

Preparation, Structure, and Reactions of Stable Mono(alkylthio)carbene Complexes of the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$ System¹

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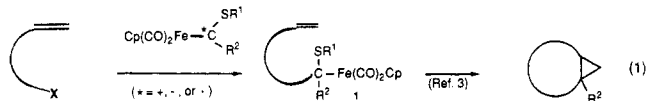
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The reaction of $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{SPh}$ ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) with trityl hexafluorophosphate produces the cationic (phenylthio)carbene complex $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHSPH}]^+\text{PF}_6^-$ (**2b**), whereas the reaction of the iron acyl $\text{Cp}(\text{CO})_2\text{FeC}(\text{O})\text{CH}_3$ with trifluoromethanesulfonic anhydride and thiols followed by anion exchange gives the more highly substituted complexes $[\text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{SR})\text{CH}_3]^+\text{PF}_6^-$ (**2c**, $\text{R} = \text{CH}_3$; **2d**, $\text{R} = \text{Ph}$). The complexes **2b-d** are reasonably stable compounds that have been characterized spectroscopically and, in the cases of **2b** and **2c**, by X-ray diffraction. Complex **2b** exhibits the more common "upright" conformation, but **2c** occurs with a "crosswise" or "orthogonal" conformation. Complexes **2b-d** undergo addition of carbon-based nucleophiles, including organolithium, -magnesium, and -copper reagents and enolates.

We have previously demonstrated that compounds of the general type $\text{Cp}(\text{CO})_2\text{FeC}(\text{SR}^1)\text{R}^2\text{R}^3$ ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) possess latent carbene-like reactivity and serve as quite useful reagents for the cyclopropanation of alkenes.³ Related studies, primarily of the corresponding alkoxy compounds $\text{Cp}(\text{CO})_2\text{FeC}(\text{OR}^1)\text{R}^2\text{R}^3$, have been reported by Brookhart,⁴ Casey,⁵ and many other workers in this area.^{6,7} However, our sulfide-based reagents have

proven to be advantageous in many cases because of high stability and/or greater efficiency of their cyclopropanation reactions. In the course of developing further applications of compounds of this type, we recognized the need for methods that would permit the direct one-step introduction of the intact $[\text{Cp}(\text{CO})_2\text{FeC}(\text{SR}^1)\text{R}^2]$ unit into various carbon frameworks. This need is especially important for the efficient construction of substrates (e.g. **1**) for intramolecular cyclopropanation reactions (eq 1).^{3e} Previously,



(1) (a) Presented by C.K. at the 191st National Meeting of the American Chemical Society, New York, NY, April 1986; paper ORGN 126. (b) Taken in part from the Ph.D. Dissertation of G.-H.K., State University of New York at Stony Brook, 1985.

(2) (a) University of Notre Dame. (b) State University of New York at Stony Brook.

(3) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473, (b) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869. (c) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (d) Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231. (e) Iyer, R. S.; Kuo, G.-H.; Helquist, P. *J. Org. Chem.* **1985**, *50*, 5898.

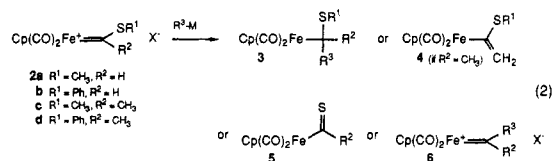
(4) For recent work from the Brookhart Laboratory see: (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B.; *Ibid* **1983**, *105*, 6721. (c) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

(5) (a) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (b) Casey, C. P.; Miles, W. H. *J. Organomet. Chem.* **1983**, *254*, 333. (c) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

(6) For leading references to the work of other research groups in this general area see: (a) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794. (b) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7. (c) Riley, P. E.; Capshaw, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408. (d) Sanders, A.; Bauch, T.; Magatti, C. V.; Lorenc, C.; Giering, W. P. *J. Organomet. Chem.* **1976**, *107*, 359. (e) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2584. (f) Allison, N. T.; Kawada, Y.; Jones, W. M. *Ibid.* **1978**, *100*, 5224. (g) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *Ibid.* **1979**, *101*, 585. (h) Bates, D. J.; Rosenblum, M.; Samuels, S. B. *J. Organomet. Chem.* **1981**, *209*, C55. (i) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305. (j) Bly, R. S.; Hossain, M. M.; Lebiada, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549. (k) Guerschais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 835. (l) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 612. (m) Bodnar, T. W.; Cutler, A. R. *Ibid.* **1985**, *4*, 1558. (n) Barefield, E. K.; McCarten, P.; Hillhouse, M. C. *Ibid* **1985**, *4*, 1682. For related studies of rhenium carbene complexes see: (o) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (p) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *Ibid.* **1983**, *105*, 5804. (q) Stenstrom, Y.; Klauk, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155.

we have prepared the above-mentioned reagents, including examples of **1**, by a multistep pathway that was satisfactory for our initial studies of the simpler compounds of this type but is undesirable for the more complex systems required in natural product syntheses that we are interested in pursuing.

We believed that nucleophilic addition of the appropriate alkylmetal reagents, or other carbanionic species, to the cationic (alkylthio)carbene complexes **2** would meet our needs in providing facile access to the desired adducts **3**, but we were also cognizant of other possible outcomes of these reactions (see 4-6, eq 2).^{5a} We emphasize the need



for dicarbonyl complexes **3** as reagents for subsequent

(7) For some recent reviews of carbene complexes see: (a) Brown, F. *J. Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Cardin, D. J.; Norton, R. *J. Organomet. Chem.* **1982**, *12*, 213. (c) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983. (d) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (e) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261. (f) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (g) Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249. (h) Casey, C. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3 and the earlier volumes of this series. (i) Aratani, *Pure Appl. Chem.* **1985**, *57*, 1839. (j) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (k) Brookhart, M.; Studabaker, W. B. *Ibid.*, in press.

cyclopropanation reactions; complexes containing electron-donating ligands (e.g. phosphines) in place of one or both carbonyls are of reduced reactivity in these reactions.

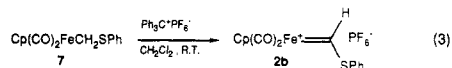
Prior to our presently reported work, there were no reports that combined the four factors of very *direct* means of preparation, good *stability* of simple mono(alkylthio)carbene complexes, use of the parent dicarbonyl system **2**, and subsequent addition of carbon-based nucleophiles. Besides more complex examples, Angelici did study $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHSCH}_3]^+\text{CF}_3\text{SO}_3^-$ (**2a**), but it was prepared by a rather long route, and it was reported to be somewhat unstable.⁸ Hughes, on the other hand, prepared the phosphine-containing complexes $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}=\text{C}(\text{SR})\text{CH}_3]^+\text{BF}_4^-$.⁹ Furthermore, the addition of heteronuclear rather than carbon-based nucleophiles were emphasized in all of these previous studies. More commonly studied than these thiocarbene complexes have been other heterosubstituted carbene complexes, especially the alkoxy derivatives,^{4,5,6h,j,m,8a,9,10} although (alkylthio)carbene complexes of other metal systems have also been reported.¹¹

In this paper, we wish to report the preparation, structural study, and addition reactions of complexes of type **2** that do indeed meet our requirements.

