ORGANOMETALLICS

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Organometallics, **1983**, 2 (8), 1018-1026• DOI: 10.1021/om50002a014 • Publication Date (Web): 01 May 2002

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Reactions of the Thiocarbene Complex $Cp(CO)_2Fe[CH(SMe)]^+$ with Nucleophiles

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Received January 13, 1983

The thiocarbene complexes $Cp(CO)(L)Fe[CH(SMe)]^+$, where L = CO, PPh_3, or $P(OPh)_3$, are prepared by H^- addition to $Cp(CO)(L)Fe[C(SMe)_2]^+$ to give $Cp(CO)(L)Fe[CH(SMe)_2]$, which upon treatment with CF_3SO_3H, HBF_4, or $(Ph_3C)PF_6$ provides $Cp(CO)(L)Fe[CH(SMe)]^+$. Reactions of the electrophilic $Cp(CO)_2Fe[CH(SMe)]^+$ with a range of phosphines and phosphites, L (PPh_2Me, PPh_3, PPh_2Cl, PCl_3, $P(OPh)_3$, $P(OCH_2)_3CMe$, PPh_2H, $P\text{-}c\text{-}Hx_2H$, $PPhH_2$, $P\text{-}c\text{-}HxH_2$), give the carbene adducts (or ylides) $Cp(CO)_2Fe[CH(SMe)(L)]^+$, most of which are air-stable, while the PCl_3 adduct is too unstable to isolate. An X-ray structural determination of $Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]PF_6$ (monoclinic, $P2_1/c$, $a = 10.359$ (3) Å, $b = 12.284$ (4) Å, $c = 16.234$ (4) Å, $\beta = 95.25$ (3)°, $V = 2057$ Å^3, $Z = 4$) confirms that the P atom is bonded to the carbene carbon in this and the other adducts. When $Cp(CO)_2Fe[CH(SMe)(PPh_3)]^+$ is heated at 200 °C, $Cp(CO)_2Fe(PPh_3)^+$ (88% yield) and *cis*- and *trans*-(MeS)CH=CH(SMe) are formed among other products. When $Cp(CO)_2Fe[CH(SMe)(PR_2H)]^+$, where R = Ph or c-Hx, is pyrolyzed, rearrangement to the phosphine complex $Cp(CO)_2Fe[PR_2(CH_2SMe)]^+$ (20% yield) occurs. The phosphonium proton in $Cp(CO)_2Fe[CHSMe)(PPh_2)H)]^+$ is removed by *n*-BuLi or Et_3N to give $Cp(CO)_2Fe[CH(SMe)(PPh_2)]$, which upon alkylation with $MeOSO_2F$ yields $Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]^+$. The carbene ligand in $Cp(CO)_2Fe[CH(SMe)]^+$ reacts rapidly with water to give equal amounts of $Cp(CO)_2Fe(CH_2SMe)$ and $CpFe(CO)_3^+$ together with MeSH; deuterium-labeling experimental results are consistent with a mechanism involving a formyl $Cp(CO)_2Fe[C(=O)H]$ intermediate. Diazomethane (CH_2N_2) reacts with $Cp(CO)_2Fe[CH(SMe)]^+$ to yield the complex $Cp(CO)_2Fe[SMe(CH=CH_2)]^+$ in which the olefin is coordinated to the metal through the S atom.

Introduction

In recent years, the preparations and reactions of dithiocarbene (=$C(SR)_2$) complexes have been of interest in this laboratory.[2-4] One of those studies[5] led to the synthesis of the relatively unstable thioalkoxy secondary carbene complex $Cp(CO)_2Fe=CH(SMe)^+$. Since only three other secondary thiocarbene complexes have been reported[6-8] and very little is known about their chemistry, we have improved the synthesis of $Cp(CO)_2Fe=CH(SMe)^+$ and explored its reactivity.

Results and Discussion

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$, 2. Since $Cp(CO)_2Fe[CH(SMe)]^+$ was prepared from $Cp(CO)_2Fe[CH(SMe)_2]$, **2**, a large scale synthesis of the later known compound[5] was required. The previously reported synthesis[5] of **2** from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$, **1**, and $LiAlH_4$ proceeded in 91% yield; however, attempts to scale up the reaction to larger quantities gave $[Cp(CO)_2Fe]_2$ as the major product. With use of $Li[Et_3BH]$ as the hydride source, as it was in a reaction with $Cp(CO)_2Fe[C(Me)(OMe)]^+$,[9] **2** was obtained in good yield (eq 1) even on a several-gram scale. Also the phosphine- and phosphite-substituted carbene complexes[10] could be converted to the corresponding alkyl products (eq 1), although these compounds **3** and **4** are oils which were characterized by their IR and ^1H NMR spectra (Tables I and II).

$$Cp(CO)(L)Fe[C(SMe)_2]PF_6 + Li[Et_3BH] \xrightarrow{THF} \underset{\mathbf{2-4}}{Cp(CO)(L)Fe[CH(SMe)_2]} + LiPF_6 + \{Et_3B\} \quad (1)$$

2, L = CO, 85% yield; **3**, L = PPh_3, 62% yield; **4**, L = $P(OPh)_3$, 76% yield

The mild hydride donor $Li[HAl(O\text{-}t\text{-}Bu)_3]$ also reacts with **1** to give **2** in high yield (80–85%); however, it fails to react with the less electrophilic PPh_3- and $P(OPh)_3$-substituted carbene complexes. Complexes **2–4** are bright yellow, air-sensitive materials which are soluble in most organic solvents; their IR and NMR spectra are given in Tables I and II.

Synthesis of $Cp(CO)(L)Fe[CH(SMe)]^+$. The room-temperature reaction of **2** with strong acids (CF_3SO_3H and HBF_4) rapidly results in the removal of MeSH and formation in good yields of the secondary thiocarbene complex (eq 2). The carbene can also be generated by removal

$$\underset{\mathbf{2}}{Cp(CO)_2Fe[CH(SMe)_2]} + HX \text{ or } (Ph_3C)PF_6 \rightarrow \underset{\mathbf{5-7}}{\{Cp(CO)_2Fe[CH(SMe)]\}X} \quad (2)$$

5, X = CF_3SO_3, 74% yield; **6**, X = BF_4, 75% yield; **7**, X = PF_6, 75% yield

of SMe^- by $Ph_3C^+PF_6^-$. Compounds **5–7** are bright yellow powders that are stable to O_2 but decompose upon exposure to traces of moisture to yield $CpFe(CO)_3^+$, which always contaminates these complexes. Compounds **5** and

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[1] Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

[2] Angelici, R. J.; McCormick, F. B.; Pickering, R. A. "Fundamental Research in Organometallic Chemistry, Proceedings, China-Jpn-U.S. Trilateral Seminar on Organometallic Chemistry, 1st, 1980"; Tsutsui, M., Ishii, Y., Huang, Y., Eds., Van Nostrand Reinhold: New York, 1982; pp 347–371.

[3] Pickering, R. A.; Angelici, R. J. *J. Organomet. Chem.* **1982**, *225*, 253.

[4] McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1118.

[5] McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1111.

[6] Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

[7] McCormick, F. B., Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57.

[8] Battioni, J. P.; Chottard, J. C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, 2056.

[9] Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

[10] McCormick, F. B.; Angelici, R. J. *J. Organomet. Chem.* **1981**, *205*, 79.

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Table I. IR Data for the Complexes in CH_2Cl_2 Solvent

complex	IR ν(CO), cm^{-1}
$Cp(CO)_2FeCH(SMe)_2$ (**2**)	2018 s, 1968 s[a]
$Cp(CO)(PPh_3)FeCH(SMe)_2$ (**3**)	1960[a]
$Cp(CO)(P(OPh)_3)FeCH(SMe)_2$ (**4**)	1963[a]
$Cp(CO)_2Fe[CH(SMe)]CF_3SO_3$ (**5**)	2067 s, 2026 s
$Cp(CO)_2Fe[CH(SMe)]BF_4$ (**6**)	2067 s, 2028 s
$Cp(CO)_2Fe[CH(SMe)]PF_6$ (**7**)	2069 s, 2029 s
$\{Cp(CO)(PPh_3)Fe[CH(SMe)]\}CF_3SO_3$ (**8**)	2006
$\{Cp(CO)(P(OPh)_3)Fe[CH(SMe)]\}CF_3SO_3$ (**9**)	2011
$\{Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]\}PF_6$ (**11**)	2021 s, 1971 s
$\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$ (**12a**)	2027 s, 1975 s
$\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}PF_6$ (**12b**)	2027 s, 1975 s
$\{Cp(CO)_2Fe[CH(SMe)(PClPh_2)]\}BF_4$ (**13**)	2030 s, 1982 s
$\{Cp(CO)_2Fe[CH(SMe)(PCl_3)]\}BF_4$ (**14**)	2031 s, 1982 s
$\{Cp(CO)_2Fe[CH(SMe)(P(OPh)_3)]\}PF_6$ (**15**)	2032 s, 1986 s
$\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}CF_3SO_3$ (**16a**)	2041 s, 1992 s
$\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$ (**16b**)	2042 s, 1992 s
$\{Cp(CO)_2Fe[CH(SMe)(PPh_2H)]\}CF_3SO_3$ (**17**)	2033 s, 1980 s
$\{Cp(CO)_2Fe[CH(SMe)(P\text{-}c\text{-}Hx_2H)]\}CF_3SO_3$ (**18**)	2025 s, 1975 s
$\{Cp(CO)_2Fe[CH(SMe)(PPhH_2)]\}CF_3SO_3$ (**19**)	2036 s, 1987 s
$\{Cp(CO)_2Fe[CH(SMe)(P\text{-}c\text{-}HxH_2)]\}PF_6$ (**20**)	2036 s, 1986 s
$\{Cp(CO)_2Fe(PPh_2CH_2SMe)\}PF_6$ (**21**)	2057 s, 2012 s
$\{Cp(CO)_2Fe(P\text{-}c\text{-}Hx_2CH_2SMe)]\}CF_3SO_3$ (**22**)	2049 s, 2005 s
$Cp(CO)_2Fe[CH(SMe)PPh_2]$ (**23**)	2008 s, 1958 s

[a] In hexane solvent.

