However, it should be noted that $U(C_5H_5)_3$ yields are relatively low, and any radical must be sufficiently constrained that attack on the cyclopentadienyl rings predominates. Alternatively, the lower thermal stability of the $U(C_5H_5)_3R$ complexes may allow more facile population of the known, possibly concerted, ring hydrogen abstraction thermolysis pathway.[4b,c] It is not even certain that hydrogen abstraction from solvent molecules must be exclusively free radical in nature. For example, recent results in organoactinide $M[(CH_3)_5C_5]_2R_2$ chemistry reveal examples of facile, nonradical thermal hydrocarbon metathesis (e.g., eq 16).[1d]

$$M\text{-}R + C_6D_6 \rightarrow M\text{-}C_6D_5 + RD \qquad (16)$$

It is also interesting to note in Table II that the olefin produced in $U(C_5D_5)_3$(*n*-butyl) experiments contains appreciable amounts of deuterium. The mechanism of deuterium transfer from the rings to the olefin likely involves initial transfer to the metal to produce a metal deuteride, followed by reversible addition and elimination of the olefin. Facile deuteride–ring methyl scrambling is observed in $\{U[(CH_3)_5C_5]_2D_2\}_2$.[1d,64] When the $U(C_5H_5)_3R$ compounds are photolyzed in THF, the yield of $U(C_5H_5)_3$ (isolated as the THF adduct) increases significantly. This reaction was not investigated in detail; however, it is possible that the donor solvent alters the reaction pathway by intercepting intermediates such as C (with THF displacing the olefin) or by stabilizing caged radical pairs.[62]

Conclusions

This study demonstrates that nonthermal transformations can be brought about readily by the UV photolysis of organoactinides. In certain systems, photoinduced β-hydride elimination is facile and represents an efficient and clean route to new organoactinide hydrides and to actinide organometallics in unusual oxidation states. Such processes are, however, highly sensitive to the nature of the metal coordination sphere and to the 5f electron configuration; they may also be dependent, to a significant degree, on the properties of the solvent.

Acknowledgment. We are grateful to the National Science Foundation for support of this research (CHE8009060) and to Professor F. D. Lewis and Dr. W. A. Wachter for helpful discussions.

Registry No. 1, 58920-13-1; **2**, 80410-04-4; **3**, 54067-92-4; **4**, 58920-16-4; **5**, 80410-05-5; **6**, 80410-06-6; **7**, 80410-07-7; **8**, 52550-20-6; **9**, 63372-74-7; **10**, 37298-79-6; **11**, 37298-84-3; **12**, 80410-08-8; **13**, 80410-09-9; **14**, 37205-28-0; **15**, E = H, 80410-10-2; $Th(C_5H_5)_3Cl$, 1284-82-8; $U(C_5H_5)_3Cl$, 1284-81-7; $Th(\eta^5\text{-}C_9H_7)_3(n\text{-}C_4H_9)$, 63643-43-6; $Th(C_9H_7)_3$, 80410-11-3; $Th(C_9H_7)_3Cl$, 11133-05-4; $Th(C_9H_7)_3I$, 66775-24-4; $Th(\eta^5\text{-}C_5H_5)_4$, 1298-75-5; $U(C_5H_5)_3\cdot THF$, 74237-38-0; $(Th[\eta^5\text{-}(CH_3)_5C_5]_2H_2)_2$, 67506-92-7; $Th[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$, 67506-90-5; $Th(C_5H_5)_3I$, 80410-12-4; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; I_2, 7553-56-2; $CHCl_3$, 67-66-3; CH_3OH, 67-56-1; NH_4Cl, 12125-02-9; $U(C_5H_5)_3$, 54007-00-0; propene, 115-07-1; *n*-butane, 106-97-8; 1-butene, 106-98-9; methane, 74-82-8; hydrogen, 1333-74-0; ethane, 74-84-0; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; propane, 74-98-6.

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[64] Fagan, P. J.; Marks, T. J., unpublished results.