Results and Discussion

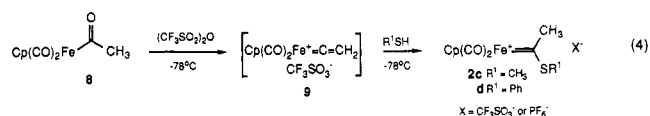
Preparations. In the simplest case, we begin with the (phenylthio)methyl complex **7**, which is very readily available by alkylation of sodium cyclopentadienyldicarbonylferrate with chloromethyl phenyl sulfide,^{8a,b,d,e,12} in analogy with a few other metal alkyl derivatives,^{6d,f,o,p,8d,10d} the reaction of **7** with trityl hexafluorophosphate (the tetrafluoroborate gives poorer results) gives

the desired (phenylthio)carbene complex **2b** (eq 3), which



after recrystallization is obtained in 80% yield. This complex, a golden yellow, crystalline solid, is a fairly stable compound that may be handled in the air for at least short periods of time, although for the purpose of long-term storage, we keep it under a nitrogen atmosphere at 25 °C. We have not been as successful in applying this method of preparation, however, to **2a**, previously obtained by Angelici by a completely different route.^{8a,b} When $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{SCH}_3$ ^{8a,b,12} is allowed to react with trityl salts, mixtures of products are obtained in which small, varying amounts of **2a** appear to be present as indicated by a peak at δ 15.46 (CH_3NO_2) in the ¹H NMR spectrum (vide infra),^{8b} as well as $\text{Cp}(\text{CO})_3\text{Fe}^+$ and several peaks corresponding to S-methyl groups, but attempts to isolate pure **2a** from these mixtures have not been possible. These observations are consistent with Angelici's report that **2a** is not very stable.^{8a,b}

For the preparation of other (alkylthio)carbene complexes, we proceed according to the approach that Hughes has used for phosphine-substituted analogues.⁹ We begin with the stable acetyl complex **8**, which itself is obtained by the straightforward acylation of sodium cyclopentadienyldicarbonylferrate.^{4a,15} Reaction of **8** with trifluoromethanesulfonic anhydride is followed within a few minutes by the addition of thiols. The vinylidene complex **9** is apparently formed as an intermediate,¹⁶ but as expected, this dicarbonyl derivative is much less stable than the phosphine-containing analogue $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}=\text{C}=\text{CH}_2]^+$, studied previously.^{9,17} The presumed **9** undergoes addition of thiols to give the desired thiocarbene complexes **2c** and **2d** as the overall products in ca. 70% yield (eq 4).



These thiol adducts are isolated as yellow solids, but because of somewhat limited stability of the initially obtained trifluoromethanesulfonate salts (particularly in the case of the methanethiol adduct **2c**), they are subjected to simple anion exchange to give the hexafluorophosphate salts. These compounds, which are also yellow solids, are stable in the air for several days at 25 °C.

Characterization. The infrared spectra show CO absorptions for $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHSPh}]^+\text{PF}_6^-$ (**2b**) at 2073 and 2034 cm^{-1} , for $[\text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{SCH}_3)\text{CH}_3]^+\text{PF}_6^-$ (**2c**) at 2058 and 2018 cm^{-1} , and for $[\text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{SPh})\text{CH}_3]^+\text{PF}_6^-$ (**2d**) at 2062 and 2022 cm^{-1} , in agreement with the values reported previously^{8a} for $[\text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{SR}^1)\text{CH}_3]^+\text{PF}_6^-$.

(8) (a) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1111, 1118. (b) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018, 1583. (c) Matachek, J. R.; Angelici, R. J.; Schugart, K. A.; Haller, K. J.; Fenske, R. F. *Ibid.* **1984**, *3*, 1038. (d) McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* **1981**, *20*, 4108.

(9) (a) Boland, B. E.; Fam, S. A.; Hughes, R. P. *J. Organomet. Chem.* **1979**, *172*, C29. (b) Boland-Lussier, B.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. (c) Boland-Lussier, B. E.; Hughes, R. P. *Ibid.* **1982**, *1*, 635.

(10) (a) Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188. (b) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (c) Priester, W.; Rosenblum, M. J. *Chem. Soc., Chem. Commun.* **1978**, 26. (d) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. (e) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471. (f) Marten, D. F. *J. Chem. Soc., Chem. Commun.* **1980**, 341. (g) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (h) Curtis, P. J.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 747. (i) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764. In addition, the general class of neutral, heterosubstituted carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{YR}^1)\text{R}^2$, first reported by Fischer, may be noted: (j) Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353.

(11) For a few examples of (alkylthio)carbene complexes of other metal systems see: (a) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73. (b) Pickering, R. A.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2977. (c) McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57. (d) Battioni, J.-P.; Chottard, J.-C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, 2056. (e) Steinmetz, A. L.; Hershberger, S. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 461. (f) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Ibid.* **1984**, *3*, 1124. (g) Raubenheimer, H. G.; Kruger, G. J.; van A. Lombard, A.; Linford, L.; Viljoen, J. C. *Ibid.* **1985**, *4*, 275. (h) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167. (i) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778. See also the many references cited in these papers. Many others are reviewed in ref 7, e.g. ref 7c, pp 11, 15–16, and 23–24.

(12) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 486.

(13) For an excellent discussion of the infrared characteristics of related iron carbene complexes, see ref 8a. For a comparison of other oxygen- and sulfur-containing complexes in the $\text{Cp}(\text{CO})_2\text{Fe}$ system, see ref 6q. For a recent discussion of the relative abilities of oxygen- and sulfur-containing substituents to stabilize adjacent carbenium ion sites, see: Bernardi, F.; Bottoni, A.; Venturini, A. *J. Am. Chem. Soc.* **1986**, *108*, 5395. For earlier work, see: Taft, R. W.; Martin, R. H.; Lampe, F. W. *J. Am. Chem. Soc.* **1965**, *87*, 2490.

(14) For an excellent discussion of the NMR behavior of related iron carbene complexes, see ref 5c and the papers cited therein.

(15) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.

(16) For the more stable complex $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}=\text{C}=\text{CH}_2]^+\text{BF}_4^-$, the vinylidene and Cp hydrogens appear at δ 5.30 and 5.25, respectively (see ref 9b). The ¹H NMR spectrum –70 °C of our reaction mixture exhibits a broadened singlet at δ 5.28, supposedly due to coincidental overlap of the vinylidene and Cp hydrogens.

(17) For some examples of related vinylidene complexes and their nucleophilic addition reactions see ref 9, 10f, and: (a) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232. (b) Selegue, J. P. *Ibid.* **1982**, *104*, 119. (c) Wong, A.; Gladysz, J. A. *Ibid.* **1982**, *104*, 4948. (d) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(18) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Organomet. Chem.* **1980**, *193*, C23. (b) Manganiello, F. J.; Radcliffe, M. D.; Jones, W. M. *Ibid.* **1982**, *228*, 273.

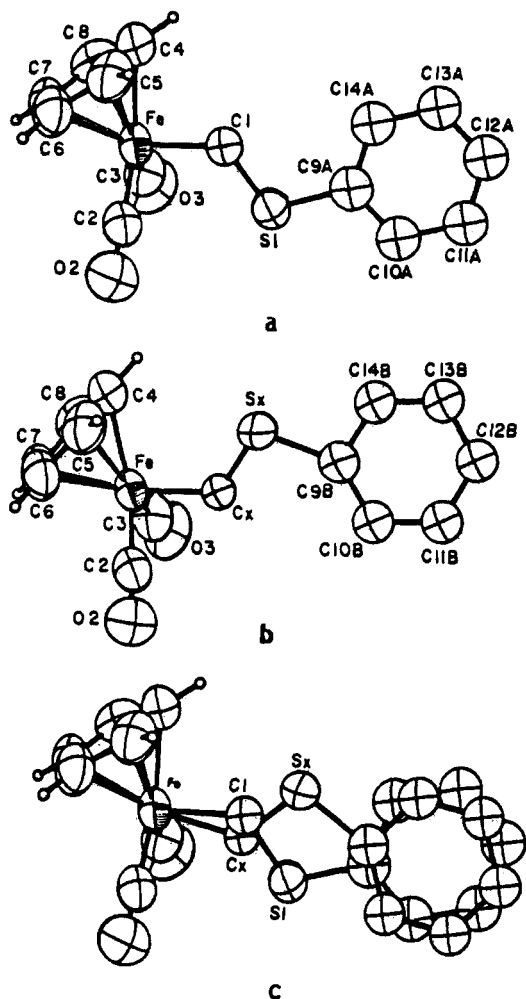


Figure 1. ORTEP diagram showing conformers of cationic carbene complex **2b**: (a) 80% contributor; (b) 20% contributor; (c) superimposition of both contributors.