Table II. ^1H NMR Data for the Complexes[a]

complex	Cp	CH	SMe	other
5[b]	5.11	14.86 (br)[c]	3.00	
7[b]	5.15	15.24 (br)	3.12	
8[d]	4.84 (d, J_{PH} = 1.10)	14.94	2.99 (d, J_{PH} = 0.73)	7.4 (m, Ph)
9[d]	4.79 (d, J_{PH} = 1.10)	14.92	2.96	7.27 (m, Ph)
11[d]	5.16	3.75 (d, J_{PH} = 2.93)	1.36 (d, J_{PH} = 0.73)	7.7 (m, Ph), 2.45 (d, J_{PH} = 12.46, PMe)
12b[d]	5.25	4.28 (d, J_{PH} = 1.46)	1.67 (d, J_{PH} = 0.74)	7.35 (m, Ph)
13[d]	5.21	4.16 (d, J_{PH} = 11.73)	1.65	7.7 (m, Ph)
15[d]	5.25	3.41 (d, J_{PH} = 7.33)	2.12 (d, J_{PH} = 1.71)	7.35 (m, Ph)
16b[d]	5.13	2.67 (d, J_{PH} = 2.44)	2.22	4.74 (d, J_{PH} = 5.37, OCH_2), 0.94 (CMe)
17[d]	5.14	3.46 (dd, J_{PH} = 1.47, J_{HH} = 10.63)	1.59 (d, J_{PH} = 0.73)	7.22 (m, Ph), 7.45 (dd, J_{PH} = 501.31, J_{HH} = 10.63, PH)
18[d]	5.16	3.18 (dd, J_{PH} = 1.47, J_{HH} = 2.93)	2.21 (d, J_{PH} = 1.10)	1.83 (m, c-Hx), 5.78 (dm, J_{PH} = 439, PH)
19[d]	5.18	3.06 (dd, J_{PH} = 1.28, J_{HH} = 9.9)	1.79	[7.25 (dm, J_{PH} = 482.02), 6.98 (dm, J_{PH} = 502.18) PH], 7.7 (m, Ph)
20[e]	5.15	2.87 (dm, J_{PH} = 7.7)	2.29	1.90–1.4 (m, c-Hx), [6.16 (dm, J_{PH} = 470.84), 5.83 (dm, J_{PH} = 472.29) PH]
21[b]	5.38 (d, J_{PH} = 1.46)		1.99 (d, J_{PH} = 1.46)	3.82 (d, J_{PH} = 6.1, SCH_2), 7.7 (m, Ph)
22[d]	5.41 (d, J_{PH} = 1.47)		2.32 (d, J_{PH} = 1.84)	3.21 (d, J_{PH} = 9.53, SCH_2), 1.83 (m, c-Hx)
23[g]	4.36	3.50 (d, J_{PH} = 4.39)	1.56	7.91-7.1 (m, Ph)

[a] Chemical shifts in δ and coupling constants in hertz. [b] CD_2Cl_2 solvent. [c] δ 15.79 in CF_3SO_3H solvent. [d] CD_3CN solvent. [e] $CDCl_3$ solvent. [f] CD_3NO_2 solvent. [g] C_6D_6 solvent.

7 are sparingly soluble in CH_2Cl_2 but dissolve readily in THF, MeCN, and CF_3SO_3H.

Complexes **3** and **4** react analogously with CF_3SO_3H to give the corresponding carbene complexes $\{Cp(CO)(PPh_3)Fe[CH(SMe)]\}CF_3SO_3$, **8**, and $\{Cp(CO)(P(OPh)_3)Fe[CH(SMe)]\}CF_3SO_3$, **9**, which, although they are more resistant to reaction with moisture, could only be obtained as oils which were characterized by their IR and NMR spectra (Tables I and II).

The ν(CO) absorptions of **5** and **6** (2067 and 2027 cm^{-1} in CH_2Cl_2) are somewhat lower than those (2085 and 2043 cm^{-1} in CH_3NO_2)[11] in the oxygen analogue $Cp(CO)_2Fe[CH(OMe)]^+$, **10**; these results suggest that the SMe group has a higher σ donor/π acceptor ratio than OMe, a trend that was observed previously[5] in other related carbene complexes. In the proton NMR spectrum (Table II) of **5** in CD_2Cl_2 solvent, the carbene proton occurs as a broad singlet at δ 14.86 which is downfield from that (δ 12.88 in CF_3CO_2H)[11] observed for the corresponding proton in **10**;

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[11] Cutler, A. *J. Am. Chem. Soc.* **1979**, *101*, 604.

Table III. ^{13}C NMR Data for the Complexes in CD_3CN Solvent[a]

complex	CO	Cp	SMe	CH	other
9	212.2 (d, J_{PC} = 39.07)	88.8	34.6	320.6 (d, J_{PC} = 33.21)	[150.5 (d, J_{PC} = 9.7), 130.7, 126.5, 121.0 (d, J_{PC} = 5.85) Ph]
11	214.5	89.3	22.5	7.5 (d, J_{PC} = 25.4)	[134.7 (d, J_{PC} = 3.9), 133–130, 127.7, 126.6, 124.3, 123.2, Ph], 5.4 (d, J_{PC} = 11.72, PMe)
12b	215.5 (d, J_{PC} = 5.86), 213.0	89.7	23.2	6.0 (d, J_{PC} = 25.39)	[135.1 (d, J_{PH} = 7.81), 130.5 (d, J_{PH} = 11.72), 125.7, 122.0 Ph]
13	214.4 (d, J_{PC} = 5.86), 213.2	89.3	22.7	12.7 (d, J_{PC} = 15.62)	[136.3, 134.0, 133.6, 126.5, 122.7, Ph]
15[b]	214.5, 213.6	88.1	20.5	10.8 (d, J_{PC} = 130.86)	[150.7 (d, J_{PC} = 13.68), 131.7, 128.3 (d, J_{PC} = 3.90), 120.6, Ph]
16b	214.0 (d, J_{PC} = 3.66), 213.1	87.4	23.5	−5.1 (d, J_{PC} = 101.32)	80.7 (d, J_{PC} = 6.1, OCH_2), 36.3 (d, J_{PC} = 34.2, *C*Me), 13.0 (C*Me*)
17[c]	214.9 (d, J_{PC} = 5.86), 213.8	88.5	23.3	5.6 (d, J_{PC} = 21.49)	135–130 (Ph)
18	216.2 (br), 215.0	89.2	23.3	−1.3 (d, J_{PC} = 19.53)[d]	34–26 (c-Hx)
19[b]	213.3 (br), 212.3[e]	87.6	22.2	1.5 (d, J_{PC} = 11.72)	135–130 (Ph)
20	214.2 (d, J_{PC} = 5.86), 213.8	87.6	22.4	−4.3 (d, J_{PC} = 19.53)	[31.8 (d, J_{PH} = 37.11), 28.3, 26.5, 25.9, c-Hx]

[a] Chemical shifts in ppm and coupling constants in hertz. [b] $(CD_3)_2CO$ solvent. [c] CD_3NO_2 solvent. [d] $CDCl_3$ solvent. [e] CD_2Cl_2 solvent.

similar chemical shift differences for the S and O analogues of $(Ph_3P)_2(CO)(L)Os[CH(XMe)]^+$[6] and $Cp(Ph_3P)(NO)Re[CH(XMe)]^+$[7,12] (X = O, S) were previously reported.

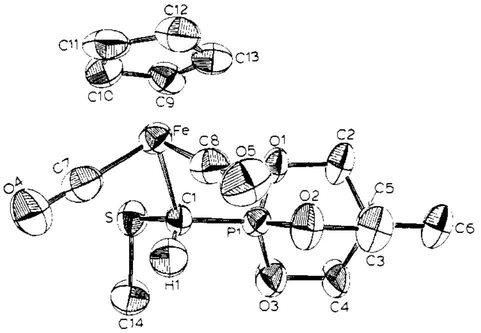

Figure 1. ORTEP drawing of $Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]^+$.