Stable Precursors of Transition-Metal Carbene Complexes. Simplified Preparation and Crystal Structure of (η^5-Cyclopentadienyl)[(dimethylsulfonium)methyl]dicarbonyliron(II) Fluorosulfonate

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Abstract: The sulfonium salt $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2S(CH_3)_2^+\ FSO_3^-$ (4), a possible precursor of an iron–carbene complex, is prepared in one simple sequence of reactions starting with commercially available $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The structure of **4** was determined by single-crystal X-ray diffraction techniques. This salt crystallizes in the space group *Pbca* (orthorhombic) with $a = 13.340$ (7) Å, $b = 15.096$ (3) Å, $c = 14.388$ (6) Å, and $Z = 8$. The structure was solved straightforwardly by a combination of Patterson and difference Fourier peak searches and was refined to values of $R = 0.045$ and $R_w = 0.057$. One structural parameter which is consistent with **4** behaving as a carbene-like complex is the Fe–C σ-bond length of 2.036 (3) Å, which is somewhat shorter than in the cases of other related iron alkyls. However, other structural parameters do not provide consistent support for the iron–carbene nature of **4**. Alternatively, the shortening of the Fe–C bond may be due to the operation of an inductive effect of the sulfonium group.

Transition-metal carbene complexes have been the subject of intensive investigation during the past two decades.[1] In recent years the involvement of these species in various important types of reactions has been realized. Among these reactions are alkene metathesis[2] and the conversion of alkenes into cyclopropanes.[1,3] One system that has been studied especially thoroughly is the cationic (η^5-cyclopentadienyl)dicarbonylalkylideneiron(II) group

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[1] For some selected reviews of transition-metal carbene complexes, see: (a) Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407–423; **1972**, *30*, 353-372. (b) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545–574. (c) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem. 16*, 487–613. (d) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99–144. (e) Dōtz, K. H. *Naturwissenschaften* **1975**, *62*, 365–371. (f) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32. (g) Casey, C. P. *J. Organomet. Chem. Libr.* **1976**, *1*, 397–421. (h) Casey, C. P. *CHEMTECH* **1979**, 378–383. (i) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122. (j) Cardin, D. J.; Norton, R. J. *Organomet. Chem.* **1980**, *8*, 286–292; see also the earlier volumes of this series.

[2] For some recent reviews on the mechanism of alkene metathesis, see: (a) Rooney, J. J.; Stewart, A. *Catalysis (London)* **1977**, *1*, 277–334. (b) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283–317. (c) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1–50. (d) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492.

[3] For some more recent examples of the conversion of alkenes into cyclopropanes by the action of a transition-metal carbene complexes, see: (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282–7292.

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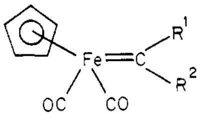
of carbene complexes (**1**).[4] Interest in these compounds arose



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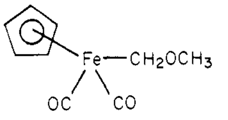

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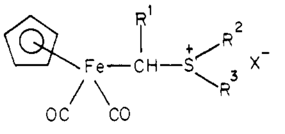

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initially when Pettit reported in 1966 that the methyl ether derivative **2** reacts with alkenes in the presence of fluoroboric acid to give cyclopropanes, apparently via the intermediacy of the parent methylene complex (**1**, $R^1 = R^2 = H$).[4a] Since that time a number of other workers have studied the chemical, physical, and bonding properties of this system,[4] and in particular, we have developed the use of the sulfonium salts **3** as possible precursors of the alkylidene complexes **1**.[5] These salts, which may formally be considered to be iron complexes of sulfonium ylides, react with a range of alkenes in a synthetically useful manner to produce the corresponding cyclopropanes in good yields. In this paper we report a simplified preparation of one of these sulfonium salts and the determination of its crystal structure as a probe for studying the basis of its carbene-like reactivity.

Experimental Section

General Procedures. All reactions of air- and moisture-sensitive materials were performed under nitrogen through use of double-manifold techniques and Schlenk glassware.[6] Air-sensitive solutions were transferred with hypodermic syringes or double-ended needles. Tetrahydrofuran and 1,4-dioxane were distilled from dark blue or dark purple solutions of sodium benzophenone radical anion or dianion under nitrogen. Bis[(η_5-cyclopentadienyl)dicarbonyliron(I)] was obtained commercially from Alfa Ventron or was prepared by the published procedure.[7] Cyclooctene and chloromethyl methyl sulfide were obtained from Aldrich, and methyl fluorosulfonate was obtained from Tridom Chemical Co. (Fluka). The latter two organic reagents were used without further purification whereas the cyclooctene was distilled before use.

