we undertook synthetic studies of the series of complexes $[Cp'Fe(L_1)(L_2)(L_3)]^+$ and $Cp'Fe(L_1)(L_2)R$.



Iron sandwich compounds are known with the C_5Me_5 ligand: decamethylferrocene was reported by Bercaw together with a very useful synthesis of pentamethylcyclopentadiene² and $[Cp'Fe(CO)_2]$ (Fp'_2) was reported by King.³ Sometime ago, we synthesized $Fp'Br$,^{4a} a useful precursor to $[Cp'(\eta^6\text{-arene})Fe]^+$ sandwiches.⁴ In preliminary communications, we reported several routes to pi-

ano-stool Fp' complexes $(Fp'CO)^+$,^{5a} Fp'^-K^+ ,^{5a} and $(Cp'FeL_1L_2L_3)^+$ ^{5b} that we describe in detail here. In studying the basic chemistry of these complexes, we were ultimately aiming at the reduction of coordinated CO^{6a} and CO_2 ,^{6b} thus stabilizing labile fragments such as formyl, hydroxymethyl, methylene, and alkylidenes and paramagnetic (Fe^I and Fe^{II}) complexes. These studies will be reported fully in subsequent articles.

A report on the "preparation and hydride reduction of the electron-rich cations $(Fp'L)^+$ ($L = CO, PPh_3, PMe_3$) and $[Cp'Fe(dppe)CO]^+$ " by Davies^{5c} appeared recently, but no characterization of these cations was given.

Results and Discussion

1. Synthesis of $[Fp'(CO)]^+$ Using a Fischer-Type Ligand-Exchange Reaction. The dimer Fp'_2 , **1**, is the starting point of all the syntheses. King's preparation ($Fe(CO)_5 + Cp'H$, 2,2,5-trimethylhexane, reflux, 48% yield on a 5-mmol scale)³ was slightly improved by using xylenes as solvent (reflux, 2 days). On a 180-mmol scale, a 65% yield was obtained after purification by filtration on alumina. $Fp'Br$, obtained by the known procedure from Fp'_2 and Br_2 ,^{4a} is useful for the preparation of $(Fp'CO)^+PF_6^-$, **3e**, by a Fischer-type reaction⁷ using $AlCl_3$ and 40 atm of CO^{5a} (eq 1). This procedure was first used for the synthesis of the parent complex $(FpCO)^+PF_6^-$, **2a**.⁷ Whereas the latter complex is also available inter alia by reaction between ferrocene and CO,^{7c} this route cannot be applied in the permethylated series because decamethylferrocene is inert toward the ligand-exchange reaction⁸ (eq 2).

The synthesis of **3e** proceeds in 67% yield using 40 atm of CO at 60 °C in heptane. This yield is higher than those obtained in the preparation of $[Cp'(\eta^6\text{-arene})Fe]^+PF_6^-$ complexes^{4a} because the three CO ligands are less bulky

(1) For some leading references, see: (a) Green, M. L. H. "Organometallic Compounds"; Methuen: London, 1968; Vol. II. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Transition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. (c) King, R. B. In "The organometallic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New-York, 1981. (d) Wilkinson, G., Stone, F. G. A., Abel, W. E., Eds. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford, 1982; Vols. IV and VIII. (e) Rosenblum, M. *Acc. Chem. Res.* 1974, 7, 122. (f) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* 1981, 206, 77. (g) King, R. B. *Organomet. Synth.* 1965, 1, 151.

(2) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* 1977, 136, 1 and references therein.

(3) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* 1967, 8, 287. (b) For a valuable review of King's work using Cp' , see: King, R. B. *Coord. Chem. Rev.* 1976, 20, 155.

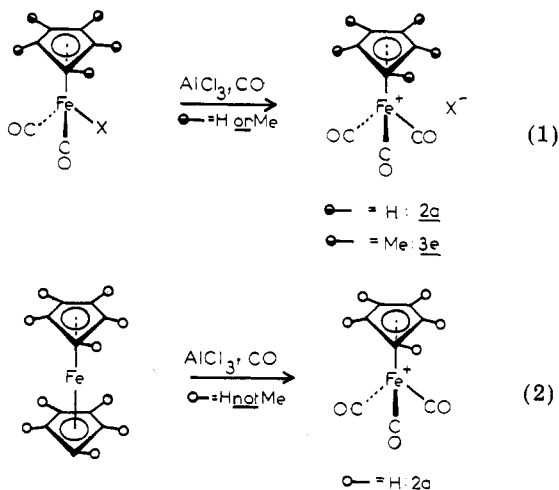
(4) (a) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* 1981, 103, 758. (b) Astruc, D.; Hamon, J.-R.; Román, E.; Michaud, P. *Ibid.* 1981, 103, 7502.

(5) (a) Catheline, D.; Astruc, D. *J. Organomet. Chem.* 1982, 226, C52. (b) Catheline, D.; Astruc, D. *Ibid.* 1983, 248, C9. (c) Davies, S. G.; Simpson, S. J.; Thomas, S. E. *Ibid.* 1983, 254, C29.

(6) (a) Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* 1983, 430. (b) Lapinte, C.; Astruc, D., work in progress.

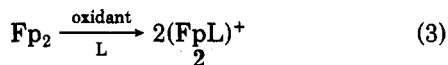
(7) (a) Fischer, E. O.; Fichtel, K. *Chem. Ber.* 1961, 3172. (b) Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* 1971, 3172. (c) Román, E.; Astruc, D. *Inorg. Chem.* 1979, 11, 3284.

(8) (a) Bublitz, D. E. *Can. J. Chem.* 1964, 42, 2381. (b) Astruc, D. *Tetrahedron* 1983, 39 (Report No. 157), 4027.



than an arene, especially a peralkylated one. The pale yellow complex **3e** is less fragile hydrolytically than its Cp homologue **2a**, and, in particular, its isolation after hydrolysis does not require the caution necessary for the preparation of **2a**.

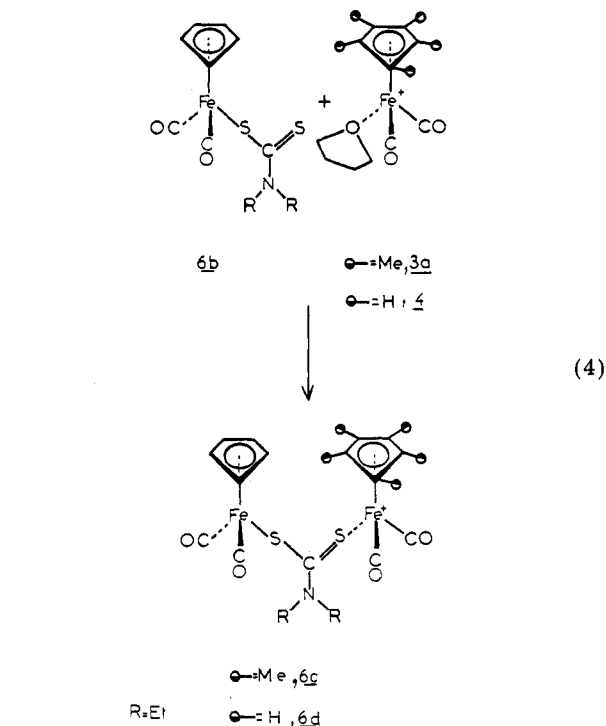
2. Syntheses of (Fp'L)⁺ by Oxidative Cleavage of Fp'₂ Using Ferricinium. **3e** is a key compound, and we have shown that its reduction by main-group and transition-metal hydrides leads to the hydroxymethyl and methyl complexes^{6a} whereas the reduction of **2a** gives CpFe(CO)₂H.⁹ Thus we have been looking for other simple syntheses of **3e**, in particular those involving the use of CO at atmospheric pressure. The oxidative cleavage of the Fe-Fe bond in Fp₂ has been used to synthesize the cationic complexes (Fp'L)⁺. AgBF₄,¹⁰ FeCl₃,¹¹ O₂/HBF₄,¹² Ph₃C⁺,¹³ and electrochemical oxidations¹⁴ have all been used (eq 3).