The instabilities of **5**–**7** made it impossible to obtain their ^{13}C NMR spectra. However, the more stable $P(OPh)_3$-substituted complex **9** in CD_3CN solvent gives a ^{13}C NMR spectrum which exhibits a doublet for the C(carbene) at 320.6 ppm (J_{PC} = 33.21 Hz). Interestingly, the spectrum also shows the cyanocarbon of the solvent as a broad peak at 132.2 ppm, as compared with 118.2 ppm for pure CD_3CN. The broadening and downfield shift may be due to a weak interaction between the nitrogen lone pair of the acetonitrile and the electrophilic C(carbene) of **9**. To our knowledge, no carbene–acetonitrile adducts have been isolated; however, ion cyclotron resonance experiments have detected $Cp(CO)_2Fe(CH_2NCMe)^+$ as a product of the gas-phase reaction between $Cp(CO)_2FeCH_2^+$ and MeCN.[13]

Reactions of $Cp(CO)_2Fe[CH(SMe)]^+$ with Tertiary Phosphines and Phosphites. The C(carbene) atom of transition-metal carbene complexes is frequently the site of attack by a variety of nucleophiles.[14] Phosphines are among the nucleophiles which react in this manner. Recent examples are the reactions of $Cp(CO)_2Fe[CH(Me)]^+$,[9] $Cp(CO)_2Fe[CMe_2]^+$,[15] and $(CO)_5W[CH(Ph)]$[15] with PPh_3 or $P(OMe)_3$ to give the stable adducts $Cp(CO)_2Fe[CH(Me)(PPh_3)]^+$, $Cp(CO)_2Fe[CMe_2(P(OMe)_3)]^+$, and $(CO)_5W[CH(Ph)(PPh_3)]$. Similarly, $Cp(CO)_2Fe[CH(SMe)]^+$ reacts at room temperature with a range of tertiary phosphines and phosphites to give the adducts $Cp(CO)_2Fe[CH(SMe)(L)]^+$ according to eq 3. All of the

$$Cp(CO)_2Fe[CH(SMe)]^+ + L \rightarrow Cp(CO)_2Fe[CH(SMe)(L)]^+ \quad (3)$$

$$L = PPh_2Me\ (\mathbf{11}),\ PPh_3\ (\mathbf{12}),\ PPh_2Cl\ (\mathbf{13}),\ PCl_3\ (\mathbf{14}),\ P(OPh)_3\ (\mathbf{15}),\ P(OCH_2)_3CMe\ (\mathbf{16})$$

adducts were isolated except that of PCl_3 which was unstable and characterized only by its IR spectrum (Table I) which was very similar to that of the other much more stable adducts. There was no adduct formation between **5** and MeCN, THF, Me_2S, or $AsPh_3$.

The ^1H NMR resonance of the methine hydrogen, which occurs as a doublet due to coupling with the P atom, in these adducts (Table II) is upfield, as much as 12 ppm, from that of the parent carbene complex and is in the range of saturated iron–alkyl complexes such as $Cp(CO)_2Fe[CH(SMe)_2]$[5] (δ 3.97) and $Cp(CO)_2Fe[C(H)S(CH_2)_3S]$ (δ 4.01).[16] In their ^{13}C NMR spectra (Table III), the methine carbon occurs as a doublet due to ^{31}P coupling; it has a chemical shift in the range of −5 to 12 ppm. These chemical shifts compare with −23.3 ppm for the methine carbon in $[Cp(CO)_2FeCH_2PPh_3]BF_4$.[17]

The two CO groups frequently are observed as three lines in ^{13}C spectra of the adducts (Table III). Since the methine carbon is a chiral center, the two CO groups are nonequivalent and would be expected to have different chemical shifts and different coupling constants to the P atom. Thus, the three lines probably arise from a significantly larger J_{PC} coupling constant to one of the CO ligands than to the other. This type of diastereotopism was previously observed in $Cp(CO)_2Fe[CH(OMe)Me]$.[18] In the PPh_2Me adduct **11**, the optically active center also causes the phenyl carbon resonances of the PPh_2Me ligand to be nonequivalent; thus two sets of these resonances are observed.

To ensure that the ylide ligands $[CH(SMe)(PR_3)]$ were bonded to the iron through the carbon rather than the

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(12) Tam, W.; Lin, G. Y.; Wong, W. K.; Kid, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(13) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2584.

(14) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(15) (a) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (b) Casey, C. P.; Polichnowski, S. W.; Schusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282.

(16) McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* **1981**, *20*, 4108.

(17) Reger, D. C.; Culbertson, E. C. *J. Organomet. Chem.* **1977**, *131*, 297.

(18) Brookhart, M.; Tucker, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.

Table IV. Bond Angles (deg) and Distances (Å) and Their Standard Deviations (in Parentheses) for $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$ [a]

A. Angles

Fe-C7-O4	176.8 (11)	H1-C1-P1	108.8 (-)
Fe-C8-O5	175.7 (10)	S-C1-P1	111.1 (5)
Fe-C1-H1	97.2 (-)	C14-S-C1	103.0 (5)
Fe-C1-S	110.9 (4)	C7-Fe-C8	94.5 (5)
Fe-C1-P1	112.8 (4)	C1-Fe-C7	87.5 (4)
H1-C1-S	115.3 (-)	C1-Fe-C8	92.9 (4)

B. Distances

Fe-C1	2.085 (9)	Fe-C13	2.16 (1)
Fe-C7	1.78 (1)	C7-O4	1.13 (1)
Fe-C8	1.78 (1)	C8-O5	1.14 (1)
Fe-C9	2.13 (1)	C1-S	1.809 (9)
Fe-C10	2.11 (1)	C1-H1	1.054 (-)
Fe-C11	2.08 (1)	C1-P1	1.732 (9)
Fe-C12	2.12 (1)	S-C14	1.82 (1)

[a] In Tables IV and V, the values in parentheses denote the estimated standard deviations in the last digits.

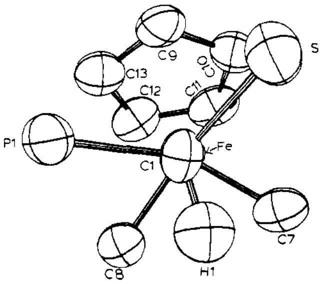

Figure 2. Newman projection of the $CpC_2FeCHSP$ core viewing down the C1–Fe bond. Torsion angles (deg): C7–Fe–C1–H1 (43.4°); C7–Fe–C1–P1 (157.4°); C7–Fe–C1–S (77.2°); C8–Fe–C1–S (171.5°); C8–Fe–C1–P1 (63.0°); C8–Fe–C1–H1 (50.9°).

sulfur, which was the case in $(CO)_5W[C(SMe)_2PR_3]$,[19] an X-ray structural determination of $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$, **16b**, was undertaken. The overall molecular structure of the cation is a three-legged piano stool in which the CO groups and the methine carbon C1 are the legs (Figure 1). The angles (Table IV) between the legs average 91.6° which is slightly greater than that (90°) expected for a regular octahedron. A Newman projection down the C1–Fe bond (Figure 2) shows that the complex adopts a sterically hindered staggered conformation with the bulky $P(OCH_2)_3CMe$ and SMe groups nearest the Cp ring.

The Fe–C1 bond distance in **16b**, 2.085 (9) Å, is comparable to Fe–C single bond distances in $Cp(CO)_2Fe–R$ complexes which range from 2.06 to 2.11 Å.[16,20-24] It is longer than that (2.036 Å) in $Cp(CO)_2Fe[CH_2(SMe_2)]^+$.[25] The C1–S bond length (1.809 (9) Å) in **16b** is very similar to those obtained in microwave studies of MeSH (1.819 Å)[26] and Me_2S (1.802 Å).[27] The P1–C1 distance (1.732 (9) Å) is in the general range for terminal phosphine carbene adducts: $Me_3AuCH_2PPh_3$ (1.755 Å),[28] $(CO)_3Ni[CH(Me)\text{-}P\text{-}c\text{-}Hx_3]$ (1.745 Å),[29] *trans*-$[Pt(CH_2PEt_3)(PEt_3)_2I]^+$ (1.77 Å),[30] and $\{(1,5\text{-}C_8H_{12})Pd[CH(SiMe_3)PPhMe_2](SiMe_3)Cl\}^+$ (1.780 Å).[31] Thus the P1–C1 bond may be considered predominately a single bond.

Table V. Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)[a] $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$

atom	*x*	*y*	*z*
Fe	0.2654 (1)	0.3525 (1)	0.2579 (1)
S	0.1779 (2)	0.3879 (2)	0.0648 (1)
P1	0.4451 (2)	0.3198 (2)	0.1107 (1)
O1	0.4991 (5)	0.4376 (4)	0.1160 (4)
O2	0.5394 (6)	0.2489 (5)	0.1673 (4)
O3	0.4634 (6)	0.2823 (6)	0.0219 (4)
O4	0.0277 (8)	0.2254 (7)	0.2486 (5)
O5	0.4294 (8)	0.1764 (6)	0.3287 (4)
C1	0.2864 (8)	0.3096 (7)	0.1356 (5)
C2	0.6396 (10)	0.4476 (9)	0.1032 (7)
C3	0.6764 (10)	0.2538 (8)	0.1488 (6)
C4	0.6033 (10)	0.2930 (11)	0.0007 (6)
C5	0.6853 (9)	0.3356 (8)	0.0755 (6)
C6	0.8297 (11)	0.3414 (10)	0.0569 (7)
C7	0.1211 (11)	0.2733 (8)	0.2503 (6)
C8	0.3661 (11)	0.2441 (8)	0.2981 (6)
C9	0.2904 (12)	0.5205 (8)	0.2314 (7)
C10	0.1706 (11)	0.5038 (8)	0.2647 (7)
C11	0.1927 (12)	0.4592 (8)	0.3422 (7)
C12	0.3336 (13)	0.4475 (9)	0.3622 (6)
C13	0.3902 (11)	0.4849 (8)	0.2896 (7)
C14	0.1492 (13)	0.2976 (12)	0.9763 (7)
P2	0.2111 (3)	0.9609 (3)	0.1274 (2)
F1	0.1081 (9)	0.0540 (7)	0.1006 (6)
F2	0.3126 (9)	0.8683 (6)	0.1571 (5)
F3	0.2901 (10)	0.0413 (7)	0.1861 (7)
F4	0.1344 (13)	0.9374 (11)	0.2079 (8)
F5	0.2873 (15)	−0.0130 (16)	0.0583 (8)
F6	0.1252 (16)	0.8784 (10)	0.0795 (12)

[a] Positional parameters are listed in fractional unit-cell coordinates.