Table I. Crystal Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2S(CH_3)_2{}^+FSO_3{}^-$ (**4**) and Data Collection Procedures

formula	$C_{10}H_{13}FFeS_2O_5$
mol wt	352.19
space group	*Pbca* (orthorhombic)
a, Å	13.340 (7)
b, Å	15.096 (3)
c, Å	14.388 (6)
V, Å^3	2897.5
Z	8
ρ(calcd), g/cm^3	1.615
ρ(measd)	1.57
cryst shape, mm	1.12 × 0.31 × 0.21
radiation	Mo Kα(λ 0.71073 Å) with a graphite monochromator
scan mode	ω-2θ
2θ range deg	$0 < 2\theta < 48$
reflctns	2601 collected, 1608 unique with $\lvert F_o\rvert^2 > 3\sigma\lvert F_o\rvert^2$ used; 172 variables
linear abs coeff, cm^{-1}	13.669
error in obsrvn of unit weight, *e*	2.079
temp, °C	22
R	0.045
R_w	0.057

The IR spectra were obtained with a Pye-Unicam Model SP-1000 spectrophotometer as KBr wafers and were calibrated with a polystyrene standard. The ^1H NMR spectra were recorded at 60 MHz with a Varian EM-360 spectrometer or at 80 MHz with a Varian HFT-80 spectrometer using acetone-d_6 solutions and were calibrated with internal acetone. The chemical shifts are expressed in parts per million (δ) downfield from Me_4Si, and the ^1H NMR peak areas are expressed as the number of hydrogen atoms (H). Analtyical GLPC was performed with a Hewlett-Packard Model 5711 gas chromatograph equipped with a flame ionization detector, a linear temperature programmer, a Hewlett-Packard Model 3380A electronic reporting integrator, and a 6 ft × $^1/_8$ in. 5% OV-1 column.

Preparation of (η^5-Cyclopentadienyl)dicarbonyl[(dimethylsulfonium)methyl]iron(II) Fluorosulfonate (4). The following procedure is an improved and simplified modification of our earlier procedure.[5a,8] A 250-mL round-bottom flask was equipped with a magnetic stirring bar, a pressure-equalizing addition funnel, and a three-way stopcock (atop the funnel). The two arms of the stopcock were connected to a nitrogen manifold and a pressure-release bubbler. Into the flask were placed freshly cut pieces of sodium (0.92 g, 40 mmol), and a nitrogen atmosphere was established within the assembled apparatus. Mercury (92 g) was slowly added from the funnel, and the resulting mixture was stirred as the 1% sodium amalgam was formed. [**Caution**: The initial dissolution of the sodium in the mercury is very exothermic; the apparatus should be shielded, and the pressure-release bubbler must be connected to the outlet of the stopcock because of the very sudden increase of pressure.] After the amalgam cooled to room temperature, the addition funnel was replaced by a stopcock, and tetrahydrofuran (90 mL) was added to the flask followed by bis[(η^5-cyclopentadienyl)dicarbonyliron(I)] (5.66 g, 16 mmol). After the dark brown mixture was stirred for 2 h at 25 °C under nitrogen, chloromethyl methyl sulfide (2.68 mL, 32 mmol) was added dropwise with a syringe. After 1 h, the mixture was diluted with methylene chloride (90 mL). The yellow-green solution was removed from the mercury with a double-ended needle and transferred to a Schlenk filter tube containing a layer of diatomaceous earth covered with a piece of filter paper and placed under nitrogen. By application of slight vacuum to the vacuum flask, a dark amber-colored filtrate was collected in a round-bottom flask equipped with a septum-covered side arm. To the filtrate was added methyl fluorosulfonate (2.58 mL, 32 mmol) with a syringe, and immediately, yellow flakes precipitated from the reaction mixture. The solid was isolated in the air by suction filtration with a Buchner funnel. After being washed with two 5-mL portions of methylene chloride, the solid was allowed to dry in the air, leaving 6.57 g (58%) of **4** as small, yellow plates: mp 110–116 °C dec; IR (KBr) 2012 and