We found that ferricinium is a very efficient and clean reagent to effect the transformation of eq 3 with Fp'₂ as well as with Fp₂. In practice, this oxidation proceeds at room temperature in various coordinating solvents S (THF,¹⁵ acetone, acetonitrile, and pyridine) to give stable complexes (Fp'S)⁺PF₆⁻, **3a-d** in quantitative crude yields. (Fp'THF)⁺PF₆⁻, **3a**, is an excellent intermediate for the preparation of the complexes (Fp'L)⁺PF₆⁻, **3e-g** (Scheme I). The general method consists of adding an excess (2/1) of L to a THF solution of **3a** without isolating **3a**. In some instances, the cleaner route is to isolate **3a** and to effect the ligand substitution in CH₂Cl₂ in order to solubilize the reactants. CO, PPh₃, and P(OPh)₃ give high yields of complexes (Fp'L)⁺PF₆⁻, **3e-g**, in this way. In particular, this method affords an excellent route to (Fp'CO)⁺PF₆⁻, **3e**, under ambient conditions.

3. Bimetallic Complexes and Anionic Ligands. The free sulfur atom of monodentate Fe^{II} dithiocarbamates

(dtc)¹⁶ can serve as the L ligand. The reaction between **3a** and Fp[η¹-SC(S)NET₂],¹⁷ **6b**, gives the binuclear complex **6c** in a 80% yield as red plates (eq 4). In **6c**, the dtc ligand acts as a dissymmetric bridging ligand, one sulfur being a one-electron ligand and the other one a two-electron donor.



This chemistry works for FpL⁺ as well as for Fp'L⁺. For instance, (FpCO)⁺PF₆⁻ can be made conveniently by using

(16) For the reactivity of the free sulfur atom in monodentate dithiocarbamates, see: (a) Román, E.; Catheline, D.; Astruc, D.; Batail, P.; Ouahab, L.; Varret, F. *J. Chem. Soc., Chem. Commun.* 1982, 129. (b) Catheline, D.; Román, E.; Astruc, D., submitted for publication in *Inorg. Chem.*

(17) (a) O'Connor, Ch.; Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. A* 1969, 84. (b) Román, E.; Catheline, D.; Astruc, D. *J. Organomet. Chem.* 1982, 236, 229.

(9) Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* 1961, 3172.

(10) (a) Giering, W. P.; Rosenblum, M. *J. Chem. Soc., Chem. Commun.* 1971, 441. (b) Williams, W. F.; Lawlor, F. J. *J. Chem. Soc. D* 1973, 1329.

(11) Johnson, E. C.; Meyer, T. J.; Winterton, N. *Inorg. Chem.* 1971, 10, 1673.

(12) Dombeck, B. D.; Angelici, R. J. *Inorg. Chim. Acta* 1973, 7, 345.

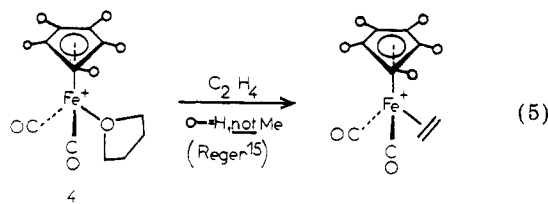
(13) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* 1976, 114, 307.

(14) [Fp(acetone)]⁺ was characterized in solution. Ferguson, J. A.; Meyer, T. J. *Inorg. Chem.* 1971, 10, 1025.

(15) (a) [Fp(THF)]⁺BF₄⁻, prepared by Reger from FpI and AgBF₄ in THF, is a useful precursor to (FpL)⁺ including [Fp(olefin)]⁺ as shown by these authors: Reger, D. L.; Coleman, C. J. *Organomet. Chem.* 1977, 131, 153. (b) Reger, D. L.; Coleman, C. J.; McElligot, P. J. *Ibid.* 1979, 171, 73.

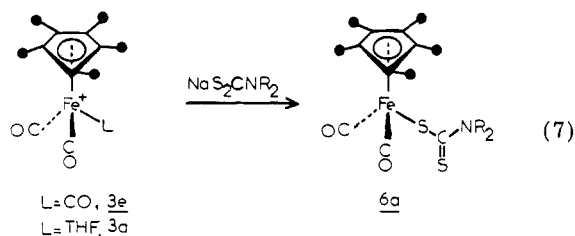
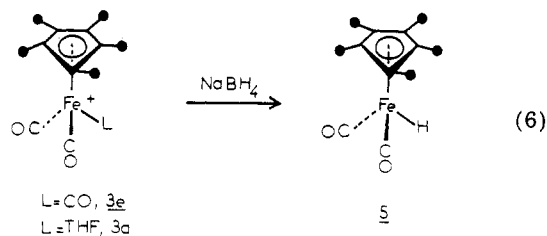
this route, as can $[\text{FpSC}(\text{NEt}_2)\text{S} \rightarrow \text{Fp}]^+\text{PF}_6^-$. The cyclopentadienyls display distinct NMR parameters.

While $(\text{FpTHF})^+\text{PF}_6^-$, **4**, reacts with olefins,¹⁵ giving $[\text{Fp}(\text{olefin})]^+$ (eq 5), only decomposition to **3e** is observed in the case of **3a** under forcing conditions with ethylene (eq 5, heating or pressure of ethylene or in the presence of BF_3 ,¹⁵ in various solvents). This failure can be com-



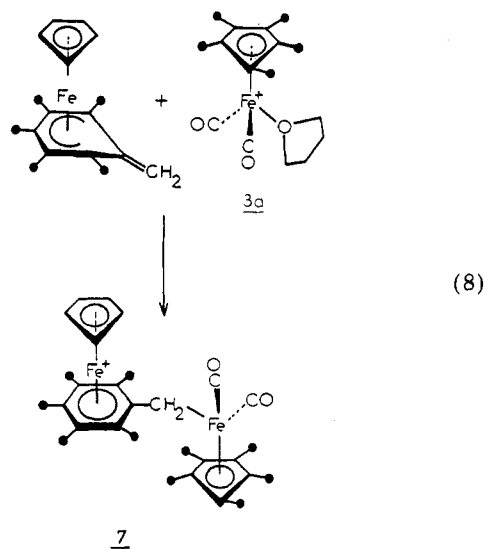
pared to difficulties previously noted in the synthesis of complexes $[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{olefin})]^+$ for analogous stereoelectronic reasons (increase of steric bulk, electron-releasing effect of the ancillary ligands).¹⁵ Reger first reported in 1977 $[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{C}_2\text{H}_4)]^+\text{BF}_4^-$ from $[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{THF})]^+\text{BF}_4^-$ and C_2H_4 and the failure to make such complexes with olefins other than C_2H_4 , which can be attributed to their unstability.^{15a} However in 1979 the synthesis of these complexes by Reger appeared using $[\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}] + \text{AgBF}_4$.^{15b}

We also attempted to synthesize neutral $\text{Fp}'\text{R}$ complexes from $[\text{Fp}'(\text{THF})]^+$ and anionic ligands. NaBH_4 gives a 60% yield of $\text{Fp}'\text{H}$,⁶ **5**, which we had previously reported from $[\text{Fp}'(\text{CO})]^+$ and NaBH_4 in high yield (eq 6). NaS_2CNR_2 reacts with **3e** to give $\text{Fp}'[\eta^1\text{-SC}(\text{S})\text{NMe}_2]$, **6a**, in only a 15% yield. As in the synthesis of $\text{Fp}'\text{H}$ and especially in the latter case, reaction with $[\text{Fp}'(\text{CO})]^+$, **3e**, gave a much better yield (90%) than that with $[\text{Fp}'(\text{THF})]^+$. It is noteworthy that this is so far the only route to **6a** (eq 7).