Adducts **12a** and **16b** are thermally stable when refluxed in CH_2Cl_2 and THF for 2 h and heated to 100 °C in the solid state under an N_2 atmosphere for 15 min. However, when heated for 2 h at 200 and 180 °C, respectively, **12a** and **16b** are converted to $[Cp(CO)_2Fe(PPh_3)]BF_4$ (88%) and $[Cp(CO)_2Fe(P(OCH_2)_3CMe)]PF_6$ (65%), respectively (eq 4). These products were identified by comparing their

$$Cp(CO)_2Fe[CH(SMe)(L)]^+ \xrightarrow{\Delta} Cp(CO)_2Fe(L)^+ + cis/trans\text{-}(MeS)CH{=}CH(SMe) + HC(SMe)_3 + Cp_2Fe \tag{4}$$

$$L = PPh_3\ (\mathbf{12a}),\ P(OCH_2)_3CMe\ (\mathbf{16b})$$

spectra with those of authentic samples prepared via the reaction of $Cp(CO)_2Fe(THF)^+$ and L.[32] The CCl_4-soluble products from the pyrolysis of **12a** were separated and identified by GC–MS spectra as *cis*- and *trans*-(MeS)-CH=CH(SMe) in about equal amounts, $HC(SMe)_3$, and ferrocene. Although the formation of the olefin probably results from some type of coupling of two CH(SMe) fragments, the origin of the $HC(SMe)_3$ is not obvious.

Reactions of $Cp(CO)_2Fe[CH(SMe)]^+$ with Primary and Secondary Phosphines. Like the reactions with tertiary phosphines (eq 3), R_2PH and RPH_2 (R = Ph or

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[19] Pickering, R. A.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 817.

[20] Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* **1966**, *88*, 4371.

[21] Churchill, M. R.; Ni Chang, S. W. Y. *J. Am. Chem. Soc.* **1973**, *95*, 5931.

[22] Pope, L.; Sommerville, P.; Laing, M.; Hindson, K. J.; Moss, J. R. *J. Organomet. Chem.* **1976**, *112*, 3090.

[23] Grompper, R.; Bartmann, E.; Nöth, H. *Chem. Ber.* **1979**, *112*, 218.

[24] Ariyaratue, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1969**, 1309.

[25] O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1809.

[26] Kojima, T.; Nichikawa, T. J. *J. Phys. Soc. Jpn.* **1957**, *12*, 680.

[27] Pierce, L.; Hayashi, M. J. *J. Chem. Phys.* **1961**, *35*, 479.

[28] Stein, J.; Fackler, J. P., Jr.; Paparizos, C.; Chen, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 2192.

[29] Bannett, B. C.; Kruger, C. *J. Cryst. Mol. Struct.* **1972**, *2*, 271.

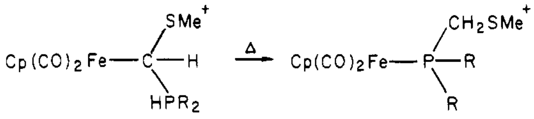
[30] Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Organomet. Chem.* **1982**, *228*, C71.

[31] Buchanan, R. K.; Pierpont, C. G. *Inorg. Chem.* **1979**, *12*, 3608.

[32] Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

c-Hx) react with $Cp(CO)_2Fe[CH(SMe)]^+$ at room temperature to give air-stable adducts $Cp(CO)_2Fe[CH(SMe)(L)]^+$ in moderate isolated yields: $\{Cp(CO)_2Fe[CH(SMe)(PHPh_2)]\}CF_3SO_3$, **17**, 62%; $\{Cp(CO)_2Fe[CH(SMe)(PH\text{-}c\text{-}Hx_2)]\}CF_3SO_3$, **18**, 39%; $\{Cp(CO)_2Fe[CH(SMe)(PH_2Ph)]\}CF_3SO_3$, **19**, 58% $\{Cp(CO)_2Fe[CH(SMe)(PH_2\text{-}c\text{-}Hx)]\}PF_6$, **20**, 52%. The large J_{PH} coupling constants (470–502 Hz) observed in the ^1H NMR spectra of these complexes (Table II) are characteristic[33] of H atoms bound directly to a phosphorus atom. The ^{31}P NMR spectrum of **20** consists of an apparent triplet with a J_{PH} value of 470 Hz. The two PH hydrogens in **19** and **20** are diastereotopic because of the adjacent chiral methine carbon and have different chemical shifts and J_{PH} coupling constants (Table II). These NMR results, together with the $\nu(CO)$ values which are very similar to those of the tertiary phosphine adducts, indicate that complexes **17**–**20** are simple adducts as found for the tertiary phosphines and phosphites.

There was some reason to expect the primary and secondary phosphine adducts to rearrange to give an Fe–P bond. It has been observed[34] that the reaction of $(CO)_5Cr[C(OMe)Ph]$ with Me_2PH gives the adduct $(CO)_5Cr[C(OMe)(Ph)(PMe_2H)]$ which upon stirring in acetone rearranges to give the phosphine complex $(CO)_5Cr[P(Me)_2[CH(Ph)(OMe)]]$. Also the reaction of $(CO)_5W[C(SMe)_2]$ with PPh_2H is believed to initially give the adduct, which rapidly rearranges to yield the final phosphine product $(CO)_5W[PPh_2[CH(SMe)_2]]$.[3,19] In contrast to these examples, **17** is stable in acetone for at least 12 h and shows no noticeable decomposition in refluxing CH_2Cl_2 or THF for 2 h. However, when heated in the solid state at 168 °C, **17** rapidly rearranges to give a low yield (20%) of $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}PF_6$, **21** (after exchange of the $CF_3SO_3^-$ anion for PF_6^-). Likewise, **18** is converted into $\{Cp(CO)_2Fe[P\text{-}c\text{-}Hx_2(CH_2SMe)]\}CF_3SO_3$, **22**, (20% yield) upon heating at 200 °C (eq 5).



$$Cp(CO)_2Fe{-}\overset{SMe^+}{\underset{HPR_2}{C}}{-}H \xrightarrow{\Delta} Cp(CO)_2Fe{-}\overset{CH_2SMe^+}{\underset{R}{P}}{-}R \qquad (5)$$

21, R = Ph
22, R = c-Hx

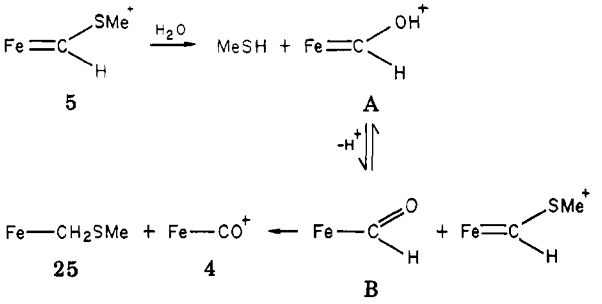
Other products of the pyrolysis are not soluble in common organic solvents. IR spectra (Table I) of **21** and **22** show two strong $\nu(CO)$ bands in the region characteristic of $Cp(CO)_2Fe(PR_3)^+$ complexes.[35] In their ^1H NMR spectra (Table II), the PH signal is no longer present and a new resonance appears with $J_{PCH} < 10$ Hz, which is consistent with values (0.5–20 Hz) for phosphines of the type R_2PCH_2R.[33]

The P-H proton in **17** is readily removed with n-BuLi at −78 °C to give $Cp(CO)_2Fe[CH(SMe)PPh_2]$, **23**, predominately; the reaction can be reversed by adding CF_3SO_3H (eq 6). Likewise, **23** may be formed from **17** by

$$\underset{\mathbf{17}}{Cp(CO)_2Fe[CH(SMe)(PPh_2H)]^+} \underset{CF_3SO_3H}{\overset{n\text{-BuLi or }Et_3N}{\rightleftharpoons}} \underset{\mathbf{23}}{Cp(CO)_2Fe[CH(SMe)(PPh_2)]} \qquad (6)$$

deprotonation with Et_3N in CH_2Cl_2 at room temperature.

Scheme I



Fe = $Cp(CO)_2Fe$

In both reactions, small amounts (5–10%) of the rearranged product $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}CF_3SO_3$ are also formed. The air-sensitive **23**, which was characterized by its IR and NMR spectra (Tables I and II), reacts rapidly with $MeOSO_2F$ to give an 82% yield of $\{Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]\}PF_6$, **11**, whose spectra are identical with those of **11** prepared from **5** and PPh_2Me (eq 3). Thus the P atom in **23** behaves as a moderately nucleophilic phosphine in its reactions with CF_3SO_3H and $MeOSO_2F$.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with H_2O. Compound **5** is very sensitive to moisture and reacts upon contact with water to give $[CpFe(CO)_3]CF_3SO_3$, **24**, and $Cp(CO)_2FeCH_2SMe$, **25**, in a 1:1 ratio. The latter product, **25**, was identified by comparing its IR and ^1H NMR spectra with an authentic sample prepared by the reaction of $CpFe(CO)_2^-$ and $ClCH_2SMe$.[36] In addition, MeSH was identified by GC to be the major organic product. Thus, the H_2O reaction proceeds according to eq 7. In order to gain some understanding of the mechanism of this reaction, the deuterated analogue of **5**, $Cp(CO)_2Fe[CD(SMe)]CF_3SO_3$, was reacted with H_2O under the same room-temperature conditions. The mass spectrum of product **25** did not show a parent ion for $Cp(CO)_2FeCD_2SMe$ (M), but two intense peaks for fragments resulting from the loss of one and two CO groups, M − CO at *m/e* 212 and M − 2CO at *m/e* 184, from this dideuterated compound were observed. Thus, both deuterium atoms in $Cp(CO)_2FeCD_2SMe$ originated from $Cp(CO)_2Fe[CD(SMe)]^+$ and the H_2O hydrogen is not involved.

$$\underset{\mathbf{5}}{2Cp(CO)_2Fe[CH(SMe)]CF_3SO_3} + H_2O \rightarrow \underset{\mathbf{25}}{Cp(CO)_2Fe(CH_2SMe)} + \underset{\mathbf{24}}{[CpFe(CO)_3]CF_3SO_3} + MeSH \qquad (7)$$

A possible mechanism for this reaction is shown in Scheme I. Given the electrophilic character of the carbene ligand in **5**, the initial step is probably H_2O attack at the carbene followed by loss of MeSH with formation of the hydroxycarbene intermediate A. Although there is no spectroscopic evidence for A, a related hydroxycarbene $Cp(CO)_2Fe[C(OH)Me]^+$ has been prepared[37] and shown to be in equilibrium with $Cp(CO)_2Fe[C({=}O)Me]$ and H^+. Similarly, $Cp(NO)(PPh_3)Re[C({=}O)H]$ is reversibly protonated to give the hydroxycarbene $Cp(NO)(PPh_3)Re[C(OH)H]^+$.[12] Moreover, $(PPh_3)_2(CO)_2(Cl)Os[CH(SMe)]^+$ has been reported[6] to react with H_2O, yielding the stable formyl complex $(PPh_3)_2(CO)_2(Cl)Os[C({=}O)H]$. Thus, H^+ dissociation from A to give the formyl intermediate B is quite resonable. An attempt to detect B by ^1H NMR

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[33] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974; p 180.