$\text{CHSCH}_3]^+\text{CF}_3\text{SO}_3^-$ (**2a**) at 2067 and 2026 cm^{-1} , and for the methoxy analogue $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHOCH}_3]^+\text{PF}_6^-$ at 2085 and 2043 cm^{-1} .^{10d} These values are also suggestive of the PhS substituent being a better electron donor than the CH_3O group but a poorer donor than the CH_3S group in these complexes.¹³ Very indicative of the carbene character of complex **2b** are the ^1H NMR absorption at δ 15.52 (CD_2Cl_2) for the hydrogen on the carbene center and the ^{13}C NMR absorption at δ 317.35 ($J_{\text{C-H}} = 158$ Hz) (CD_3NO_2) for the carbene carbon itself.¹⁴ The literature value for the ^1H NMR of the closely related $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHSCH}_3]^+\text{CF}_3\text{SO}_3^-$ (**2a**) is δ 14.86 (CD_2Cl_2),^{8b} and the corresponding ^1H and ^{13}C NMR values for $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHOCH}_3]^+\text{PF}_6^-$ are δ 13.13 (CD_3NO_2 , or δ 12.88 in $\text{CF}_3\text{CO}_2\text{H}$) and δ 321.9 (CD_3NO_2),^{5c,d,10d} respectively, but solvent effects complicate the interpretation of chemical shift differences. For the methyl-substituted thiocarbene complexes **2c** and **2d**, ^{13}C NMR peaks are seen at δ 345.4 (CD_3NO_2) and 351.7 (CD_3NO_2), respectively.

We have also studied the structures of two of these thiocarbene complexes, namely, **2b** and **2c**, by X-ray diffraction. The structure of the molecular cation of **2b** (Figure 1) consists of a central iron atom about which is coordinated a η^5 -cyclopentadienyl ring, two carbonyl ligands, and a (phenylthio)carbene fragment.

Two separate carbene fragments were described by least-squares refinement resulting in two randomly distributed models as 80% (Figure 1a) and 20% (Figure 1b) contributors that differ in the relationship of the phe-

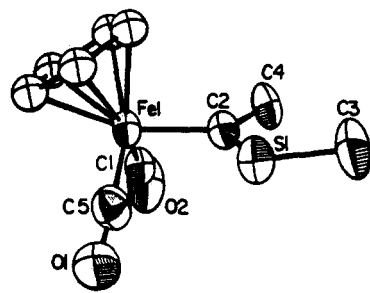


Figure 2. ORTEP diagram of cationic carbene complex **2c**.

Table I. Selected Bond Angles (deg) and Bond Lengths (Å) for **2b**

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C3	Fe	C2	95.4 (4)	Fe	C2	O2	176.4 (7)
C3	Fe	C1	92.6 (4)	Fe	C3	O3	177.4 (9)
C3	Fe	Cx	81 (1)	Fe	C1	S1	125.2 (7)
C2	Fe	C1	94.2 (4)	Fe	Cx	Sx	122 (3)
C2	Fe	Cx	85 (1)	C8	C4	C5	108.7 (8)
C6	C5	C4	106.4 (8)	C7	C6	C5	109.0 (8)
C6	C7	C8	108.6 (8)	C7	C8	C4	107.2 (8)
C1	C7	C4	88.7 (4)	Cx	Fe	C4	103 (1)
atom 1	atom 2	dist	atom 1	atom 2	dist		
Fe	C1	1.88 (1)	Fe	C6	2.107 (8)		
Fe	C2	1.784 (9)	Fe	C7	2.086 (8)		
Fe	C3	1.764 (8)	Fe	C8	2.108 (8)		
Fe	C4	2.092 (8)	Fe	Cx	1.90 (4)		
Fe	C5	2.101 (8)	S1	C1	1.62 (1)		
Sx	Cx	1.64 (4)	P1	F4	1.525 (7)		
P1	F1	1.518 (6)	P1	F5	1.541 (7)		
P1	F2	1.565 (6)	P1	F6	1.563 (7)		
P1	F3	1.526 (7)	C3	O3	1.139 (8)		
C4	C5	1.414 (13)	C2	O2	1.137 (9)		
C5	C6	1.411 (12)	C6	C7	1.388 (12)		
C7	C8	1.402 (12)	C8	C4	1.412 (14)		

^a Numbers in parentheses are estimated standard deviations in the least significant digit(s).

nylthio group to the Cp ring. This difference can best be described by a rotation about the Fe-carbene bond of approximately 180°. The angle between the plane of the phenyl ring and the plane defined by Fe,C1,S1 is 23° (80% model, Figure 1a), and for Fe,Sx,Cx it is 33° (20% model, Figure 1b). These deviations from strict planarity can be attributed to the interaction of the ortho hydrogens of the phenyl ring with the carbene hydrogen. A calculation of the carbene hydrogen using the assumption that the carbene is sp^2 -hybridized places the two hydrogen atoms 2.19 Å apart, which is closer than the sum of the van der Waals radii of two hydrogen atoms (2.4 Å). The length of the Fe-carbene (C1 crystallographic numbering) bond is reasonable at 1.88 (10) Å, but that of the S1-carbene bond is short at 1.62 (10) Å in the 80% model; the values for the 20% model are 1.89 (38) and 1.64 (42) Å, respectively. For the purpose of comparison of the values with earlier X-ray data, typical Fe-C(sp^3) bond lengths occur within the range of 2.08–2.10 Å, Fe-C(sp^2) values are most typically in the range of 1.98–2.00 Å, and for actual Fe=C bond lengths of known carbene complexes, the range is 1.91–2.00 Å.^{19,26}

The structure of the molecular cation of **2c** (Figure 2) consists of a central iron atom about which is coordinated a η^5 -cyclopentadienyl ring, two carbonyl ligands, and a methyl(thiomethyl)carbene fragment. The length of the Fe1-carbene (C2 crystallographic numbering) bond is 1.94

(19) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* 1980, 102, 2458.

Table II. Selected Bond Lengths and Angles of **2c**^a

Bond Lengths (Å)			
bond	d, Å	bond	d, Å
Fe1-C1	1.77 (2)	C2-S1	1.64 (2)
Fe1-C2	1.94 (2)	S1-C3	1.80 (2)
Fe1-C5	1.73 (3)	Cp-Fe1	(2.07) ^b
C2-C4	1.47 (2)		
Bond Angles (deg)			
A-B-C	∠, deg	A-B-C	∠, deg
Fe-C2-S1	117 (1)	C1-Fe-C5	93 (1)
C2-S1-C3	107 (1)	C1-Fe-C2	90 (1)
Cp-Fe-C2	88	C5-Fe-C2	95 (1)
C4-C2-S1	121 (1)	C4-C2-Fe	122 (1)

^aThe estimated standard deviations of the least significant digits are given in parentheses. ^bAverage value for the rigid group.

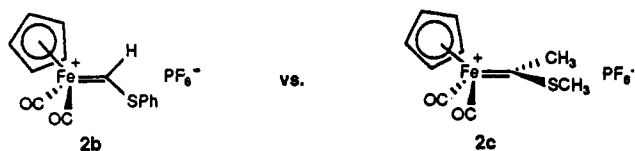
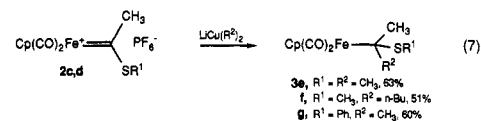
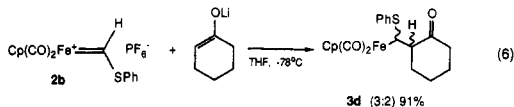
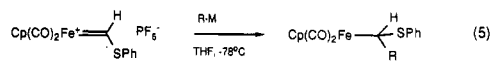


Figure 3. Comparison of conformations for cationic carbene complexes **2b** and **2c**.

(2) Å, and the S1-carbene is again short at 1.64 (2) Å. Tables I and II list selected bond lengths and angles for carbene complexes **2b** and **2c**, respectively.