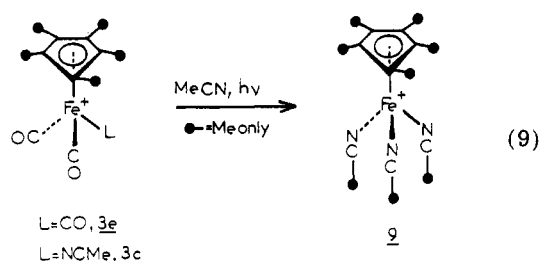


The neutral carbon nucleophile $[\text{Cp}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)\text{-Fe}]^{4b,18}$ reacts with **3a** in THF at -30°C (2 h) to form a metal-carbon bond giving a 50% yield of the bimetallic complex **7** (eq 8) together with $[\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)\text{Fe}]^+\text{PF}_6^-$, **8**,¹⁹ and **1** resulting from electron transfer. The Cp analogue of **7** is known from the reaction of $[\text{Cp}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)\text{Fe}]$ with FpCl .^{4b}

4. Synthesis of $[\text{Cp}'\text{Fe}(\text{NCMe})_3]^+\text{PF}_6^-$ by Photolysis of $(\text{Fp}'\text{L})^+$ ($\text{L} = \text{CO}$ and NCMe) and Access to $[\text{Cp}'\text{Fe}(\text{L}_1)(\text{L}_2)(\text{L}_3)]^+$. Photolysis in CH_3CN of pale yellow



$[\text{Fp}'(\text{CO})]^+\text{PF}_6^-$, **3e**, or of yellow $[\text{Fp}'(\text{NCMe})]^+\text{PF}_6^-$, **3c**, gives the thermally stable purple complex $[\text{Cp}'\text{Fe}(\text{NCMe})_3]^+$, **9**^{5b} (eq 9). Large crystals are obtained upon recrystallization from CH_3CN . UV photolysis of $\text{Cp}'(\eta^6\text{-arene})\text{Fe}^+\text{PF}_6^-$ fails to give ligand exchange under any conditions.



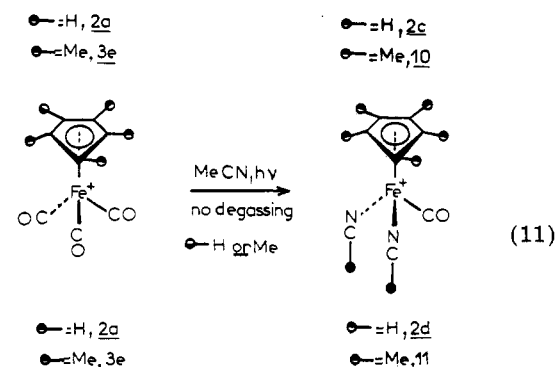
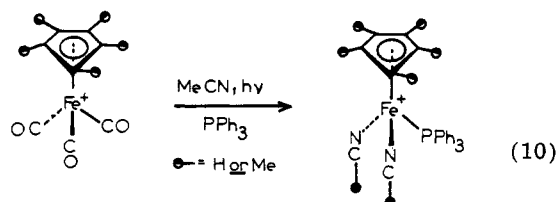
9 is extremely water sensitive, and the acetonitrile ligands are very labile. Attempts to record a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** at room temperature in CD_3CN solution failed because of fast exchange with the solvent. Only the C_5Me_5 signals are clearly observed (C_5 , 78.9 ppm; Me, 9.3 ppm); the ligand and solvent peaks cannot be distinguished. A good spectrum is obtained at -60°C in $\text{CD}_3\text{-COCD}_3$ solution. The CN carbon is found 20 ppm downfield from uncoordinated acetonitrile. In solvents other than MeCN, **9** decomposes at or below room temperature. The Cp analogue²⁰ is thermally unstable, but photolysis of $(\text{FpCO})^+\text{PF}_6^-$ or $[\text{Cp}(\eta^6\text{-arene})\text{Fe}]^+\text{PF}_6^-$ in CH_3CN in the presence of an added ligand gives $[\text{Cp}'\text{Fe}(\text{NCMe})_2\text{L}]^+$ [eq 10, $\text{L} = \text{CO}$ (**2b**), PPh_3 (**2c**), cyclohexene (**2d**), dimethylthiophene (**2e**)]. $[\text{Cp}'\text{Fe}^+(\text{NCMe})_3]^+$ was characterized recently at low temperature by ^1H NMR.²⁰ **9** reacts with CO, PPh_3 , dppe, or cyclooctatetraene to give the replacement of one, two, or three acetonitrile ligands (Scheme II). Whereas the first two CH_3CN ligands must be exchanged in CH_3CN as a solvent, replacement of the third CH_3CN ligand can only be achieved in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ (except with COT that also replaces all the three CH_3CN ligands in CH_3CN).

If photolysis of $[\text{Fp}(\text{CO})]^+\text{PF}_6^-$ or $[\text{Fp}'(\text{CO})]^+\text{PF}_6^-$ is carried out in CH_3CN without degassing the solution, the red complexes $[\text{Cp}'\text{Fe}(\text{NCMe})_2(\text{CO})]^+\text{PF}_6^-$, **2b**, and $[\text{Cp}'\text{Fe}(\text{NCMe})_2(\text{CO})]^+\text{PF}_6^-$, **10**, respectively, are obtained in high yields^{5b} (eq 11). Under these conditions CO is not removed from the cell and we know that the reaction product between **9** and CO is **10**.

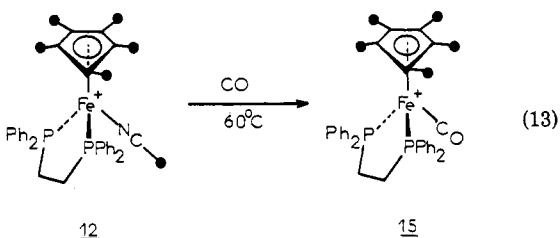
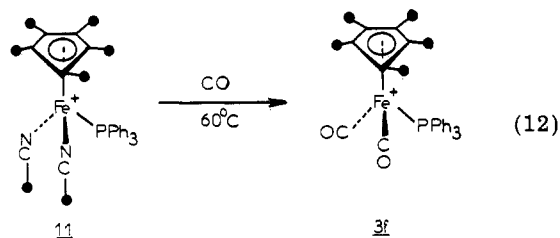
(18) Hamon, J.-R.; Astruc, D.; Román, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2431.

(19) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2261.

(20) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1986.