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Table II. Positional and Thermal Parameters and Estimated Standard Deviations for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2S(CH_3)_2{}^+FSO_3{}^-$ (4)[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.08654 (5)	0.18451 (4)	0.14264 (4)	4.00 (3)	3.07 (3)	3.01 (3)	−0.47 (2)	−0.53 (2)	−0.08 (2)
S1	0.09242 (7)	0.38571 (7)	0.06596 (7)	3.47 (4)	3.50 (5)	2.80 (4)	−0.05 (4)	−0.15 (3)	0.15 (3)
S2	0.29490 (9)	0.41022 (9)	0.33733 (8)	3.73 (5)	6.69 (6)	4.60 (5)	0.59 (5)	−1.04 (4)	−1.40 (5)
O1[b]	0.2617 (4)	0.3182 (3)	0.3475 (4)	10.6 (4)	6.8 (3)	14.7 (4)	−1.4 (2)	−3.6 (1)	0.9 (3)
O2[b]	0.3371 (3)	0.4115 (4)	0.2477 (3)	8.9 (3)	17.3 (5)	5.2 (2)	0.3 (3)	1.2 (2)	−0.6 (3)
O3[b]	0.2058 (3)	0.4627 (3)	0.3398 (3)	6.8 (2)	11.3 (3)	10.9 (3)	5.1 (2)	−1.4 (2)	−1.9 (3)
O4	0.3036 (3)	0.1858 (3)	0.1360 (3)	4.3 (1)	6.8 (2)	13.0 (3)	1.6 (2)	−0.9 (2)	−1.4 (2)
O5	0.0839 (4)	0.1632 (3)	0.3415 (2)	16.4 (4)	7.8 (2)	3.7 (2)	−3.9 (2)	−1.8 (2)	1.4 (2)
O6[b]	0.3633 (3)	0.4311 (3)	0.4054 (3)	6.4 (2)	13.5 (4)	8.3 (2)	0.8 (2)	−3.5 (2)	−4.5 (2)
C1	0.0949 (4)	0.4943 (3)	0.1153 (3)	7.0 (3)	3.3 (2)	4.4 (2)	−0.3 (2)	−0.2 (2)	0.3 (2)
C2	0.2202 (3)	0.3731 (3)	0.0310 (3)	3.4 (2)	5.4 (3)	5.2 (3)	−0.2 (1)	1.0 (2)	0.9 (2)
C3	0.0797 (3)	0.3173 (3)	0.1664 (3)	4.2 (2)	3.2 (2)	2.4 (2)	−0.1 (2)	0.0 (2)	−0.2 (1)
C4	0.2182 (4)	0.1864 (3)	0.1368 (4)	4.9 (2)	3.5 (2)	6.7 (2)	0.6 (2)	−0.9 (2)	−0.6 (2)
C5	0.0857 (4)	0.1718 (3)	0.2637 (3)	9.2 (4)	3.9 (2)	3.9 (2)	−1.8 (2)	−1.6 (2)	0.7 (2)
C6	0.0743 (4)	0.0818 (3)	0.0465 (4)	7.1 (3)	4.6 (2)	6.3 (3)	−0.1 (2)	−1.0 (2)	−2.8 (2)
C7	0.0471 (4)	0.1622 (3)	0.0039 (3)	6.7 (3)	5.9 (3)	3.3 (2)	−1.8 (2)	−0.8 (2)	−0.4 (2)
C8	−0.0347 (4)	0.1960 (3)	0.0502 (4)	4.8 (2)	5.5 (3)	6.2 (3)	−0.6 (2)	−2.9 (2)	−0.7 (2)
C9	−0.0592 (4)	0.1374 (4)	0.1219 (4)	5.1 (2)	8.2 (3)	6.0 (3)	−3.1 (2)	0.4 (2)	−2.0 (2)
C10	0.0079 (4)	0.0671 (3)	0.1198 (4)	9.5 (3)	4.2 (2)	5.4 (3)	−3.4 (2)	−1.8 (2)	0.3 (2)
HC6	0.1297 (0)	0.0431 (0)	0.0300 (0)	5.0000 (0)					
HC7	0.0827 (0)	0.1879 (0)	−0.0482 (0)	5.0000 (0)					
HC8	−0.0713 (0)	0.2498 (0)	0.0342 (0)	5.0000 (0)					
HC9	−0.1098 (0)	0.1432 (0)	0.1679 (0)	5.0000 (0)					
HC10	0.0094 (0)	0.0164 (0)	0.1576 (0)	5.0000 (0)					
H1C1	0.0996 (0)	0.5384 (0)	0.0685 (0)	5.0000 (0)					
H2C1	0.0333 (0)	0.5049 (0)	0.1499 (0)	5.0000 (0)					
H3C1	0.1492 (0)	0.5005 (0)	0.1576 (0)	5.0000 (0)					
H1C2	0.2327 (0)	0.4109 (0)	−0.0236 (0)	5.0000 (0)					
H2C2	0.2641 (0)	0.3948 (0)	0.0789 (0)	5.0000 (0)					
H3C2	0.2357 (0)	0.3153 (0)	0.0159 (0)	5.0000 (0)					
H1C3	0.0215 (0)	0.3320 (0)	0.2070 (0)	5.0000 (0)					
H2C3	0.1328 (0)	0.3320 (0)	0.2285 (0)	5.0000 (0)					