[34] Kreissel, H.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262.

[35] Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

[36] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 486.

[37] Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188.

spectrometry at −40° C in CD_2Cl_2 was unsuccessful; however, it might be expected to be unstable and transfer a hydride ion to unreacted starting carbene as in the last step of Scheme I. Many formyl complexes are known to be excellent hydride donors.[38a] For example, in a reaction very similar to the last step in Scheme I, $Cp(NO)(PPh_3)Re[C(=O)H]$ readily transfers H^- to $Cp(NO)(PPh_3)Re(CH_2)^+$ to afford $Cp(NO)(PPh_3)Re(CO)^+$ and $Cp(NO)(PPh_3)Re(CH_3)$.[12] Likewise, the reaction of $Cp(CO)_2Fe[CH(OMe)]^+$ with I^- to give MeI, $Cp(CO)_2FeCH_2OMe$, and $CpFe(CO)_3^+$ is postualted to proceed through the formyl intermediate B which transfers a hydride to $Cp(CO)_2Fe[CH(OMe)]^+$ to give the observed products.[11] There is good evidence[38b] for the existence of $Cp(DPPE)Fe[C(=O)H]$. These related studies, together with the deuterium labeling experiment and the observed 1:1 ratio of **24**–**25**, indicate that Scheme I is a reasonable pathway for reaction 7.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with CH_2N_2. When CH_2N_2–Et_2O is added to a CH_2Cl_2 solution of **5**, gas evolution, presumably N_2, is apparent (eq 8).

$$\underset{\mathbf{5}}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} + CH_2N_2 \rightarrow \underset{\mathbf{26}}{\{Cp(CO)_2Fe[SMe(CH{=}CH_2)]\}CF_3SO_3} + N_2 \quad (8)$$

After 45 min of reaction, the vinyl methyl sulfide complex $\{Cp(CO)_2Fe[SMe(CH{=}CH_2)]\}CF_3SO_3$, **26**, is obtained in 76% yield as a yellow oil, which crystallizes with difficulty to give red needles of **26** (10%). The compound was characterized by its IR, ^1H NMR, and ^{13}C NMR spectra which suggest that the $MeSCH{=}CH_2$ ligand is coordinated to the Fe through the sulfur rather than the olefin. The vinyl protons in the ^1H NMR spectrum of **26** occur as an ABX pattern (see Experimental Section) and are shifted to lower field than those in the free olefin $MeSCH{=}CH_2$[39] as expected for S bonding. Coordination through the double bond of an olefin often results in an upfield shift of the olefin protons.[40,41] While there are many known $Cp(CO)_2Fe(olefin)^+$[41] and $Cp(CO)_2Fe(SR_2)^+$[35,42,43] complexes, **26** is the first example of a vinyl sulfide complex, and it appears to prefer coordination through the S atom. The $\nu(CO)$ values of **26** are very close to those reported for $Cp(CO)_2Fe(SR_2)^+$ complexes.[35,42,43] The vinyl carbon atoms in the ^{13}C NMR spectrum of **26** are observed at 130.8 and 124.1 ppm, which are characteristic of unsaturated carbons,[44] whereas olefinic carbons of η^2-olefinic complexes of Fe often occur below 100 ppm.[41] Thus, the spectroscopic results support S atom coordination of the $MeSCH{=}CH_2$ ligand in **26**.

A few other reactions of carbene complexes with CH_2N_2 have been reported to lead either to η^2-olefin complexes[45] or free olefins.[14,46] In these reactions, as in eq 8, it is likely that the carbene ligand is initially attacked by CH_2N_2 to give an intermediate which liberates N_2 and rearranges to the final product.

Experimental Section

General Procedures. All reactions were carried out under an N_2 atmosphere. CH_2Cl_2 was dried over CaH_2; THF was distilled from Na–benzophenone, and Et_2O was distilled from K–benzophenone before use. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer; band positions were calibrated against gaseous CO and are believed to be accurate to within ±2 cm^{-1}. Proton NMR spectra were obtained with Varian 360 (60 MHz), Perkin-Elmer R20B (60 MHz), or JEOL FX-90Q (89.55 MHz) spectrometers. ^{13}C NMR spectra were obtained with Bruker WM 300 (75.43 MHz) or JEOL FX-90Q (22.5 MHz) instruments. ^{31}P spectra were run on the Bruker WM 300 (121.44 MHz) spectrometer. To reduce data acquisition time, $Cr(acac)_3$ (35 mg/mL) was added to ^{13}C and ^{31}P samples. Chemical shifts of ^1H and ^{13}C nuclei are reported in δ units relative to tetramethylsilane (Me_4Si); ^{31}P resonances upfield from the H_3PO_4 internal reference (in a capillary insert) are given in negative values (ppm).

GC traces were recorded on a Varian 1700 gas chromatograph equipped with a 30-ft 5% SE30 capillary column. Mass spectra and GC–MS spectra were performed on a Finnigan 400 GC-MS with an INCOS 2300 data system, GC Model 9610. Decomposition and melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

All alkylphosphines and $P(OPh)_3$ were purchased from Strem Chemical and used without further purification. A sample of $P(OCH_2)_3CMe$ was kindly supplied by Steve Socol; PCl_3 and $ClPPh_2$ were distilled before use. CH_2N_2–Et_2O[47] and $ClCH_2SMe$[48] were synthesized according to the literature references; CH_2N_2–Et_2O was dried with anhydrous Na_2CO_3 before use.

Samples of $LiAlH_4$, $LiAlD_4$, $LiAl(O\text{-}t\text{-}Bu)_3H$, and n-BuLi (2.5 M in hexane) were obtained from Alfa; $Li(BEt_3H)$ (1 M in THF), HBF_4–Et_2O, CF_3SO_3H, and $(Ph_3C)PF_6$ were purchased from Aldrich; $(Cp(CO)_2Fe)_2$ was obtained from Strem Chemical, and $MeOSO_2F$ was acquired from Tridom Chemical (Fluka).

The exchange of PF_6^- with other anions was performed by dissolving the desired complex in either acetone containing 10 equiv of $(NH_4)PF_6$ or acetonitrile with 10 equiv of KPF_6. The mixture was stirred for 0.5 h, and the solvent was removed under reduced pressure. The resulting residue was extracted with CH_2Cl_2, the combined extracts were filtered through a frit, and the resulting solution was concentrated under reduced pressure. A layer of another organic solvent (Et_2O, hexane, or EtOH) was placed over the CH_2Cl_2 solution, and the mixture was slowly chilled to −20 °C to induce crystallization.

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$, 2, from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$, 1, and $Li(AlH_4)$. A solution of 100 mL of THF containing $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$, **1**,[49] (0.10 g, 0.23 mmol) was treated with $Li[AlH_4]$ (0.020 g, 0.47 mmol); the yellow solution turned dark brown immediately and evolution of gas was apparent. The mixture was stirred for an additional 20 min, and the solvent was then removed under reduced pressure to afford a smelly brown solid. The residue was then extracted by rapidly stirring for 30 min with 20 mL of hexane. The resulting extract was then filtered through Celite on a glass frit under an N_2 atmosphere. Upon evaporation under reduced pressure, a yellow oil of $Cp(CO)_2Fe[CH(SMe)_2]$ (0.056 g, 85%), **2**, was obtained. The IR and ^1H NMR spectra of the oily **2** were in accord with the previously recorded spectra of this compound;[5] the oil was used in subsequent reactions without further purification. When this reaction was scaled up 10-fold, the major organometallic product obtained upon extraction was $[Cp(CO)_2Fe]_2$.

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$, 2, from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$, 1, and $Li(Et_3BH)$. A suspension of **1** (2.0 g, 4.6 mmol) in 20 mL of THF was treated dropwise with $Li(Et_3BH)$ (4.8 mL, 4.8 mmol), diluted with 5 mL of THF, via a 25 mL addition funnel in a period of 15 min. The deep brown mixture was allowed to react for an additional 20 min; the solvent was removed in vacuo, affording a brown oil. The oil was extracted as described in the preceding synthesis to furnish **2** (1.3 g, 85%).

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[38] (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (b) Davies, S. G.; Simpson, S. J. *J. Organomet. Chem.* **1982**, *240*, C48.

[39] Ceccarelli, G.; Chiellini, E. *Org. Magn. Reson.* **1970**, *2*, 409.

[40] Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 1653.

[41] Faller, J. S.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101.

[42] Sawai, T.; Martin, J. P.; Butler, I. S.; Simkin, D. *J. Phys. (Orsay, Fr.)* **1974**, *35*, *Suppl. 6*, 247.