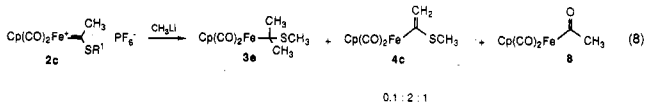
The technical problems described in the Experimental Section have prevented us from obtaining X-ray data of higher quality, but the data are at least adequate to reveal an interesting conformational difference between **2b** and **2c**. Complex **2b** possesses a so-called "upright" conformation (Figure 3) in the solid state (i.e. the dihedral angle of 4° between the Cp(center)-Fe-C(carbene) and S-C(carbene)-Fe planes approaches 0°). This conformation is in agreement with theoretical predictions for the parent methylene complex $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CH}_2]^+$ and with NMR measurements of various examples of more highly substituted alkylidene complexes of this series, although the predicted and the measured barriers to rotation about the Fe-C bonds in these species are relatively small (ca. 6–10 kcal/mol).^{5c,6f,18} On the other hand, complex **2c** exists in a "crosswise" or "orthogonal" conformation (Figure 3) in the solid state (i.e. the corresponding dihedral angle of 84° approaches 90°). This conformation is contrary to the discussion above, but it is readily rationalized by a combination of an electronic donor effect of the added methyl substituent on the carbene center (probably a small effect) and a steric effect due to nonbonded interactions between the Cp ligand and either of the two substituents on the carbene center. Previously, Jones reported solid-state cross-wise conformations for cycloheptatrienyliene complexes of this series,¹⁹ and Casey considered the possibility of a crosswise conformation of the isopropylidene complex.^{5c} We should point out, however, that we cannot make any definitive comments on the solution conformations of **2b** and **2c** in that low-temperature solubility limitations have prevented us from doing adequate dynamic NMR experiments. Down to -100 °C (CD₂Cl₂), we see no significant changes in the ¹H NMR spectrum of either complex **2b** or **2c**.

Addition Reactions. The new (alkylthio)carbene complexes reported in this paper undergo addition of types of carbon-based nucleophilic reagents that will be of use in our planned applications of organoiron intermediates in natural products synthesis. These addition reactions are summarized in eq 5–7. The adducts of **2b** are ac-



companied by small amounts of the (phenylthio)methyl complex **7** as an unavoidable contaminant that is difficult to remove chromatographically from the simpler adducts.

In the case of the secondary carbene complex **2b**, simple organometallic reagents (i.e. organolithium and Grignard reagents) undergo additions rather cleanly (eq 5). However, in the cases of the tertiary complexes **2c** and **2d**, the difficulties that we anticipated earlier (see eq 2) actually do arise in that we observe only small amounts of the desired adducts **3** when simple organometallic reagents are used. The principal products are instead the elimination products **4** and acyl complex **8**.^{4a,15} The latter compound is likely to arise from nucleophilic attack on the S-CH₃ group of **2c** to give the thioacyl derivative **5** that then undergoes hydrolysis to **8** during product isolation. A typical result is shown for the case of methyl lithium (eq 8), but similar results are also obtained with methyl-



magnesium bromide and *n*-butyllithium. Fortunately, the well-known cuprates,²⁰ which behave as less basic species than organolithium or Grignard reagents, undergo the desired addition reactions much more successfully (eq 7). Similar observations have been made by Casey in the case of alkoxycarbene complexes.⁵

Special mention should be made of the addition of an enolate to complex **2b** (eq 6). Adducts related to **3d** are expected to serve as key intermediates in many applications in synthesis.

Conclusion

As a result of the work reported herein, (alkylthio)carbene complexes of the Cp(CO)₂Fe series are now readily available as well-characterized compounds of good stability and of useful reactivity in addition reactions. Applications of this chemistry in natural products synthesis are presently being pursued in our further work. These studies of (alkylthio)carbene complexes and their adducts also contribute to the ever increasingly broad role that the Cp(CO)₂Fe unit plays as one of the most useful groups in organometallic chemistry.²¹

Experimental Section

General Remarks. All reactions and other manipulations of air-sensitive compounds were performed under a nitrogen at-

(20) (a) Posner, G. H. *Org. React. (N.Y.)* 1972, 19, 1. (b) Posner, G. H. *Ibid.* 1975, 22, 253. (c) Normant, J. F. *Pur. Appl. Chem.* 1978, 50, 709.

(21) For a recent review by the leading practitioner of Cp(CO)₂Fe chemistry in general, see: Rosenblum, M.; Bucheister, A.; Chang, T. C. T.; Cohen, M.; Marsi, M.; Samuels, S. B.; Scheck, D.; Sofen, N.; Watkins, J. C. *Pure Appl. Chem.* 1984, 56, 129. See also: (b) Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W.; Eds.; Pergamon: Oxford, 1982; Vol. 8, pp 939–1011.

mosphere by using double-manifold techniques²² or in a Vacuum Atmospheres Dri-Lab glovebox. Solutions were transferred with double-ended needles (cannulas) or hypodermic syringes. Glassware was flame-dried or taken directly from a drying oven into the glovebox before use.

Tetrahydrofuran (THF) and diethyl ether were freshly distilled under nitrogen from dark blue or purple solutions of sodium benzophenone radical anion or dianion. Triphenylcarbenium (trityl) salts were obtained commercially (Aldrich) but were recrystallized from CH_2Cl_2 /benzene. Grignard reagents were prepared in the usual manner in THF and were then titrated.²³ Organolithium reagents were obtained commercially (Aldrich) and titrated.²⁴ Most other commercial solvents and reagents were distilled or recrystallized and then stored under nitrogen prior to use.

A Neslab Cryo-Cool Model CC-100F with an acetone bath was employed for low-temperature reactions of long duration. For shorter duration, dry ice/acetone (-78°C), dry ice/carbon tetrachloride (-23°C), or ice/water baths were used. ^1H NMR spectra were recorded on Varian HFT-80 (80 MHz), Magnachem A-200 (200 MHz), and Nicolet NT-300 (300 MHz) spectrometers. ^{13}C NMR spectra were recorded on these same instruments at 20, 50, and 75 MHz, respectively. The IR spectra were obtained with Pye-Unicam Model SP-1000, Perkin-Elmer Model 1420, and IBM 32FTIR spectrophotometers and were calibrated with a polystyrene standard. Mass spectra were recorded with Hewlett-Packard Model 2981A, AEI Model MS-30, and Hewlett-Packard Model 5890A BG-70-250 spectrometers using electron-impact ionization at 70 eV, chemical ionization (methane reagent gas), or fast atom bombardment (xenon source). Melting points were determined in capillaries with a Thomas-Hoover oil immersion apparatus and are corrected. Elemental analyses were performed by Galbraith (Knoxville, TN) and M-H-W Laboratories (Phoenix, AZ) and are reported when they agree with the calculated values within $\pm 0.4\%$. In other cases, the homogeneity of the compounds was determined by TLC, and molecular formulas were determined by high resolution mass spectrometry. Chromatographic purifications were performed under nitrogen with a modified "flash" chromatography technique developed in these laboratories^{22c} or with radial chromatography ("Chromatotron") on silica gel or basic alumina. Crude products were generally purified by bulb-to-bulb ("Kugelrohr") distillation at reduced pressure.

(η^5 -Cyclopentadienyl)dicarbonyl((phenylthio)carbenium)iron Hexafluorophosphate (**2b**). In the glove box, (η^5 -cyclopentadienyl)dicarbonyl((phenylthio)methyl)iron (**7**) (1.48 g, 5.0 mmol) was placed in a 100-mL flask equipped with a stirring bar. Methylene chloride (20 mL) was added followed by triphenylcarbenium hexafluorophosphate (1.7 g, 5.0 mmol). The mixture was stirred magnetically for 5 min. The orange solution turns dark green immediately. Anhydrous ether (40 mL) was added slowly to precipitate **2b**. Filtration through a medium frit followed by washing with ether (3×10 mL) and then drying under vacuum yielded 1.76 g (80%) of **2b** as golden yellow crystals: mp 126°C dec; ^1H NMR (200 MHz, CD_2Cl_2) δ 15.52 (s, $\text{Fe}^+=\text{CH}$), 7.62 (s, C_6H_5), 5.64 (s, C_5H_5); ^{13}C NMR (75 MHz, CD_3NO_2) δ 317.35 ($\text{Fe}=\text{CH}$, $J_{\text{C-H}} = 158$ Hz), 208.72 ($\text{FeC}\equiv\text{O}$), 142.31, 133.29, 131.52, 128.45 (C_6H_5), 90.40 (C_5H_5); IR (FT, CH_2Cl_2) 2073, 2034 cm^{-1} ($\text{FeC}\equiv\text{O}$). Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_6\text{FeO}_2\text{PS}$: C, 37.86; H, 2.50. Found: C, 37.52; H, 2.78.