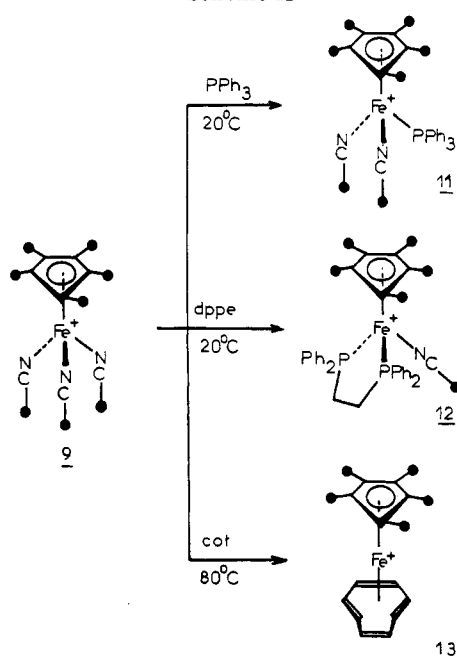
Yellow crystalline mixed phosphine-carbonyl complexes are easily obtained by reaction of the mixed acetonitrile-carbonyl complexes 11 and 12 with CO (3 atm) at 60 °C in $C_2H_2Cl_2$ ²¹ (eq 12 and 13). $[Cp^*Fe(CO)_2(PPh_3)]^+PF_6^-$, **3f**, can also be obtained more simply by thermal reaction of $(Fp^*CO)^+PF_6^-$ with PPh_3 in acetone (reflux, 24 h) or by reaction of **3a** with PPh_3 in CH_2Cl_2 (Scheme I).



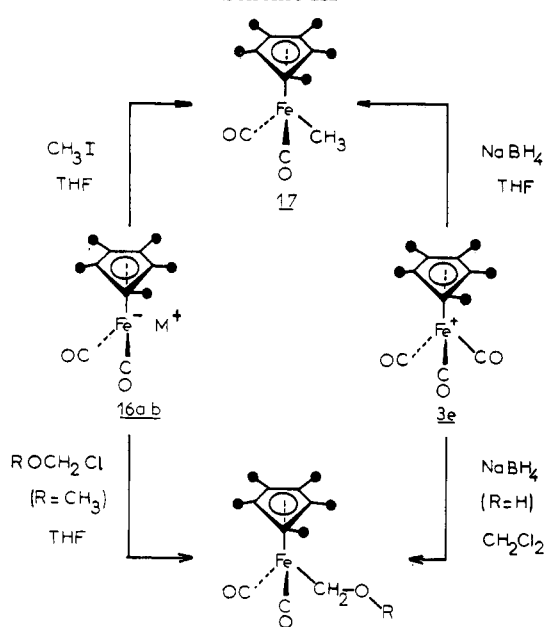
Attempts to coordinate olefins or arenes by reaction with **9** failed under a variety of conditions.²³ Apparently conjugated cyclic polyenes such as cyclooctatetraene are the only favorable cases (Scheme II) although $[Cp^*Fe(NCMe)_2(cyclohexene)]^+PF_6^-$ could be synthesized^{5b} as in eq 10.

5. Synthesis and Characterization of the Anion Fp'^- . Fp'^- can be synthesized as its red Na^+ or K^+ salt using Na/Hg or K mirror in THF. However, Fp'^-Na^+

Scheme II



Scheme III



cannot be made on large scale unless a very large contact surface of Na/Hg is used because (i) its formation is slow due to the insolubility of Fp'^- , **1**, and (ii) the red anion progressively turns orange, a feature not observed when a K mirror is used. Alkylation with CH_3I or $ClCH_2OCH_3$ can be achieved in high yields by using either the red salt in THF or the orange solution. The structure of the orange species Fp'^-Hg , already reported by King^{24c} in the Fp series, will be reported later. The reduction of Fp'^- by Na/Hg was mentioned in a footnote recently.^{24d} Fp'^-K^+ , **16a**, was synthesized by reduction of Fp'^- on a K mirror in 50 mL of THF on a 10-mmol scale overnight at ambient

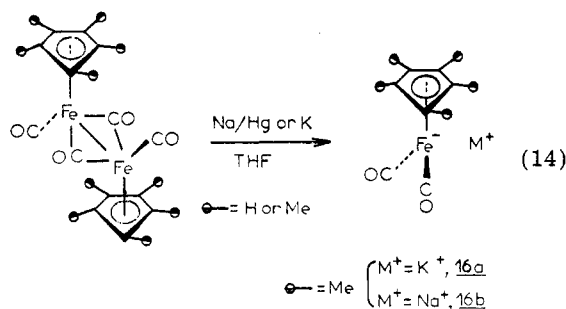
(21) Catheline, D. Thesis, Rennes, 1982.

(22) (a) King, R. B. *Acc. Chem. Res.* 1970, 3, 417. (b) King, R. B. *Organomet. Synth.* 1965, 1.

(23) (a) Photolytic (sunlight) arene exchange in $Cp^*(\eta^6\text{-arene})Fe^+$ cations in dichloromethane has been reported: Swann, R. T.; Boekelheide, V. *J. Organomet. Chem.* 1982, 231, 143. Laganis, E. D.; Firske, R. O.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* 1981, 2657, 78. Gill, T. P.; Mann, K. R. *Inorg. Chem.* 1980, 19, 3007. Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* 1981, 216, 65. (b) $[Cp^*Ru(NCMe)_3]^+PF_6^-$ reacts with arenes to give $[Cp^*(\eta^6\text{-arene})Ru]^+PF_6^-$: Gill, T. P.; Mann, K. R. *Organometallics* 1982, 1, 485. (c) That reaction of $[Cp^*(NCMe)_3]^+$ with arene gives $[Cp^*(\eta^6\text{-arene})M]^+$ with $M = Ru$,^{23b} not with $M = Fe$, can be explained by the ability of Ru to stabilize $\eta^6\text{-arene}$ ligands: Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* 1972, B28, 2049.

(24) For comparison, the infrared spectrum of Fp'^-K^+ displays carbonyl bands at 1868, 1792, and 1772 cm^{-1} in THF^{24a} and at 1880 and 1735 cm^{-1} in Nujol.^{24b} Splitting of the asymmetric CO stretch, observed in THF solution, was attributed to ion pair formation:^{24a} (a) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* 1975, 99, 263. (b) Plotkins, J. S.; Shore, S. G. *Inorg. Chem.* 1981, 20, 284. (c) King, R. B.; *J. Inorg. Nucl. Chem.* 1963, 25, 1296. (d) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* 1982, 1, 1254 (ref 13).

temperature (1 h on a 1-mmol scale).