[43] William, W. E.; Lalor, F. J. *J. Chem. Soc.* **1973**, *1329*.

[44] Kalabin, G. A.; Trofimov, B. A.; Bzhezovskii, V. M.; Kushnarev, D. F.; Amasova, S. V.; Gusmova, N. K.; Al'pert, M. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, *24*, 501.

[45] Mitsudo, T.; Watanabe, H.; Watanabe, K.; Watanabe, Y.; Takegami, Y. *J. Organomet. Chem.* **1981**, *214*, 87.

[46] Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. *Tetrahedron Lett.* **1973**, 1421.

[47] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 191, Procedure B.

[48] Bardwell, F. G.; Pitt, B. M. *J. Am. Chem. Soc.* **1955**, *77*, 572.

[49] McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231.

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$, 2, from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$, 1, and $Li[Al(O\text{-}t\text{-}Bu)_3H]$. A sample of 1 (2.0 g, 4.6 mmol) was suspended in 20 mL of THF, $Li[Al(O\text{-}t\text{-}Bu)_3H]$ (1.5 g, 5.8 mmol) was added, and the mixture was stirred for 30 min. The solvent was then evaporated under vacuum, and the resulting residue was extracted as noted above. This gave a mixture of 2 and a white inert solid which totaled 1.5 g. The concentration of 2 in the mixture was determined by the intensities of the ν(CO) absorbances of the complex to be 80–85%. This mixture was used directly in the preparations of 5, 6, and 7.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)]\}X$ [X = CF_3SO_3 (5), BF_4 (6)]. A rapidly stirred solution containing 2 (0.10 g, 0.35 mmol) in 15 mL of Et_2O was treated dropwise via a syringe with CF_3SO_3H until precipitation ceased (ca. 50 μL); a golden precipitate and MeSH, identified by its disagreeable odor, were found. The solvent was carefully removed by decantation, and the remaining solid was washed a few times with dry Et_2O and pumped dry to afford $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$, 5 (0.10 g, 74%). The complex is very sensitive to water and modestly to light and should be stored in the dark under N_2 at –20 °C. Even taking those precautions, decomposition of 5 is apparent after 2 weeks of storage. Thus, it is best used immediately.

A ^{13}C NMR spectrum of the compound was not obtained due to extensive decomposition during data acquisition even without the addition of $Cr(acac)_3$ which apparently accelerates the decompositon.

Like CF_3SO_3H, HBF_4–Et_2O also produced the corresponding carbene complex $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$, 6, in 75% yield upon reaction with 2. It exhibited similar spectral and stability characteristics to 5.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)]\}PF_6$, 7. A solution of 2 (0.20 g, 0.70 mmol) in 15 mL of dry Et_2O was transferred via cannula to a rapidly stirred solution of $(CPh_3)PF_6$ (0.18 g, 0.63 mmol) in 10 mL of CH_2Cl_2 at –40 °C. The resulting orange solution was slowly warmed to room temperature; a yellow precipitate had formed. An additional 15 mL of Et_2O was added to induce further precipitation. The suspension was filtered through a fine frit, and the remaining solid was washed with Et_2O and then dried under vacuum to afford the (0.20 g, 75%) crude product $\{Cp(CO)_2Fe[CH(SMe)]\}PF_6$, 7. The substance is sparingly soluble in CH_2Cl_2 and was recrystallized from CH_2Cl_2–Et_2O to afford golden platelike crystals, though it was found to occlude diethyl ether as established by its ^1H NMR spectrum.

Preparation of $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$. A sample of 1 (0.10 g, 0.23 mmol) was suspended in 100 mL of THF; $Li[AlD_4]$ (0.025 g, 0.60 mmol) was added, and the mixture was stirred for 20 min. The resulting brown solution was evaporated to dryness, and the remaining residue was extracted with hexane. Workup as for 2 gave $Cp(CO)_2Fe[CD(SMe)_2]$ (0.046 g, 70%). The crude product was then dissolved in 10 mL of Et_2O, and 30 μL of CF_3SO_3H was added. Following the established workup procedures for 5, $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ (0.041 g, 65%) was isolated. The ν(CO) absorptions of this product are identical with those of 5.

Synthesis of $\{Cp(CO)(PPh_3)Fe[CH(SMe)]\}CF_3SO_3$, 8. To 10 mL of a THF solution of $\{Cp(CO)(PPh_3)Fe[C(SMe)_2]\}PF_6$ (0.10 g, 0.15 mmol)[10] was added $(Et_3BH)Li$ (0.16 mL, 0.16 mmol) dropwise, and the mixture was allowed to react for 30 min. The solvent was then removed under vacuum, and the remaining residue was extracted with 20 mL of a mixture of hexane–diethyl ether (75:25), giving a yellow oil of $Cp(CO)(PPh_3)Fe[CH(SMe)_2]$, 3 (0.048 g, 62%), upon evaporation. This oily 3 was then dissolved in 5 mL of Et_2O, and 50 μL of CF_3SO_3H was injected into the solution, providing a bright yellow solution and oil. The solution was decanted, and the yellow oil was characterized by IR and ^1H NMR spectra to be 8 (0.041 g, 71%). The crude substance obtained could not be crystallized; it is slightly soluble in Et_2O and resists hydrolysis.

Synthesis of $\{Cp(CO)(P(OPh)_3)Fe[CH(SMe)]\}CF_3SO_3$, 9. As in the preparation of 8, $\{Cp(CO)(P(OPh)_3)Fe[C(SMe)_2]\}PF_6$ (0.10 g, 0.13 mmol)[10] reacted with $(Et_3BH)Li$ (0.15 mL, 0.15 mmol) in 10 mL of THF to give a yellow oil of $Cp(CO)(P(OPh)_3)Fe[CH(SMe)_2]$, 4 (0.056 g, 76%). The crude 4 further reacted with CF_3SO_3H (50 μL) in 5 mL of Et_2O to provide a yellow oil of 9 (0.047 g, 72%). Although it could not be recrystallized from CH_2Cl_2–Et_2O, spectral characterization indicated that it was quite pure. Like 8, 9 is moisture stable.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with $MePPh_2$. Freshly prepared 5 (0.12 g, 0.31 mmol) was suspended in 10 mL of CH_2Cl_2; $MePPh_2$ (0.10 g, 0.51 mmol) was added. The mixture was stirred for 20 min, giving a golden yellow solution. The solvent was removed under vacuum, and the resulting oily residue was washed a few times to remove excess phosphine. The anion of the remaining oil was metathesized with KPF_6 in MeCN. Recrystallization from CH_2Cl_2–Et_2O at –20 °C afforded deep orange crystals of $\{Cp(CO)_2Fe[CH(SMe)(MePPh_2)]\}PF_6$, 11 (0.13 g, 72%). Complex 11 is moisture and air stable and can be stored indefinitely at –20 °C under an N_2 atmosphere. Anal. Calcd for $C_{22}H_{22}O_2SP_2F_6Fe$: C, 45.37; H, 3.78. Found: C, 46.00; H, 4.08.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$ with PPh_3. Into a CH_2Cl_2 suspension of 6 (0.10 g, 0.31 mmol) was introduced PPh_3 (0.16 g, 0.62 mmol). The mixture was stirred until all of 6 went into solution (ca. 30 min). The solvent was then removed under reduced pressure, and the residue was washed with Et_2O. It was recrystallized from CH_2Cl_2–Et_2O at –20 °C, giving $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$, 12a (0.16 g, 86%). Complex 12a is a bright yellow, air-stable material; it may be stored at –20 °C under an N_2 atmosphere for months with no noticeable physical changes. Anal. Calcd for $C_{27}H_{24}O_2PSF_4BFe$: C, 55.32; H, 4.10. Found: C, 55.23; H, 4.06.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}PF_6$, 12b. Complex 5 (0.12 g, 0.31 mmol) was allowed to react with PPh_3 (0.16 g, 0.62 mmol) to give an oily product; the residue was metathesized with $[NH_4]PF_6$ in acetone. Upon workup and recrystallization from CH_2Cl_2–Et_2O at –20 °C, $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}PF_6$, 12b, was obtained in 82% yield: ^{31}P NMR (CD_3CN) 31.7 (s, PPh_3), –142.3 ppm (h, J_{PF} = 706.26 Hz, PF_6^-).

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(PPh_2Cl)]\}BF_4$, 13. A freshly distilled sample of PPh_2Cl (0.14 g, 0.62 mmol) was injected into a suspension of 6 (0.10 g, 0.31 mmol) in 10 mL of CH_2Cl_2. The reaction was allowed to proceed for 30 min. Upon recrystallization from CH_2Cl_2–Et_2O at –20 °C, dark orange crystals of $\{Cp(CO)_2Fe[CH(SMe)(PPh_2Cl)]\}BF_4$, 13 (0.11 g, 62%), were obtained. The material decomposes when exposed to the ambient environment for a few hours.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$ with PCl_3. A sample of 6 (0.10 g, 0.31 mmol) reacted with 100 μL of freshly distilled PCl_3 in 10 mL of CH_2Cl_2. An infrared spectrum of the solution showed two strong ν(CO) bands (2031, 1982 cm^{-1}) which are consistent with the phosphine adduct $\{Cp(CO)_2Fe[CH(SMe)(PCl_3)]\}BF_4$, 14. However, the product was not sufficiently stable to be isolated nor characterized by NMR spectrometry.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(P(OPh)_3)]\}PF_6$, 15. A sample of $P(OPh)_3$ (0.20 g, 0.67 mmol) was allowed to react with 5 (0.12 g, 0.31 mmol) in CH_2Cl_2 for 30 min. The resulting solution was pumped dry; the residue was metathesized with KPF_6 in MeCN and recrystallized from CH_2Cl_2–Et_2O at –20 °C, affording dark brown crystals of $\{Cp(CO)_2Fe[CH(SMe)(P(OPh)_3)]\}PF_6$, 15 (0.15 g, 72%). Compound 15 is quite stable toward moisture and air. Anal. Calcd for $C_{27}H_{24}O_5SP_2F_6Fe$: C, 46.83; H, 3.47. Found: C, 46.03; H, 3.66.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}X$ [X = CF_3SO_3 (16a), PF_6 (16b)]. A freshly sublimed sample of $P(OCH_2)_3CMe$ (0.10 g, 0.68 mmol) reacted with 5 (0.12 g, 0.31 mmol) to give crude $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}CF_3SO_3$, 16a, upon evaporation. The mixture was washed with Et_2O and then recrystallized from CH_2Cl_2–Et_2O at –20 °C to yield a golden powder of 16a (0.14 g, 87%). This compound exhibits remarkable stability toward air; it eventually turned black when exposed to laboratory lighting for a few days under N_2.