X-ray Structure Determination of 2b. A yellow, irregular crystal of **2b**, formed by diffusion of ether into a cooled saturated methylene chloride solution, having approximate dimensions of $0.30 \times 0.20 \times 0.40$ mm was mounted in a glass capillary with its long axis roughly parallel to the phi axis of the goniometer. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained for least-squares refinement, using the setting angles of 25 reflections in the range $24^\circ < |\theta| < 28^\circ$, measured by the computer-controlled diagonal slit method of centering (there were $(11 \pm 2)\theta$ pairs). The monoclinic cell parameters and calculated volume are $a = 7.267$ (2) Å, $b = 14.245$ (4) Å, $c = 16.668$ (3) Å, $\beta = 96.84$ (2)°, and $V = 1713.0$ Å³. For $Z = 4$ and $fw = 444.12$ g/mol, the calculated density is 1.72 g/cm³. The observed density was 1.72 g/cm³ (floatation in $\text{CH}_2\text{Br}_2/\text{CCl}_4$). As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.20° with a takeoff angle of 2.8° , indicating good crystal quality. From the systematic absences of $h0l$, $l = 2n$, and $0k0$, $k = 2n$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$ (No. 14).

The data were collected at room temperature by using the $\theta/2\theta$ scan technique. The scan rate varied from 1.0 to $4.1^\circ/\text{min}$ (in ω). The variable scan rate allows rapid data collection for intense reflection where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 54.9° . The scan range (in degrees) was determined as a function of θ to correct for the separation of the $K\alpha$ doublet; the scan width was calculated as follows: ω scan width = $0.8 + 0.35 \tan \theta$. Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was 2.0 mm wide by 4.0 mm high. The diameter of the incident beam collimator was 1.5 mm, and the crystal to detector distance was 21 cm. For intense reflections the attenuator was automatically inserted in front of the detector; the attenuator factor was 19.0.

A total of 4311 reflections were collected, of which 3912 were unique and not systematically absent. As a check on crystal and electronic stability, four representative reflections were measured every 60 min of X-ray exposure. The slopes of the least-squares lines through a plot of intensity vs. time were -0.12 , -0.19 , -0.17 , and -0.12% per hour over 85.5 h of X-ray exposure which corresponds to a total loss in intensity of 12.6%. A linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.070 with an average value of 1.032.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 11.5 cm^{-1} for Mo $K\alpha$ radiation. An empirical absorption correction based on a series of psi scans was applied to the data. Relative transmission coefficients ranged from 0.906 to 1.000 with an average value of 0.947. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 362 observed and accepted reflections was 1.6% based on intensity and 1.4% based on F_o .

The structure was solved by using the Patterson heavy-atom method that revealed the position of the Fe atom. The remaining atoms were located in succeeding difference Fourier syntheses. A reasonable isotropic model with $R = 15\%$ was obtained. However, there was a difference peak of approximately $3 e/\text{Å}^3$ located within bonding distance of the C1 carbon atom (carbene). At this point a disorder problem was realized. Refinement of the multiplicity of this difference peak and that of the sulfur atom gave values of 0.2 and 0.8, respectively, which indicated that the difference peak was a sulfur atom. Further refinement failed to find the corresponding carbene carbon or the phenyl ring associated with the 0.2 occupancy sulfur atom. We concluded that the remaining atoms of the 0.2 occupancy ligand were too close to those of the 0.8 occupancy ligand to be resolved in difference Fourier maps. This conclusion was confirmed by the successful refinement of 0.2 occupancy atoms calculated in positions close to those of the 0.8 occupancy ligand. Both phenyl rings were refined as isotropic rigid groups and the two carbons as isotropic carbon atoms with their occupancy values set at 0.8 and 0.2. The temperature factors of the remaining atoms were treated anisotropically resulting in R values of 0.077 and 0.101. Hydrogen atoms were calculated for the cyclopentadienyl ligand and added to the structure factor calculations, but their positions were not refined.

The standard deviation on intensities, $\sigma(F_o^2)$, is defined as follows

$$\sigma(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/LP^2$$

where S is the scan rate, C is the total integrated peak count, R

(22) (a) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969. (b) Burlitch, J. M. *How to Use Ace No-Air Glassware*; Ace Glass: Vineland, New Jersey, 1971. (c) Kremer, K. A. M.; Helquist, P. *Organometallics* 1984, 3, 1743.

(23) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* 1967, 9, 165.

(24) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* 1976, 41, 1879.

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	2b	2c
formula	$\text{C}_{14}\text{H}_{11}\text{FeF}_6\text{O}_2\text{-PS}$	$\text{C}_{10}\text{H}_{11}\text{FeF}_6\text{O}_2\text{PS}$
fw	444.12	396.07
cryst dimens, mm	$0.30 \times 0.20 \times 0.40$	$0.41 \times 0.21 \times 0.24$
temp, °C	21 ± 1	23 ± 1
space group	$P2_1/c$	$P2_12_1$
a, Å	7.267 (2)	7.818 (2)
b, Å	14.245 (4)	11.696 (2)
c, Å	16.668 (3)	16.228 (4)
β , deg	96.84 (2)	
V, Å ³	1713.0	1483.9
Z	4	4
d(calcd), g/cm ³	1.722	1.773
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	11.5	13.2
scan type	$\theta/2\theta$	$\theta/2\theta$
scan rate, deg/min	$1.03\text{--}4.12$ (in ω)	$2.35\text{--}4.12$ (in ω)
scan width, deg	$0.9 + 0.350 \tan \theta$	$1.0 + 0.350 \tan \theta$
max 2θ , deg	54.9	52.9
no. of reflctns measd	4311 total, 3912 unique	1901 total, 1813 unique
solutn	Patterson method	Patterson method
reflctns included	2070 with $F_o^2 > 2.0\sigma(F_o^2)$	1184 with $F_o^2 > 2.0\sigma(F_o^2)$
GOF	2.29	2.85
R	0.0718	0.103
R_w	0.0952	0.127

is the ratio of scan time to background counting time, B is the total background count, L_p is the Lorentz-polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.060.

Scattering factors were taken from Cromer and Waber.^{25a} Anomalous dispersion effects were included in F_o^{25c} . The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.^{25b} Only the 2070 reflections having intensities greater than 2.0 times their standard deviation were used in the refinements. Least-squares weights were calculated as $w = 4F_o^2/\sigma^2(F_o^2) - 1/\sigma^2(F_o)$. The final cycle of refinement included 194 variable parameters and converged (largest parameter shift was 0.08 times its estimated standard deviation) with unweighted and weighted agreement: $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0718$ and $R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2} = 0.0952$. The standard deviation of an observation of unit weight was 2.29. There were 17 correlation coefficients greater than 0.50. The highest correlation coefficient was 0.60 between β 's of F3. The highest peak in the final difference Fourier had a height of 0.848 e/Å³ with an estimated error based on ΔF^{25d} of 0.10. Nine of the ten highest difference peaks were located near the PF₆ anion. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$ and various classes of indices showed one reflection; the (3,2-5) suffered from nonsystematic errors and was rejected. Further plots indicated no unusual trends.

All calculations were performed on a VAX-11/730 computer using SDP-PLUS^{25e} and locally modified versions of Levy's ORFLS and ORFFE and Zalkin's FORDAP. The final refinement features are listed in Table III, and the fractional coordinates are given in Table IV.