$\text{Fp}'\text{-K}^+$, **16a**, is only sparingly soluble in THF at 20 °C but much more soluble at 60 °C; thus warm dark red THF solutions of $\text{Fp}'\text{-K}^+$ can be filtered, which avoids the transfer of colloidal potassium. Both **16a** and **16b** in THF solution display two infrared²⁴ stretches at 1805 and 1870 cm^{-1} ; removal of the solvent in vacuo gives a crude sample of **16a** for which a Mössbauer spectrum recorded at 77 K shows a clean doublet ($\text{IS} = 0.11 \text{ mm s}^{-1}$ vs. Fe; $\text{QS} = 2.00 \text{ mm s}^{-1}$), these values being very close to those for $\text{Fp}'\text{-Na}^+$ ($\text{IS} = 0.11 \text{ mm s}^{-1}$ vs. Fe; $\text{QS} = 2.06 \text{ mm s}^{-1}$). Addition of CH_3I to a suspension of $\text{Fp}'\text{-K}^+$, **16a**, immediately gives a quantitative crude yield of $\text{Fp}'\text{CH}_3$, **17** (Scheme III). Sublimation gives yellow needles in 85% overall yield from Fp'_2 . Addition of $\text{ClCH}_2\text{OCH}_3$ to orange or red solutions of $\text{Fp}'\text{-Na}^+$ or $\text{Fp}'_2\text{Hg}$ gives $\text{Fp}'\text{CH}_2\text{OCH}_3$, **18**, also known in the Fp series.²⁵ Orange **18** is much more stable and less air sensitive than its Fp analogue and can be obtained in 70% yield after preparative thick-layer chromatography. Note that we have also obtained $\text{Fp}'\text{CH}_3$ and $\text{Fp}'\text{CH}_2\text{OH}$ by NaBH_4 reduction of $[\text{Fp}'(\text{CO})]^+\text{PF}_6^-$.^{6a}

Concluding Remarks

Several classical FpR (FpL)⁺ complexes are available via analogous routes in the pentamethyl series. These include the useful oxidative cleavage of the metal-metal bond in the dimers Fp_2 and Fp'_2 and the alkylation of the anions Fp'^- and Fp'^- . In some instances, however, the Fp' chemistry seems more restricted than that of Fp. Olefins could not be coordinated by reaction with $[\text{Fp}'(\text{THF})]^+$ nor with $[\text{Cp}'\text{Fe}(\text{NCMe})_3]^+$ whereas the corresponding Cp chemistry is successful. The synthesis of Fp'^- proceeds more slowly than that of Fp'^- with Na/Hg, but the use of the K mirror shortens the reaction time. The synthesis of $[\text{Fp}'(\text{CO})]^+$ using ferrocene does not find its equivalent with decamethylferrocene, but the oxidative cleavage of Fp_2 and Fp'_2 using ferricinium is a good substitute for the Fischer-type synthesis since it proceeds quantitatively under 1 atm of CO. The stabilization of $[\text{Cp}'\text{Fe}(\text{NCMe})_3]^+$ by permethylation provides a significant advantage that adds to the usefulness of its synthesis from $[\text{Fp}'(\text{CO})]^+$ and $[\text{Fp}'(\text{NCMe})]^+$. Thus $[\text{Cp}'\text{Fe}(\text{L}_1)(\text{L}_2)(\text{L}_3)]^+$ complexes are now accessible with a variety of N, P, S, and even C ligands although monoolefins and arenes fail to complex. Complexes of this type are accessible in particular without CO ligands. Although $[\text{Cp}'\text{Fe}(\text{NCMe})_3]^+$ is unstable, this chemistry has its analogies in the parent Cp series since $[\text{Cp}'\text{Fe}(\text{NCMe})_2(\text{L})]^+$ are accessible (including L = olefin) by effecting the photolysis in the presence of L or, if not, without degassing. Thus while entries into the piano-stool

$\text{Cp}'\text{Fe}$ chemistry are explored, new or improved entries to $\text{Cp}'\text{Fe}$ analogues have also been found.

The reactivity of $\text{Cp}'\text{Fe}$ or Fp' complexes is also significantly different from those of Cp or Fp^{6,26} as we have shown in other papers.^{6,26} In particular, reduction of CO with NaBH_4 is much more useful in $\text{Cp}'\text{Fe}$ complexes since Cp reduction is prevented and formyl and hydromethyl complexes are stabilized.⁶

Several direct consequences of the steric effect of permethylation have also been noted in the reactions with arenes. Upon coordination, hexaethylbenzene specifically loses one Et group^{26,27} and the site of hydrogenation of anthracene is changed.²⁸

Experimental Section

Reagent grade tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen just before use. Acetonitrile and dichloromethane were distilled from phosphorus pentoxide. All other chemicals were used as received. All manipulations were done by using Schlenk techniques under argon or in a nitrogen-filled Vacuum Atmosphere Drylab. Photolyses were performed with a Hanovia lamp (250 nm, 450 W) at room temperature under a stream of argon. Infrared spectra were recorded on a Pye-Unicam SP 1100 infrared spectrometer either as a Nujol mull between KBr disks or in solution using 0.1-mm cells with KBr windows. Wavenumbers are given in inverse centimeters by using polystyrene as reference. ¹H NMR spectra were recorded with a Varian EM 360 (60 MHz, room temperature) or a Brüker WH 90 (80 MHz, FT mode, low-temperature spectra) instrument. ¹³C NMR were recorded on a Brüker WH 90 spectrometer (20.115 MHz, FT mode). All chemical shifts are reported in parts per million [δ (ppm)] with reference to internal tetramethylsilane (Me_4Si). ³¹P NMR spectra were obtained on a Brüker WH 90 instrument (32.3 MHz, FT mode); chemical shifts are reported with reference to external H_3PO_4 (85% in D_2O). Mössbauer spectra were recorded with a 25-mCi ⁵⁷Co source on Rh using a symmetric triangular sweep mode. Isomer shifts are given relative to Fe. Elemental analyses were performed by the center for microanalyses of the CNRS at Lyon-Villeurbanne.

(a) **Synthesis of Fp'_2 , 1.** Fp'_2 , **1**, was obtained as previously described by King^{2a} by using $\text{Cp}'\text{H}$ and $\text{Fe}(\text{CO})_5$ in refluxing xylenes instead of 2,2,5-trimethylhexane as solvent. Typically, 25 g (180 mmol) of $\text{Cp}'\text{H}$ and 50 mL of $\text{Fe}(\text{CO})_5$ in 100 mL of xylenes were heated with a good reflux for 2 days. An additional 30 mL of $\text{Fe}(\text{CO})_5$ was added after the first 24 h of reflux. After the mixture was cooled to room temperature, the solid was filtered off, washed with 3 × 100 mL of hexane, and filtered on alumina using CH_2Cl_2 . The filtrate was concentrated to 200 mL and cooled to -20 °C. Filtration gave 30 g (67% yield calculated vs. $\text{Cp}'\text{H}$) of purple microcrystals.

(b) **Synthesis of $(\text{Fp}'\text{S})^+\text{PF}_6^-$, 3a-d.** Fp'_2 (1.23 g, 2.5 mmol) and $\text{Cp}'_2\text{Fe}^+\text{PF}_6^-$ (1.65 g, 5 mmol) were stirred overnight in 100 mL of $\text{CH}_2\text{Cl}_2/\text{solvent}$ (2/1) mixtures. After evaporation of the solvents in vacuo and washing with ether (2 × 50 mL), the residue was recrystallized from an acetone/ether mixture (except for **3a** which was recrystallized from THF/ether).

3a (S = THF): 65% yield; ¹H NMR (CD_3COCD_3) 3.70 (m, 4 H, CH_2O), 2.17 (s, 4 H, CH_2), 1.84 (s, 15 H, C_5Me_5); ¹³C NMR (CD_3COCD_3) 212.9 (CO), 100.8 (C_5Me_5), 68.3 (CH_2O), 26.5 (CH_2), 9.42 (C_5Me_5); IR 2085, 2005 (ν_{CO}). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_3\text{FePF}_6$: C, 41.40; H, 4.99; Fe, 12.03. Found: C, 41.20; H, 4.72; Fe, 12.48.