Since 16a was obtained in powder form and was not suitable for a single-crystal X-ray determination, it was metathesized with $(NH_4)PF_6$ in acetone. 16b was isolated in 64% yield from CH_2Cl_2–Et_2O at –20 °C. Microscopic crystals were found which were suitable for X-ray analysis: ^{31}P NMR (CD_3CN) 60.4 (s, $P(OCH_2)_3CMe$), –142.3 ppm (h, J_{PF} = 708.01 Hz, PF_6^-). Anal. Calcd for $C_{14}H_{18}O_5SP_2F_6Fe$: C, 31.71; H, 3.40. Found: C, 32.14; H, 3.50.

Pyrolysis of $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$, 12a. A 13-mg sample of 12a was sealed in a 2-mL prescored ampule under an atmosphere of N_2. The bottom one-third portion of the ampule was submerged in an oil bath maintained at 200 °C for 2 min; gas evolution was apparent. The ampule was then removed from the bath and cooled to room temperature; it was broken open leaving a mixture of an amber oil and a brown residue. The oily product was separated from the mixture by extraction with CCl_4; it was found to consist of four major products by GC. They were determined by their GC–MS spectra to be *cis*- and *trans*-1,2-bis(thiomethoxyl)ethylene, tris(thiomethoxyl)methane, and ferrocene. The remaining residue was recrystallized from CH_2Cl_2–Et_2O at −20 °C, affording bright yellow crystals of $[Cp(CO)_2Fe(PPh_3)]BF_4$ (10.4 mg, 88%). This product was characterized by its IR and ^1H NMR spectra, which are consistent with reported data[35] for this compound. GC–MS spectra of the CCl_4 solution (*m/e*): *cis*- and *trans*-(MeS)CH=CH(SMe) had very similar patterns, 122 (M + 2 for ^{34}S isotope; calcd 8.8% of M, found 8.6%), 120 (M), 105 (M − Me); $HC(SMe)_3$, 156 (M + 2 for ^{34}S isotope; calcd 13.2% of M, found 10.4%), 154 (M), 107 (M − SMe); Cp_2Fe, 186 (M), 121 (M − Cp), 56 (M − 2Cp).

Pyrolysis of $\{Cp(CO)_2Fe[CH(SMe)(P(OCH)_3CMe)]\}PF_6$, 16b. A 30-mg sample of **16b** was heated at 180 °C for 2 min as described in the preceding experiment. The resulting material was recrystallized from CH_2Cl_2–Et_2O at −20 °C affording a brown powder of $[Cp(CO)_2Fe(P(OCH_2)_3CMe)]PF_6$ (17 mg, 65%). The complex was characterized by its IR, ^1H NMR, and ^{13}C NMR spectra, which are in accord with those of an authentic sample prepared from the reaction of $[Cp(CO)_2Fe(THF)]BF_4$[32] and $P(OCH_2)_3CMe$: IR (CH_2Cl_2) 2078 (s), 2039 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 5.44 (d, J_{PH} = 1.22 Hz, Cp), 4.43 (d, J_{PH} = 5.13 Hz, OCH_2), 1.93 (s, CMe); ^{13}C NMR (CD_3CN) 206.7 (d, J_{PC} = 39.06, CO), 88.7 (s, Cp), 78.7 (d, J_{PC} = 5.86 Hz, OCH_2), 33.0 (d, *J* = 39.15 Hz, *C*Me), 14.4 ppm (s, C*Me*).

Synthesis of $\{Cp(CO)_2Fe[CH(SMe)(PPh_2H)]\}CF_3SO_3$, 17. Diphenylphosphine (0.12 g, 0.64 mmol) was added to **5** (0.12 g, 0.31 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred for 20 min and then diluted with 10 mL of heptane. The solution volume was gradually reduced in vacuo until complete precipitation occurred; this gave a bright yellow, malodorous solid. The material was dissolved in a minimum amount of $MeNO_2$, and a layer of Et_2O was added to induce crystallization of $\{Cp(CO)_2Fe[CH(SMe)(PPh_2H)]\}CF_3SO_3$, **17** (0.11 g, 62%), at −20 °C. Compound **17** is very soluble in most organic solvents and only sparingly soluble in nitromethane. Anal. Calcd for $C_{22}H_{20}O_5S_2F_3PFe$: C, 46.16; H, 3.50. Found: C, 45.82; H, 3.54.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(HP\text{-}c\text{-}Hx_2)]\}CF_3SO_3$, 18. Into a CH_2Cl_2 solution of **5** (0.12 g, 0.31 mmol) was introduced HP-c-Hz_2 (0.10 g, 0.51 mmol). Upon initial workup as in the preceding synthesis, 0.12 g of the crude product $\{Cp(CO)_2Fe[CH(SMe)(HP\text{-}c\text{-}Hx_2)]\}CF_3SO_3$, **18**, was obtained. It was recrystallized from THF–hexane, giving **18** (0.069 g, 39%) as a bright yellow solid which is very soluble in polar organic solvents. Anal. Calcd for $C_{22}H_{32}O_5S_2F_3PFe$: C, 45.21; H, 5.48. Found: C, 45.47; H, 5.23.

Synthesis of $\{Cp(CO)_2Fe[CH(SMe)(PhPH_2)]\}CF_3SO_3$, 19. Phenylphosphine (0.10 g, 0.90 mmol) was injected into a CH_2Cl_2 suspension of **5** (0.12 g, 0.31 mmol). After the reaction had proceeded for 20 min, a yellow homogeneous solution was obtained. It was diluted with 10 mL of heptane; slow evaporation under reduced pressure furnished a yellow precipitate. The solid was recrystallized from CH_2Cl_2–Et_2O at −20 °C affording $\{Cp(CO)_2Fe[CH(SMe)(PhPH_2)]\}CF_3SO_3$, **19** (0.089 g, 58%). Anal. Calcd for $C_{16}H_{16}O_5S_2F_3PFe$: C, 38.72; H, 3.23. Found: C, 37.84; H, 3.29.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(c\text{-}HxPH_2)]\}PF_6$, 20. The reaction of H_2P-c-Hx (0.10 g, 0.86 mmol) and **5** (0.12 g, 0.31 mmol) in 10 mL of CH_2Cl_2 for 20 min gave a gummy residue after workup according to the procedures described in the preceding synthesis. Therefore, the residue was metathesized with KPF_6 in MeCN. Upon recrystallization, $\{Cp(CO)_2Fe[CH(SMe)(c\text{-}HxPH_2)]\}PF_6$, **20** (0.080 g, 52%), was obtained. Like the other adducts, **20** is stable in air and can be maintained indefinitely at −20 °C under N_2: ^{31}P NMR ($CDCl_3$) 13.2 (t, J_{PH} = 470.84 Hz H_2P-c-Hx), −143.5 ppm (h, J_{PF} = 710.62 Hz, PF_6^-). Anal. Calcd for $C_{15}H_{22}O_2F_6SP_2Fe$: C, 36.15; H, 4.42. Found: C, 36.99; H, 4.45.

Thermal Rearrangement of $\{Cp(CO)_2Fe[CH(SMe)(HPPh_2)]\}CF_3SO_3$, 17. A 35-mg sample of **17** sealed in a prescored ampule was heated at 168 °C for 2 min, which turned it into a caramel-like substance. The ampule was allowed to cool to room temperature and then broken open. Its contents were washed with Et_2O and then extracted with CH_2Cl_2. The extract was then metathesized with $(NH_4)PF_6$ in acetone, followed by recrystallization from CH_2Cl_2–Et_2O at −20 °C which afforded pale yellow crystals of $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}PF_6$, **21** (7 mg, 20%). Anal. Calcd for $C_{21}H_{20}O_2SF_6P_2Fe$: C, 44.37; H, 3.52. Found: C, 44.32; H, 3.22.

Thermal Rearrangement of $\{Cp(CO)_2Fe[CH(SMe)(HP\text{-}c\text{-}Hx_2)]\}CF_3SO_3$, 18. By a procedure analogous to that used in the rearrangement of **17**, 20 mg of **18** was heated at 200 °C for 2 min; 4 mg (20%) of $\{Cp(CO)_2Fe[P\text{-}c\text{-}Hx_2(CH_2SMe)]\}CF_3SO_3$, **22**, was obtained. It was characterized by its spectra (Tables I–III).

Preparations of $Cp(CO)_2Fe[CH(SMe)(PPh_2)]$, 23. A THF suspension of **17** (0.020 g, 0.035 mmol) was chilled at −78 °C with an acetone–dry ice bath. It was then treated with 19 μL of *n*-BuLi (2.5 M in hexane), and the mixture was warmed to room temperature slowly, producing a pale orange solution. The solvent was removed at reduced pressure, and the remaining residue was extracted with hexane to yield an air-sensitive glassy product of **23** (0.013 g, 78%) upon evaporation. The hexane-insoluble portion was recrystallized from CH_2Cl_2–Et_2O at −20 °C, after having been washed with Et_2O, to provide a small amount of $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}CF_3SO_3$ (0.001 g, 5%).