(η^5 -Cyclopentadienyl)dicarbonyl[methyl(methylthio)carbenium]iron Hexafluorophosphate (2c). To a stirred

Table IV. Fractional Coordinates for Complex 2b^a

atom	x	y	z
Fe	0.12503 (13)	0.15743 (6)	0.38506 (6)
S1	0.2444 (4)	0.33413 (17)	0.48920 (16)
Sx	0.1306 (17)	0.3747 (7)	0.3820 (6)
P1	0.4749 (3)	0.14493 (14)	0.69828 (13)
F1	0.6762 (9)	0.1618 (5)	0.6865 (7)
F2	0.2668 (8)	0.1291 (4)	0.7104 (5)
F3	0.4420 (16)	0.0905 (9)	0.6190 (5)
F4	0.4247 (14)	0.2421 (6)	0.6640 (7)
F5	0.5183 (11)	0.0483 (5)	0.7375 (6)
F6	0.4904 (11)	0.1967 (6)	0.7815 (5)
O2	-0.0158 (10)	0.1190 (5)	0.5387 (4)
O3	0.5139 (8)	0.1212 (6)	0.4371 (4)
C1	0.1537 (14)	0.2875 (7)	0.4046 (7)
Cx	0.192 (5)	0.2769 (27)	0.4299 (26)
C2	0.0446 (11)	0.1338 (6)	0.4801 (6)
C3	0.3603 (11)	0.1343 (6)	0.4182 (5)
C4	0.0429 (17)	0.1877 (6)	0.2632 (6)
C5	-0.1153 (12)	0.1668 (7)	0.3018 (6)
C6	-0.0932 (12)	0.0736 (6)	0.3299 (6)
C7	0.0757 (12)	0.0394 (6)	0.3116 (5)
C8	0.1602 (12)	0.1084 (8)	0.2685 (5)

^aThe estimated standard deviations of the least significant digits are given in parentheses.

solution of acetyl complex 8 (8.5 g, 38.6 mmol)^{4a,15} in ether (220 mL) at -78 °C was added a precooled solution (-78 °C) of trifluoromethanesulfonic anhydride (6.5 mL, 38.6 mmol) and ether (50 mL) dropwise. A yellow precipitate formed immediately. [If allowed to warm to above -65 °C, this yellow precipitate decomposed to a greenish-yellow oil.] This yellow solid was assumed to be the vinylidene complex 9.¹⁶ Condensed methylmercaptan (20 mL) was added to the yellow suspension at -78 °C. After the mixture was warmed to 25 °C, a deeper yellow solid formed. The flask was recooled to -20 °C, and the solid was washed with cold pentane (-20 °C, 300 mL) and dried under vacuum at -100 °C to afford 2c as a yellow powder (12.8 g, 83%): ¹H NMR (300 MHz, CD₃NO₂) δ 5.38 (s, C₅H₅), 3.56 (s, SCH₃), 3.01 (s, CH₃); ¹³C NMR (75 MHz, CD₃NO₂) δ 345.4 (Fe=C), 210.5 (FeCO), 90.1 (C₅H₅), 48.8 (CCH₃), 30.7 (SCH₃); IR (FT, CH₂Cl₂) 2058, 2018 cm⁻¹ (FeCO). This compound decomposes after 3 h at 25 °C. **Anion Exchange.** In a 50-mL round-bottom flask, 2c (120 mg, 0.3 mmol) and NH₄PF₆ (600 mg, 3.7 mmol) were dissolved in nitromethane (8 mL). The solution was stirred for 2 h at 25 °C followed by dilution with methylene chloride (40 mL). The upper liquid layer was filtered through a column of Celite (2 cm) under nitrogen. The filtrate was concentrated under vacuum and diluted with ether (40 mL) to precipitate 2c. The yellow solid was washed with cold ether (3 × 10 mL) and dried under vacuum to yield 2c as a yellow powder (56 mg, 46%): mp 136 °C dec; ¹H NMR (300 MHz, CD₂Cl₂) δ 5.36 (s, C₅H₅), 3.56 (s, SCH₃), 3.06 (s, CH₃); IR (FT, CH₂Cl₂) 2058, 2018 cm⁻¹ (FeCO).

X-ray Structure Determination of 2c. A yellow irregular crystal of 2c formed as for 2b and having approximate dimensions of 0.41 × 0.21 × 0.24 mm was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $20^\circ < |2\theta| < 26^\circ$, measured by the computer-controlled diagonal slit method of centering. The orthorhombic cell parameters and calculated volume are $a = 7.818$ (2) Å, $b = 11.696$ (2) Å, $c = 16.228$ (4) Å, and $V = 1483.9$ (7) Å³. For $Z = 4$ and $fw = 396.08$ the calculated density is 1.77 g/cm³. As a check on crystal quality, ω scans of several intense reflections were measured; the width at half-height was 0.26° with a takeoff angle of 2.8°, indicating moderate crystal quality. On the basis of the observance of the systematic absences $h00$, $h = 2n$, $0k0$, $k = 2n$, and $00l$, $l = 2n$, the space group was determined to be $P2_12_12_1$ (No. 19).

Data collections procedures were the same as described above for 2b. A total of 1901 reflections were collected, of which 1813 were unique. As a check on crystal and electronic stability, three

(25) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Cromer, D. T. *Ibid.* Table 2.31. (c) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* 1964, 17, 781. (d) Cruickshank, D. W. J. *Ibid.* 1949, 2, 154. (e) Frenz, B. A. In *Computing in Crystallography*; Schenk, H.; Olthof-Hazelkamp, R.; van Koningsveld, H.; Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71.

(26) (a) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* 1980, 102, 2458-2460. (b) Aoki, K.; Yamamoto, Y. *Inorg. Chem.* 1976, 15, 48-52. (c) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* 1972, 72, 545-574. (d) Aleksandrov, G. G.; Skripkin, V. V.; Kolobova, N. E.; Struchkov, Y. T. *Sov. J. Coord. Chem. (Eng. Transl.)* 1979, 5, 348-352; *Koord. Khim.* 1979, 5, 453-458.

Table V. Fractional Coordinates for 2c^a

atom	x	y	z
Fe1	0.3998 (3)	-0.00110 (26)	0.02659 (13)
S1	0.6192 (8)	-0.1094 (4)	0.16144 (29)
P1	0.8786 (8)	0.2154 (5)	0.2142 (3)
F1	0.7388 (23)	0.1980 (16)	0.2766 (10)
F2	0.8441 (27)	0.3429 (20)	0.2119 (12)
F3	0.914 (3)	0.0825 (20)	0.2164 (13)
F4	1.0097 (23)	0.2370 (14)	0.2848 (10)
F5	0.7441 (23)	0.1914 (16)	0.1483 (10)
F6	1.0290 (19)	0.2366 (12)	0.1493 (9)
O1	0.7476 (23)	-0.0195 (24)	-0.0412 (11)
O2	0.408 (3)	0.2460 (12)	0.0406 (9)
C1	0.413 (3)	0.1509 (17)	0.0356 (11)
C2	0.4674 (24)	-0.0168 (15)	0.1409 (10)
C3	0.644 (4)	-0.1144 (21)	0.2717 (12)
C4	0.385 (3)	0.0481 (18)	0.2075 (11)
C5	0.606 (3)	-0.0128 (21)	0.0114 (12)

^a Estimated standard deviations of the last significant digits are given in parentheses.

representative reflections were measured every 60 min of X-ray exposure. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 13.2 cm⁻¹ for Mo K α radiation. A numerical absorption correction was made by using six faces of the crystal. Relative transmission coefficients ranged from 73.580 to 81.029 with an average value of 76.864. Intensities of equivalent reflections were averaged. Ten reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 30 observed and accepted reflections was 3.7% based on intensity and 2.4% based on F_o . Psi scans of several reflections show a consistent trend with I_{\min}/I_{\max} values of about 0.66 Å. Neglecting absorption effects would leave errors as large as 34% on I untreated.