3b (S = Me_2CO): 60% yield; ¹H NMR (CD_3COCD_3) 2.10 (s, 6 H, Me_2CO), 1.86 (s, 15 H, C_5Me_5); ¹³C NMR (CD_3COCD_3) 232.0 (Me_2CO), 212.8 (CO), 100.8 (C_5Me_5), 29.9 (Me_2CO), 9.34 (C_5Me_5); IR 2055, 1990 (ν_{CO}), 1660 ($\nu_{\text{C=O}}$). Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3\text{FePF}_6$: C, 40.02; H, 4.70; Fe, 12.41. Found: C, 40.30; H, 4.99; Fe, 12.03.

(25) (a) $\text{Fp}'\text{CH}_2\text{OCH}_3$ was synthesized from $\text{Fp}'\text{-Na}^+$ and $\text{ClCH}_2\text{OCH}_3$ by Pettit, who showed that protonation gives the transient methylene complex $[\text{Fp}'(\text{CH}_2)]^+$: Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Cutler reported the reduction of $[\text{Fp}'(\text{CO})]^+\text{PF}_6^-$ by NaBH_4 in methanol giving a 40% yield of $\text{Fp}'\text{CH}_2\text{OCH}_3$: Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

(26) (a) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817. (b) Davies, S. G.; Hibberd, J.; Simpson, S. J. *J. Organomet. Chem.* **1983**, *246*, C16.

(27) Hamon, J.-R. Thesis, Rennes, 1982.

(28) Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 1115.

3c ($S = NCMe$): 60% yield; 1H NMR (CD_3CN) 2.28 (s, 3 H, MeCN), 1.82 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3CN) 211.9 (CO), 134.9 (MeCN), 100.4 (C_5Me_5), 9.65 (C_5Me_5), 4.79 (MeCN); IR 2065, 2010 (ν_{CO}), 2120 (ν_{CN}). Anal. Calcd for $C_{14}H_{18}NO_2FePF_6$: C, 38.82; H, 4.19; N, 3.23; Fe, 12.89. Found: C, 38.30; H, 4.25; N, 3.18; Fe, 12.83.

3d ($S =$ pyridine): 65% yield; 1H NMR (CD_3COCD_3) 8.65 (m, 2 H, H ortho), 8.06 (m, 1 H, H para), 7.61 (m, 2 H, H meta), 1.83 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3CN) 213.2 (CO), 158.4 (C ortho), 140.7 (C para), 128.5 (C meta), 100.1 (C_5Me_5), 9.41 (C_5Me_5); IR 2050, 1988 (ν_{CO}). Anal. Calcd for $C_{17}H_{20}NO_2FePF_6$: C, 43.34; H, 2.97; Fe, 11.85. Found: C, 42.92; H, 4.34; N, 2.66; Fe, 12.50.

(c) **Synthesis of $(Fp'THF)^+PF_6^-$, 4.** Under the same conditions (see b) Fp_2 (0.875 g, 2.5 mmol) and $Cp_2Fe^+PF_6^-$ (1.65 g, 5 mmol) were stirred overnight. After workup as in b, 1.77 g of 4 was isolated (90% yield) and was to be found pure by 1H NMR and IR by comparison with an authentic sample.¹⁵

(d) **Synthesis of $(Fp'CO)^+PF_6^-$, 3e.** Fp'_2 (2.50 g, 5 mmol) and $Cp_2Fe^+PF_6^-$ (3.31 g, 10 mol) were stirred in 100 mL of 2/1 mixture of CH_2Cl_2/THF , under CO (1 atm) for 24 h. After removal the solvent in vacuo, washing with ether (2 \times 50 mL), and recrystallization from acetone/ethanol, 2.8 g (70% yield) of 3e was collected by filtration. 3e was found to be pure by comparison of its 1H NMR spectrum with that of an authentic sample.^{5a}

(e) **Synthesis of $(Fp'L)^+PF_6^-$, 3f-g.** A 2.32-g (5-mmol) sample of $(Fp'THF)^+PF_6^-$, 3a, was dissolved in 30 mL of CH_2Cl_2 , and 10 mmoles of L was added. Stirring overnight, removal the solvent in vacuo, washing with ether (2 \times 50 mL), and recrystallization from acetone/ethanol gave pure 3f-g.

3f ($L = PPh_3$): 70% yield; 1H NMR (CD_3COCD_3) 7.40 (m, 15 H, Ph), 2.15 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3CN) 214.4 (CO, d, $^2J_{PC} = 24$ Hz), 134.4, 133.0, 130.7, 130.2 (Ph), 101.7 (C_5Me_5), 9.78 (C_5Me_5); IR 2130, 2070 (ν_{CO}). Anal. Calcd for $C_{30}H_{30}P_2O_2FeF_6$: C, 55.04; H, 4.59; P, 9.48; Fe, 8.56. Found: C, 54.99; H, 4.68; P, 9.00; Fe, 8.81; F, 17.68.

3g ($L = P(OPh)_3$): 70% yield; 1H NMR (CD_3CN) 7.36 (m, 15 H, Ph), 2.81 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3CN) 210.7 (CO, d, $^2J_{PC} = 33$ Hz), 151.7 ($C_{Ph}O$, d, $^2J_{PC} = 11$ Hz), 131.7, 127.5, 121.5 (Ph), 103.2 (C_5Me_5), 9.88 (C_5Me_5); IR 2050, 2005 (ν_{CO}). Anal. Calcd for $C_{30}H_{30}O_5P_2FeF_6$: C, 51.30; H, 4.31; P, 8.82. Found: C, 51.20; H, 4.23; P, 8.82.

(f) **Synthesis of $[Fp'SC(Net)_2SFp]^+PF_6^-$, 6c and $[Fp'SC(Net)_2SFp]^+PF_6^-$, 6d.** A 928-mg (2-mmol) sample of $(Fp'THF)^+PF_6^-$, 3a, and 710 mg (2 mmol) of $Fp[\eta^1-SC(S)Net_2]$, 6b, were stirred in 50 mL of CH_2Cl_2 at $-20^\circ C$ for 1 h. After the mixture had warmed to room temperature, the solvent was removed in vacuo. Recrystallization from acetone/ether gave 1.28 g (80% yield) of 6c, as dark red plates.

The same reaction performed with 2 mmol of 4 and 2 mmol of 6b gave 6d in 80% yield.

6c: 1H NMR ($CDCl_3$) 4.75 (s, 5 H, C_5H_5), 4.30 (q, 4 H, CH_2), 1.80 (s, 15 H, C_5Me_5), 1.33 (t, 6 H, CH_3); ^{13}C NMR 215.3, 213.1 (CO), 201.1 (CS), 99.1 (C_5Me_5), 87.6 (C_5H_5), 53.1 (CH_2), 13.1 (CH_3), 9.6 (C_5Me_5); IR 2070, 2060, 2020, 1980 (ν_{CO}), 1550 (ν_{CN}), 975 (ν_{CS}).

6d: 1H NMR (CD_3CN) 5.12 (s, 5 H, Cp), 5.05 (s, 5 H, Cp), 4.03 (q, 4 H, CH_2), 1.26 (t, 6 H, CH_3).