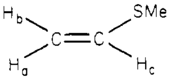
Like *n*-butyllithium, a 10-fold excess of Et_3N also worked well for the deprotonation reaction in THF and CH_2Cl_2 at room temperature. Between 75 and 80% of **23** and 8 and 12% of $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}CF_3SO_3$ were isolated.

Reaction of $Cp(CO)_2Fe[CH(SMe)(PPh_2)]$, 23, with $MeOSO_2F$. Into a 10-mL CH_2Cl_2 solution containing freshly prepared **23** (0.013 g, 0.031 mmol) from **17** and Et_3N in CH_2Cl_2 was injected 20 μL of $MeOSO_2F$. The solution was evaporated under reduced pressure to leave a glassy residue. It was then washed with Et_2O, metathesized with KPF_6 in MeCN, and recrystallized from CH_2Cl_2–Et_2O at −20 °C, giving **11** (0.015 g, 82%).

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with H_2O. To a 5-mL CH_2Cl_2 solution of **5** (0.10 g, 0.26 mmol) was added 100 μL of doubly distilled-degassed H_2O; the solution was stirred for 10 min. During this time, MeSH liberation was evident by its odor and GC. The solvent was evaporated under reduced pressure. The resulting residue was extracted with benzene to give 28 mg (45%) of **25**. The remaining residue was found to contain 42 mg (46%) of **24**. The identical reaction was repeated, and the crude mixture was analyzed by ^1H NMR spectroscopy. On the basis of the integrated Cp resonance areas, the **25**–**24** ratio wa 1:1.

Reaction of $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ with H_2O. Following the procedure for the reaction of **5** and H_2O, $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ was allowed to react with H_2O in CH_2Cl_2 for 10 min. After evaporation to dryness, the residue was extracted with benzene. A mass spectrum of this solution showed *m/e* fragments for $Cp(CO)_2FeCD_2SMe$ (*m/e* 212 (M − CO), 184 (M − 2 CO)) which was the sole product in the extract.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with CH_2N_2. To a 10-mL CH_2Cl_2 solution containing **5** (0.17 g, 0.44 mmol) was added anhydrous CH_2N_2–Et_2O[47] dropwise until the evolution of N_2 ceased (ca. 1 mL). The resulting orange solution was allowed to stir for 45 min, and a yellow solution was obtained. The solvent was removed under reduced pressure, and the oily residue was washed with Et_2O. Extraction of the oil with 10 mL of CH_2Cl_2, filtering the extract, and evaporating the solvent gave a yellow oil of $\{Cp(CO)_2Fe[SMe(CH{=}CH_2)]\}CF_3SO_3$, **26** (0.13 g, 76%). The oil was recrystallized from dichloromethane–ethanol–cyclohexane at room temperature for a few days, affording red needle crystals of **26** (0.02 g, 10%): IR (CH_2Cl_2) 2062 (s), 2019 (s) cm^{-1}; ^1H (CD_3CN)



δ δ 6.31 (m, H_c), 5.81 (m, $J_{H_aH_c}$ = 8.98 Hz, H_a), 5.71 (m, $J_{H_bH_c}$ = 16.50 Hz, H_b), 5.38 (s, Cp), 2.47 (s, SMe); ^{13}C (CD_2Cl_2) 208.4 (CO), 130.8 (=CH) 124.1 (H_2C=), 87.7 (Cp), 25.3 ppm (SMe).

Crystal Data. $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$, **16b**: M_r = 530.0; monoclinic, $P2_1/c$; *a* = 10.359 (3) Å, *b* = 12.284 (4) Å, *c* = 16.234 (4) Å, β = 95.25 (3)°, *V* = 2057 Å^3; ρ_{calcd} = 1.711 g/cm^3, *Z* = 4.

1026 *Organometallics* 1983, *2*, 1026–1031

Data Acquisition. Compound **16b** yielded yellow platelike crystals with approximate dimensions of 0.6 × 0.4 × 0.3 mm which were readily indexed by using 12 independent reflections and an automatic indexing procedure.[50] The data were collected at ambient temperature with graphite-monochromated Mo Kα (λ = 0.709 79 Å) radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory: ω scan; 4151 reflections measured in almost four octants; $2\theta \leq 45°$; decomposition corrections applied; 2502 reflections with $I \geq 3\sigma_I$ after averaging; agreement between equivalent reflections is 4.2%. Accurate cell parameters and their standard deviations were obtained from a least-squares fit to $\pm 2\theta$ values of 12 high-angle reflections.

The position of the Fe atom was located by analysis of a sharpened three-dimensional Patterson function. All the remaining non-hydrogen and H1 atoms were found by successive structure factor and electron density map calculations; a combination of block and full-matrix least-squares refinement[51] of all non-hydrogen atoms was carried out. As expected for the PF_6^-, packing disorder resulted in high conventional and weighted residuals of $R = 0.082$ and $R_w = 0.109$, respectively. The scattering factors[52] were modified for anomalous dispersion effects.[53] Bond angles, bond distances, and final atom positional parameters are summarized in Tables IV and V.

Acknowledgment. We sincerely thank Professor R. A. Jacobson and James Richardson for their assistance with the X-ray diffraction studies.

Registry No. 1, 6932-11-2; **2**, 76136-44-2; **3**, 85629-24-9; **4**, 85629-25-0; **5**, 76136-46-4; **6**, 85629-26-1; **7**, 85629-27-2; **8**, 85629-29-4; **9**, 85629-31-8; **10**, 69621-11-0; **11**, 85629-33-0; **12a**, 85629-35-2; **12b**, 85629-59-0; **13**, 85629-37-4; **14**, 85629-39-6; **15**, 85629-41-0; **16a**, 85629-43-2; **16b**, 85629-61-4; **17**, 85629-45-4; **18**, 85629-47-6; **19**, 85629-49-8; **20**, 85629-51-2; **21**, 85629-53-4; **22**, 85629-55-6; **23**, 85629-56-7; **24**, 76136-47-5; **25**, 12108-33-7.

Supplementary Material Available: Tables of calculated hydrogen atom positions, interatomic distances, bond angles, thermal parameters, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(50) Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.

(51) Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program", U.S. DOE Report; Iowa State University and Ames Laboratory: Ames, IA, 1979.

(52) Gromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71–97.

(53) Templeton, D. H. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England; 1962, Vol. III, Table 3.3.2c, pp 215-6.

Synthesis and a Multinuclear NMR Spectroscopic Study of Some $Mo(CO)_5(PPh_2XR)$ (X = O, NH; R = 1–4 Carbon Alkyls) Complexes. Steric Effects on ^{31}P and ^{95}Mo Chemical Shifts

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Received December 14, 1982

The syntheses and multinuclear NMR spectroscopic data for a series of $Mo(CO)_5(PPh_2XR)$ (X = O, NH; R = 1–4 carbon alkyls) complexes is presented. The steric effect of substitution at the α carbon of the R groups is shown to have an effect on the chemical shifts of the aromatic C(1) ^{13}C, ^{31}P, and ^{95}Mo resonances but not upon the chemical shifts of the carbonyl ^{13}C and ^{17}O resonances. In addition, the good correlation observed between the chemical shifts of the ^{95}Mo and aromatic C(1) ^{13}C resonances indicates that in the $Mo(CO)_5(PPh_2XR)$ complexes, the ^{95}Mo and aromatic C(1) ^{13}C resonances are similarly affected by changes in the R group.

Introduction

There has been considerable interest in the relationship between the chemical shifts observed for NMR active nuclei of transition-metal complexes and the steric and electronic parameters of the ligands in these complexes. In order to better understand this relationship, we have begun a study of the multinuclear NMR spectra of molybdenum carbonyl complexes containing phosphorus-donor ligands. The first complexes studied were a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ complexes (X = NH, O, S; R = alkyl, aryl, silyl). Good correlations were observed between the ^{13}C and ^{17}O chemical shifts of the trans carbonyl ligands but not between those of the cis carbonyl ligands or between the ^{31}P or ^{95}Mo chemical shifts and any other chemical shifts.[1,2] These results were only in partial agreement with previous results,[3-5] and the differences were attributed, in part, to variations in the steric and electronic properties of the P-donor ligands used in these studies.[1]

The reasons for the lack of correlation between many of the chemical shifts are not well understood. This is especially true for the ^{95}Mo chemical shift. Preliminary studies of the ^{95}Mo NMR spectra of some molybdenum carbonyl complexes demonstrated that the ^{95}Mo chemical shift was extremely sensitive to the number and type of non-carbonyl ligands[6-11] while two more systematic studies

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(1) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1983**, *241*, 201.

(2) Gray, G. M.; Kraihanzel, C. S. *Inorg. Chem.*, in press.

(3) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

(4) Kowada, Y.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1979**, 291.

(5) Hickey, J. P.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1979**, *179*, 159.

(6) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Cotton, J. D. *J. Organomet. Chem.* **1980**, *195*, C17.

(7) Dysart, S.; Georgii, I.; Mann, B. E. *J. Organomet. Chem.* **1981**, *213*, C10.

(8) LeGall, J. Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

(9) Bailey, J. T.; Clark, R. J.; Levy, G. C. *Inorg. Chem.* **1982**, *21*, 2085.

(10) Jaitner, P.; Wohlgenannt, W. *Monatsh. Chem.* **1982**, *11*, 699.

0276-7333/83/2302-1026$01.50/0