Only the 1184 reflections having intensities greater than 2.0 times their standard deviation were used in the refinements. The final cycle of refinement included 115 variable parameters and converged (largest parameter shift was 0.08 times its estimated standard deviation) with unweighted and weighted agreement factors of $R = \sum |F_o - F_c| / \sum |F_o| = 0.103$ and $R_w = [(\sum w(F_o - F_c)^2) / \sum w F_o^2]^{1/2} = 0.127$. The standard deviation of an observation of unit weight was 2.85. There was one correlation coefficient greater than 0.5 that involved parameters of the cyclopentadienyl rings, described as two equally contributing rigid groups. The highest peak in the final difference Fourier had a height of 1.57 e/Å³ (located between the iron atom and cyclopentadienyl ring) with an estimated error based on $\Delta F^{2\sigma}$ of 0.22 e/Å³. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin \theta) / \lambda$, and various classes of indices showed relatively poor agreement at low angles, most likely due to the only moderate accuracy of the cyclopentadienyl disorder model. Seven intermolecular contacts of less than 3.5 Å were found involving calculated Cp carbons and oxygen atoms of the carbonyls, the shortest contact being 3.095 Å. The final refinement features are listed in Table III, and the fractional coordinates are given in Table V.

(η^5 -Cyclopentadienyl)dicarbonyl[methyl(phenylthio)carbenium]iron hexafluorophosphate (2d). The same procedure was used as for 2c except for the replacement of methanethiol by benzenethiol. The product was isolated in a similar manner to yield the trifluoromethanesulfonate salt (81%) and then subjected to anion exchange as for 2c to yield the hexafluorophosphate salt 2d as golden yellow crystals (43%): mp 92–96 °C dec; ¹H NMR (300 MHz, CD₃NO₂) δ 7.49–7.70 (m, SC₆H₅), 5.53 (s, C₅H₅), 3.39 (s, CH₃); ¹³C NMR (75 MHz, CD₃NO₂) δ 351.7 (Fe=C), 210.0 (FeCO), 136.1, 133.6, 132.5, 131.8 (SC₆H₅), 90.8 (C₅H₅), 50.2 (CH₃); IR (FT, CH₂Cl₂) 2062, 2025 cm⁻¹ (FeCO). Anal. Calcd for C₁₅H₁₃F₆FeO₂PS: C, 37.69; H, 2.94. Found: C, 38.04; H, 2.99.

General Procedure for Reactions of Alkylmetal Reagents with 2b. (η^5 -Cyclopentadienyl)dicarbonyl[1-(phenylthio)-

alkyl]iron (3a–c). In the glovebox, 2b (0.221 g, 0.5 mmol) was placed in a 25-mL two-neck round-bottom flask fitted with a septum, a three-way stopcock, and a stirring bar. The flask was removed from the glovebox, connected to the nitrogen manifold, and cooled to -78 °C prior to addition of THF (4 mL). To the suspension was added the freshly prepared or commercially obtained alkylmetal reagent (0.5 mmol) slowly with vigorous stirring. After the addition was complete, the solution was stirred until the solid carbene complex was consumed (ca. 5–15 min). The mixture was stirred an additional 5 min before being removed from the bath, and then the solvent was removed under vacuum. The yellow residue was extracted with hexanes (3 \times 10 mL), and the combined extracts were filtered through a medium frit and then concentrated in vacuo. The yellow-brown oil was purified by column chromatography (silica gel, 4:1 hexanes/methylene chloride) to give the adducts 3a–c as yellow brown solids. These products contained varying amounts of Cp(CO)₂FeCH₂SPh (7) as a contaminant. Because of slight thermal sensitivity, microanalyses were not obtained for the adducts 3.

3a: 93% from CH₃Li and 73% from CH₃MgBr. The ¹H NMR, ¹³C NMR, and IR spectra matched those of previously reported 3a:^{3d} ¹H NMR (300 MHz, CDCl₃) δ 7.1–7.5 (m, SC₆H₅), 4.93 (s, C₅H₅), 3.78 (q, J = 6.8 Hz, CHCH₃), 1.58 (d, J = 6.8 Hz, CHCH₃); ¹³C NMR (75 MHz, CDCl₃) δ 216.09 (CO), 215.74 (CO), 141.00 (ipso), 128.45, 128.34, 124.91 (SC₆H₅), 86.09 (C₅H₅), 30.41 (FeCH), 21.12 (CH₃); IR (KBr pellet) 1990, 1930 cm⁻¹ (CO). This product was contaminated by ca. 1–2% of 7 according to ¹H NMR.

3b: 70% from *n*-C₅H₁₁MgBr; ¹H NMR (300 MHz, CDCl₃, homonuclear decoupling used) δ 7.0–7.4 (m, C₆H₅), 4.83 (s, C₅H₅), 3.62 (dd, J = 7, 5.3 Hz, FeCH(SPh)CH₂), 1.75–1.95 (apparent octet, J = 5.3 Hz, FeCH(SPh)CH₂), 0.72–1.2 (m, CH₂C₄H₉); ¹³C NMR (75 MHz, CDCl₃) δ 216.53, 215.64 (FeCO), 141.96 (ipso), 128.48, 128.41, 124.91 (SC₆H₅), 86.37 (C₅H₅), 44.69 (FeCHCH₂), 31.75, 30.43, 28.62 ((CH₂)₃), 22.63 (FeCH), 14.07 (CH₃); IR (FT, CH₂Cl₂) 2017, 1963 cm⁻¹ (CO); MS (EI), m/e 342 (M - CO), 314 (M - 2 CO), 230 (CpFeCSPh); exact mass for C₁₈H₂₂FeOS (M - CO) calcd 342.0741, found 342.0722. This product was contaminated by ca. 5–10% of 7 according to ¹H NMR.

3c: 70% from PhMgBr; ¹H NMR (200 MHz, CDCl₃) δ 6.86–7.34 (m, SC₆H₅, C₆H₅), 4.72 (s, FeCH), 4.68 (s, C₅H₅); ¹³C NMR (75 MHz, CDCl₃) δ 215.93, 214.62 (FeCO), 142.80 (ipso SC₆H₅), 131.02 (ipso C₆H₅), 128.22, 128.01, 126.15, 125.66, 124.12, 123.87 (SC₆H₅, C₅H₅), 86.61 (C₅H₅), 25.05 (FeCH); IR (FT, CH₂Cl₂) 2020, 1968 cm⁻¹ (CO); MS (EI), m/e 348 (M - CO), 320 (M - 2 CO), 230 (CpFeSPh), 199 (HC(Ph)(SPh)); exact mass for C₁₉H₁₆FeOS (M - CO) calcd 348.0271, found 348.0298.

(η^5 -Cyclopentadienyl)dicarbonyl[(phenylthio)(2-ketocyclohexyl)methyl]iron (3d). In the glovebox, 2b (0.221 g, 0.5 mmol) was placed in a solid addition arm connected to a 25-mL three-neck round-bottom flask with contained the trimethylsilyl ether of cyclohexanone (0.085 g, 0.5 mmol).²⁷ The flask was equipped with a magnetic stirring bar, a septum, and a three-way stopcock. The apparatus was removed from the glovebox and connected to the nitrogen manifold. THF (2 mL) was added to the silyl ether, and the enolate was generated²⁷ by slow addition of methylolithium (0.36 mL, 0.5 mmol, 1.4 M) at 25 °C. After the mixture was allowed to stir for 10 min, it was cooled to -78 °C, and 2b was added. After 5 min, the light brown solution became homogenous. The mixture was slowly warmed to 0 °C. Glacial acetic acid (0.28 mL, 0.5 mmol) was injected, and the mixture was quickly filtered through a small plug of flash chromatography grade silica gel. The solvent was removed under vacuum to leave a yellow residue. Column chromatography (silica gel, Et₂O/hexanes, 1:1) yielded 0.142 g (91%) of 3d as a yellow oil. The diastereomers (3:2 ratio of A:B) were not separable. A: ¹H NMR (300 MHz, CDCl₃, homonuclear decoupling used) δ 7.13 (m, C₆H₅), 4.90 (s, C₅H₅), 4.73 (d, J = 2 Hz, FeCH), 1.00–2.75 (m, C₆H₉O); ¹³C NMR (75 MHz, CDCl₃) δ 217.63, 216.30 (FeCO), 212.44 (C=O), 141.02 (ipso), 128.77, 127.94, 125.13 (SC₆H₅), 87.48 (C₅H₅), 56.87 (FeCHCH), 41.55 (C(=O)CH₂), 30.75, 25.77, 24.97, 22.07 (cyclohexyl (CH₂)₃ and FeCH). B: ¹H NMR (300 MHz, CDCl₃, homonuclear decoupling used) δ 7.13 (m, C₆H₅), 4.85 (s, C₅H₅),

(27) (a) Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* 1968, 90, 4464. (b) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* 1969, 34, 2324.