(g) **Synthesis of $Fp'R$, 5 and 6.** $(Fp'THF)^+PF_6^-$, 3a (464 mg, 1 mmol), and $NaBH_4$ (190 mg, 5 mmol) were stirred in 20 mL of CH_2Cl_2 (2 h). Evaporation of the solvent and extraction with pentane (2 \times 10 mL) gave 146 mg (60%) of yellow $Fp'H$, 5, characterized by comparison of its 1H NMR spectrum with that of an authentic sample.⁶

The same reaction between $(Fp'THF)^+PF_6^-$, 3a (464 mg, 1 mmol), and $Na^+S_2CNMe_2 \cdot 2H_2O$ (900 mg, 5 mmol) gave $Fp'[\eta^1-SC(S)NMe_2]$, 6a, in 15% yield after recrystallization from ether/hexane.

6a: 1H NMR ($CDCl_3$) 3.58 (s, 6 H, NMe_2), 1.83 (s, 15 H, C_5Me_5); ^{13}C NMR ($CDCl_3$) 214.6 (CO), 207.9 (CS), 96.1 (C_5Me_5), 45.6 (NMe_2), 9.4 (C_5Me_5); IR 2018, 1970 (ν_{CO}). Anal. Calcd for $C_{15}H_{21}NO_2S_2Fe$: C, 49.05; H, 5.76; N, 3.81; S, 17.46; Fe, 13.20. Found: C, 49.37; H, 5.98; N, 3.65; S, 18.01; Fe, 13.55.

(h) **Synthesis of $[CpFe(\eta^6-C_6Me_6CH_2)Fp]^+PF_6^-$, 7.** $Cp(\eta^5-C_5Me_5CH_2)Fe$ (282 mg, 1 mmol) and $(Fp'THF)^+PF_6^-$, 3a (464 mg, 1 mmol), were stirred in 30 mL of THF at $-30^\circ C$ for 2 h.

Filtration, concentration of the solution in vacuo, and addition of ether precipitated 337 mg (50% yield) of 7 as a yellow powder:

1H NMR (CD_3COCD_3) 4.56 (s, 5 H, Cp), 2.50 (s, 15 H, C_5Me_5), 2.23 (s, 2 H, CH_2), 1.90 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3CN) 219.1 (CO), 121.5, 99.3, 96.5, 93.4 ($C_6Me_6CH_2$), 79.4 (C_5H_5), 97.7 (C_5Me_5), 18.7, 17.9, 17.7 ($C_6Me_6CH_2$), 13.6 ($C_5Me_5CH_2$), 9.6 (C_5Me_5); IR 1990, 1935 (ν_{CO}). Anal. Calcd for $C_{38}H_{37}O_2Fe_2PF_6$: C, 51.66; H, 5.33; Fe, 16.56. Found: C, 52.05; H, 5.45; Fe, 16.78.

(i) **Synthesis of $[Cp'Fe(NCMe)_3]^+PF_6^-$, 9.** $(Fp'CO)^+PF_6^-$, 3e (2.1 g, 5 mmol), was photolyzed in 200 mL of acetonitrile. After 3 h the pale yellow solution turned deep purple. Concentration of this solution in vacuo to 20 mL and addition of diethyl ether (150 mL) afforded 9 as a purple powder. Recrystallization from acetonitrile/ether solution gave large black purple crystals (1.8 g, 80% yield): 1H NMR (CD_3COCD_3) 2.42 (s, 9 H, MeCN), 1.66 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3COCD_3 , $-60^\circ C$) 131.8 (MeCN), 78.91 (C_5Me_5), 9.0 (C_5Me_5), 3.84 (MeCN); IR 2290 (ν_{CN}); Mössbauer, IS = 0.54 mm s^{-1} vs. Fe, QS = 2.37 mm s^{-1} . Anal. Calcd for $C_{16}H_{24}N_3FePF_6$: C, 41.85; H, 5.27; N, 9.15; Fe, 12.16. Found: C, 41.84; H, 5.26; N, 9.03; Fe, 12.32.

(j) **Synthesis of $[Cp'Fe(CO)(NCCH_3)_2]PF_6^-$, 10.** $(Fp'CO)^+PF_6^-$, 3e (2.1 g, 5 mmol), was photolyzed in 200 mL of MeCN without degassing the solution. After 3 h, the pale yellow solution turned bright red. Concentration in vacuo and addition of diethyl ether caused the precipitation of 10 as a red powder in 65% yield: 1H NMR (CD_3COCD_3) 2.40 (s, 6 H, MeCN), 1.70 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2) 216.0 (CO), 132.6 (MeCN), 91.7 (C_5Me_5), 9.35 (C_5Me_5), 4.43 (MeCN); IR 2308 (ν_{CN}), 1976 (ν_{CO}). Anal. Calcd for $C_{15}H_{21}N_2OFePF_6$: C, 40.38; H, 4.74; N, 6.28; Fe, 12.52. Found: C, 40.32; H, 4.74; N, 6.10; Fe, 12.75.

(k) **Synthesis of $[Cp'Fe(NCCH_3)_2(PPh_3)]^+PF_6^-$, 11.** $[Cp'Fe(NCMe)_3]^+PF_6^-$, 9 (1.38 g, 3 mmol), and PPh_3 (790 mg, 3 mmol) were stirred at room temperature in 20 mL of CH_3CN for 0.5 h. Addition of 150 mL of diethyl ether precipitated 1.36 g (88% yield) of 11 as a red powder: 1H NMR (CD_3COCD_3) 7.59 (m, 15 H, Ph), 2.42 (s, 6 H, MeCN), 1.37 (s, 1 S, C_5Me_5); ^{13}C NMR 165.9 (MeCN), 133.1, 132.6, 132.1, 128.5, 127.5, 127.1, 126.7 (Ph), 82.0 (C_5Me_5), 1.72 (MeCN); IR 2280 (ν_{CN}).

(l) **Synthesis of $[Cp'Fe(\eta^2-dppe)(NCMe)]^+PF_6^-$, 12.** $[Cp'Fe(NCMe)_3]^+PF_6^-$, 9 (880 mg, 1.9 mol), and 1,2-bis(diphenylphosphino)ethane (dppe) (760 mg, 1.9 mmol) were stirred in 20 mL of MeCN for 12 h. Concentration in vacuo, addition of diethyl ether (150 mL), filtration, and recrystallization from THF gave 12 (1.33 g, 90%) as red microcrystals as a THF solvate: 1H NMR (CD_3COCD_3) 7.73 (m, 20 H, PPh_2), 3.33 (m, 4 H, CH_2), 2.06 (s, 3 H, CH_3CN); ^{13}C NMR (CD_3CN) 135.0 (MeCN), 133.9, 131.6, 129.7, 129.5 (Ph), 88.4 (C_5Me_5), 28.52 (br, CH_2), 9.94 (C_5Me_5), 1.67 (MeCN); IR 2280 (ν_{CN}). Anal. Calcd for $C_{38}H_{42}NP_2FeF_6$: C, 59.51; H, 5.94; N, 1.65; P, 10.96; Fe, 6.59. Found: C, 60.32; H, 5.95; N, 1.71; P, 10.24; Fe, 6.44.

(m) **Synthesis of $[Cp'Fe(\eta^6-COT)]PF_6^-$, 13.** $[Cp'Fe(NCCH_3)_3]^+PF_6^-$, 9 (694 mg, 1.5 mmol), and cyclooctatetraene (COT) (0.35 mL, 3 mmol) were refluxed in 20 mL of NCMe for 12 h. Evaporation of MeCN in vacuo to 2 mL and addition of 50 mL of diethyl ether precipitated 13, (380 mg, 57%) as an orange powder: 1H NMR (CD_3COCD_3) 6.60 (m, 2 H, H_α), 5.76 (m, 4 H, H_α and H_β), 4.83 (m, 2 H, uncomplexed CH), 1.80 (s, 15 H, C_5Me_5), ^{13}C NMR (CD_3CN) 134.1 (uncomplexed CH), 104.7 (C_α), 102.9 (C_β), 94.5 (C_α), 97.1 (C_5Me_5), 9.22 (C_5Me_5). Anal. Calcd for $C_{18}H_{23}FePF_6$: C, 49.11; H, 5.27; Fe, 12.69. Found: C, 49.00; H, 5.38; Fe, 12.68.

(n) **Synthesis of $[Cp'Fe(CO)_2(PPh_3)]^+PF_6^-$, 3f.** $[Cp'Fe(PPh_3)(NCCH_3)_2]^+PF_6^-$, 11 (728 mg, 1.1 mmol), was stirred at $60^\circ C$ in 20 mL of 1,2-dichloroethane under 3 atm of CO for 12 h. After the mixture was cooled to room temperature, the solvent was concentrated in vacuo to 2 mL. Addition of diethyl ether caused the precipitation of 470 mg (65%) of 3f, characterized as in 6.

(o) **Synthesis of $[Cp'Fe(\eta^2-dppe)CO]^+PF_6^-$, 15.** $[Cp'Fe(\eta^2-dppe)(NCMe)]^+PF_6^-$, 12 (730 mg, 0.9 mmol), was stirred at $60^\circ C$ in 20 mL of 1,2-dichloroethane under 3 atm of CO. After 12 h, the solvent was concentrated in vacuo to 2 mL and 50 mL of diethyl ether was added, giving a yellow powder. Recrystallization from acetone/ethanol mixture gave analytically pure crystals of $[Cp'Fe(\eta^2-dppe)(CO)]^+PF_6^-$, 15 (90% yield): 1H NMR (CD_3CN) 7.62 (m, 20 H, Ph), 2.47 (m, 4 H, CH_2), 1.52 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_3CN) 219.6 (CO, $^2J_{CP} = 25$ Hz), 134.7, 134.5, 134.2, 133.7, 133.4, 132.8, 132.5, 130.1, 129.9 (Ph), 96.5 (C_5Me_5),

30.7 (CH₂, t, $J_{\text{CP}} = 22$), 9.84 (C₅Me₅); IR 1940 (ν_{CO}). Anal. Calcd for C₃₇H₂₉P₃FeF₆: C, 59.04; H, 3.86; P, 12.36; Fe, 7.45. Found: C, 59.15; H, 3.88; P, 12.45; Fe, 7.55.

(p) **Synthesis of Fp⁻K⁺, 16a.** Fp'₂, 1 (4.94, 10 mmol), was stirred on a potassium mirror (780 mg, 20 mmol) in 60 mL of THF at room temperature for 2 h. After filtration the THF was removed in vacuo, giving a red powder (85% yield): IR 1870, 1805 (ν_{CO}); Mössbauer, IS = 0.11 mm s⁻¹ vs. Fe (77 K), QS = 2.00 mm s⁻¹.

(q) **Synthesis of Fp⁻Me, 17.** To a stirred suspension of Fp'⁻K⁺, 16a, prepared as in 15, from 10 mmol of Fp'₂, 1, was added MeI (3.55 g, 25 mmol) by syringe. After evaporation in vacuo, the residue was extracted with 3 × 20 mL of pentane. Evaporation of this solution gave crude 17, purified by sublimation (70 °C, 1 mmHg), yielding 17, as yellow microcrystals (80% yield calculated vs. Fp'₂): ¹H NMR (C₆D₆) 1.95 (s, 15 H, C₅Me₅), -0.08 (s, 3 H, FeMe); ¹³C NMR (CDCl₃) 219.5 (CO), 105.2 (C₅Me₅), 9.2 (C₅Me₅), -13.1 (FeMe, $J_{\text{CH}} = 133$ Hz); IR 2040, 1985 (ν_{CO}); Mössbauer, IS = 0.12 mm s⁻¹ vs. Fe (77 K), QS = 1.88 mm s⁻¹. Anal. Calcd for C₁₃H₁₈O₂Fe: C, 59.57; H, 6.92; Fe, 21.30. Found: C, 59.65; H, 7.02; Fe, 21.38.

(r) **Synthesis of Fp⁻CH₂OCH₃, 18.** Fp'₂, 1 (980 mg, 2 mmol), was reduced on Na/Hg (5 mmol of Na) in 100 mL of THF over 24 h. The solution was transferred, and 170 mg (2.1 mmol) of chloromethyl methyl ether was added by syringe. After evapo-

ration of the THF the residue was extracted with 3 × 50 mL of pentane. Concentration in vacuo and chromatographic separation on silica plates (1 mm, eluant pentane/ether (95/5), R_f 0.7), yielded 18, as an orange oil (60% yield: ¹H NMR (C₆D₆) 4.53 (s, 2 H, CH₂), 3.36 (s, 3 H, CH₃), 1.58 (s, 15 H, C₅Me₅); ¹³C NMR (C₆D₆) 218.7 (CO), 95.5 (C₅Me₅), 61.3 (o-CH₃), 73.3 (CH₂), 9.2 (C₅Me₅); IR 2010, 1990, 1940, 1930 (ν_{CO}), 1060 ($\nu_{\text{C-O}}$). Anal. Calcd for C₁₄H₂₀O₃Fe: C, 57.55; H, 6.90; Fe, 19.11. Found: C, 57.63; H, 6.91; Fe, 19.25.

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Photochemical Hydrogenolysis of the Phosphorus-Cyclopentadienyl Bond of $(\text{CO})_4\text{MnMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$ and Formation of the Phosphido-Bridged Metal Hydride Complex $(\text{CO})_4\text{Mn}[\mu\text{-P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2](\mu\text{-H})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)$

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The photolysis of $(\text{CO})_4\text{MnMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$, 1, under 1 atm of H₂ results in the formation of $(\text{CO})_4\text{Mn}[\mu\text{-P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2](\mu\text{-H})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)$, 2. Deprotonation of 2 by KOH gives $(\text{CO})_4\text{Mn}[\mu\text{-P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2]\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)^-$, 3.

We recently reported¹ the synthesis and crystal structure of $(\text{CO})_4\text{MnMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]$, a heterobimetallic compound in which the two metals are held together through both a metal-metal bond and a heterodifunctional ligand. This compound and a series of related compounds containing Mo-Re,¹ Mo-Rh,² and Mo-Ir² bonds have been studied as possible precursors to heterobimetallic dihydrides that might serve as reducing agents for polar molecules such as CO.

Reaction of $(\text{CO})_4\text{MnMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]$ with high pressure of H₂ was investigated as a possible means of cleaving the Mo-Mn bond and of obtaining a heterobimetallic hydride. However, when solutions of $(\text{CO})_4\text{MnMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]$ under 1200 psi of H₂ at 145 °C were examined by high-pressure infrared

spectroscopy, no reaction was observed, and higher temperatures led to decomposition. In a second approach to form heterobimetallic dihydrides, we investigated the reactivity of the related *p*-tolyl compound $(\text{CO})_4\text{MnMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$, 1, toward sequential treatment with acid followed by a hydride donor. The Mo-Mn bond of 1 was protonated by CF₃SO₃H, giving a cationic bimetallic bridging hydride. However, reaction of this cation with a hydride donor caused deprotonation rather than dihydride formation.³

Here we report an attempted photochemical synthesis of a heterobimetallic dihydride. However, no evidence for

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