4.45 (d, $J = 8$ Hz, FeCH), 1.00–2.75 (m, C_6H_9O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.12, 215.75 (FeCO), 213.49 (C=O), 143.36 (ipso), 128.54, 127.81, 124.97 (SC_6H_5), 86.92 (C_5H_5), 65.52 (FeCHCH), 41.97 (C(=O)CH₂), 34.51, 28.18, 24.19, 23.42 (cyclohexyl (CH₂)₃ and FeCH). **A + B**: IR (FT, CH₂Cl₂) 2018, 1958 (FeCO), 1700 (C(=O)C) cm^{-1} ; MS (EI) m/e 396 (M⁺), 340 (M – 2 CO), 230 (CpFeSPh); exact mass for FeSC₁₈H₂₀O (M – 2 CO) calcd 340.0584, found 340.0576.

General Procedure for Reactions of Dialkylcuprates with 2c,d. (η^5 -Cyclopentadienyl)dicarbonyl[1-methyl-1-(alkylthio)alkyl]iron (**3e–g**). A suspension of cuprous iodide (0.714 g, 3.75 mmol) in ether (20 mL) was cooled to -15 °C (for lithium dimethylcuprate) or to -50 °C (for lithium di-*n*-butylcuprate) under nitrogen. The alkylolithium (7.5 mmol) was added dropwise with stirring to the gray suspension. (The flask was brought to -30 °C for 10 min in the case of the di-*n*-butylcuprate.) The flask was then cooled to -78 °C, and **2c** or **2d** (1.0 g, 2.5 mmol) in methylene chloride (10 mL) was slowly added via a double-ended needle. The mixture was allowed to warm to 25 °C, and the solvent was removed in vacuo. The residue was extracted with methylene chloride (3 \times 10 mL), and the combined extracts were concentrated under vacuum to afford a brown oil. Radial chromatography (4-mm alumina, 4:1 pentane/methylene chloride) yielded the adducts **3e–g**.

3e: obtained as yellow crystals in 63% yield from **2c** and lithium dimethylcuprate: 1H NMR (300 MHz, $CDCl_3$) δ 4.84 (s, C_5H_5), 1.98 (s, SCH_3), 1.67 (s, $FeC(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.2 (FeCO), 87.1 (C_5H_5), 67.9, 39.1, 12.5; IR (Nujol) 2018, 1952 (FeCO) cm^{-1} ; MS (EI), m/e 238 (M – CO), 210 (M – 2 CO), 121 (FeCp), 89 (C(SPh)(CH₃)₂); exact mass for C₁₀H₁₄FeOS (M – CO) calcd 238.0114, found: 238.0114.

3f: obtained as an impure brown oil, containing an unidentified contaminant having strong aliphatic absorptions in the 1H NMR spectrum, in 51% yield from **2c** and lithium di-*n*-butylcuprate: 1H NMR (300 MHz, acetone-*d*₆) δ 4.96 (s, C_5H_5), 1.90 (s, SCH_3), 1.71 (s, $FeCCH_3$), 1.25–1.82 (m, 10 H, $FeC(CH_2)_3CH_3$ and impurity), 0.96 (t, $J = 7.3$ Hz, 4 H, impurity), 0.90 (t, $J = 6.9$ Hz, (CH₂)₃CH₃); ^{13}C NMR (75 MHz, acetone-*d*₆) δ 218.7, 218.2 (FeCO),

88.1 (C_5H_5), 49.5, 44.1, 36.9, 31.9, 24.0, 14.6, 12.5; MS (EI), m/e 280 (M – CO), 252 (M – 2 CO), 131 (C(SCH₃)(CH₃)(C₄H₉), 121 (CpFe); exact mass for C₁₃H₂₀FeOS (M – CO) calcd 280.0583, found 280.0564.

3g: obtained as a yellow brown oil in 60% yield from **2d** and lithium dimethylcuprate: 1H NMR (300 MHz, $CDCl_3$) δ 7.14–7.42 (m, SC_6H_5), 4.87 (s, C_5H_5), 1.49 (s, $FeC(CH_3)_2$); IR (Nujol) 2038, 1952 (FeCO) cm^{-1} ; MS, m/e 300 (M – CO), 272 (M – 2 CO), 230 (CpFeSPh), 218 (M – PhSH), 151 (C(SPh)(CH₃)₂), 121 (CpFe); exact mass for C₁₅H₁₆FeOS (M – CO) calcd 300.0271, found: 300.0265.

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Supplementary Material Available: Tables of thermal parameters, group parameters, and derived crystallographic coordinates for group atoms for complexes **2b** and **2c** and hydrogen atom coordinates and short interionic contacts for **2b** (7 pages); listings of structure factors for **2b** and **2c** (16 pages). Ordering information is given on any current masthead page.

Syntheses and Characterization of Organometallic Molybdenum–Iron–Sulfur and Molybdenum–Cobalt–Sulfur Clusters

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The photochemical reaction of [MeCpMoS(SH)]₂ (Cp = C₅H₅; MeCp = CH₃C₅H₄) with Fe(CO)₅ has resulted in the formation of [MeCpMoS₂Fe(CO)₃]₂ (I) in >50% yield. A second minor product, (MeCp)₂Mo₂S₃Fe₂(CO)₆ (II), has also been isolated from this reaction. Complex II has been prepared in better yield from the reduction of I with potassium graphite. X-ray diffraction studies of each of these complexes have been completed. I crystallizes in space group $P\bar{1}$ with $a = 6.598$ (2) Å, $b = 10.168$ (3) Å, $c = 10.203$ (3) Å, $\alpha = 99.81$ (2)°, $\beta = 107.55$ (2)°, $\gamma = 108.99$ (2)°, $V = 589.1$ Å³, and $Z = 1$. Complex II crystallizes in space group $P\bar{1}$ with $a = 12.542$ (2) Å, $b = 10.724$ (2) Å, $c = 10.296$ (1) Å, $\alpha = 121.35$ (9)°, $\beta = 93.90$ (1)°, $\gamma = 106.07$ (1)°, $V = 1088.5$ (3) Å³, and $Z = 2$. The structure of I contains a rather unusual planar array of metal ions, while II involves a butterfly arrangement of metal ions bridged by one μ_4 - and two μ_3 -sulfur ligands. The structures of these complexes are described and compared with those of related clusters. The reactions of [MeCpMoS(SH)]₂ with CpFe(CO)₂I and CpCo(CO)₂I₂ have resulted in the formation of [(MeCp)₂Mo₂S₄FeCp][I] (III) and [(MeCp)₂Mo₂S₄CoCp][(I)₂] (IV), respectively. Complex III crystallizes in space group Cc with $a = 19.348$ (10) Å, $b = 6.673$ (3) Å, $c = 17.524$ (9) Å, $\beta = 112.68$ (4)°, $V = 2087.3$ (2) Å³, and $Z = 4$. The metal ions of III lie in a plane that is perpendicular to the plane of sulfur atoms. The structure contains two μ_3 -sulfur ligands and a η^2 -S₂ ligand that bridges the two molybdenum ions. Spectral and electrochemical properties of the new clusters are discussed. Their reactions with unsaturated molecules and with electrophilic and nucleophilic reagents are compared to those of the related dinuclear molybdenum–sulfur complexes.

Introduction

The sulfido ligands in tetrasulfur-bridged cyclopentadienyl molybdenum dimers have been found to react

with hydrogen and with unsaturated molecules, and a number of hydrogenation and hydrogenolysis reactions have been catalyzed.^{1–3} It is interesting to consider the