[a] The form of the anisotropic thermal parameter is $\exp[-(^1/_4)\{B_{11}(a^*h)^2 + B_{22}(b^*k)^2 + B_{33}(c^*l)^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*k^*l\}]$. [b] The four substituents of the sulfur atom of the $FSO_3{}^-$ counterion were treated as oxygen atoms (O1, O2, O3, O6).

1962 cm^{-1}; ^{1}H NMR (acetone-d_6) 5.37 (s, 5 H), 2.99 (s, 6 H), 2.73 (s, 2 H). Crystals suitable for X-ray diffraction studies were obtained by very straightforward recrystallization from acetone in the air.

In order to examine the reactivity of this fluorosulfonate relative to the earlier reported tetrafluoroborate, we allowed a portion of **4** (2 equiv) to react with cyclooctene in refluxing dioxane for 12 h according to the previously published procedure.[5a] The ratio of the cyclopropanation product, bicyclo[6.1.0]nonane, to unreacted cyclooctene was found to be 77:23 according to analytical GLPC. In the case of the tetrafluoroborate, the corresponding ratio was 95:5.[5a]

X-ray Diffraction Studies. The reflection data for **4** were obtained with an Enraf-Nonius CAD-4A automated diffractometer controlled by a PDP 11/45 computer. Mo Kα radiation was employed. The space group *Pbca* was uniquely defined by systematic absences of reflections. According to three standard reflections which were remeasured after every 100 reflections, the mounted crystal showed no systematic indications of movement or decomposition. The data were reduced ($p = 0.04$), and a numerical correction for absorption by the crystal was applied to the data. The computer programs that were used were those of the standard Enraf-Nonius structure determination package developed by Okaya and Frenz.[9] A summary of the crystal data and collection procedures is given in Table I.

The iron atom of **4** was located very easily with a Patterson map, and the remaining nonhydrogen atoms were located by a few cycles of least squares and difference Fourier peak searches, although the fluorine and oxygen atoms of the fluorosulfonate counterion could not be distinguished from one another. Therefore, for purposes of refinement, all four substituents on sulfur in the sulfonate anion were assigned as oxygen atoms and are indicated as such in all of our tabulations of data. After refinement of the nonhydrogen atom positions using anisotropic thermal parameters, the hydrogen atoms of the methylene group (C3) were located by a difference Fourier peak search, but the positions of the remaining hydrogen atoms were calculated with the assumption of ideal geometries about the cyclopentadienyl and methyl groups. All of the hydrogen atoms were assigned isotropic temperature factors of 5.0 Å^2 and added as fixed contributions for the remainder of the refinement cycles. The function which was minimized by the least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, $R = \sum[|F_o| - |F_c|]/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, $w = 1/(\sigma^2 + 0.0016F_o{}^2)$. Anomalous dispersion corrections were made for all nonhydrogen atoms. The final positional and thermal parameters are given in Table II, and the resulting structural parameters are given in Table III.

Table III. Some Selected Bond Distances (Å) and Angles (Deg) and Estimated Standard Deviations for the Cations of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2S(CH_3)_2{}^+FSO_3{}^-$ (4)

Fe–C3	2.036 (3)	Fe–C3–S1	115.5 (2)
Fe–C4	1.759 (4)	Fe–C3–H1C3	110.6 (2)
Fe–C5	1.753 (4)	Fe–C3–H2C3	106.8 (2)
Fe–C6	2.083 (3)	S1–C3–H1C3	114.9 (2)
Fe–C7	2.092 (3)	S1–C3–H2C3	117.1 (2)
Fe–C8	2.101 (3)	H1C3–C3–H2C3	88.9 (2)
Fe–C9	2.092 (4)	C1–S1–C2	101.0 (2)
Fe–C10	2.085 (3)	C1–S1–C3	102.2 (2)
S1–C1	1.786 (3)	C2–S1–C3	104.9 (2)
S1–C2	1.788 (3)		
S1–C3	1.784 (3)		

Results

Earlier we had reported the preparation and reactivity of the dimethylsulfonium salt **3** (R^1 = H, $R^2 = R^3 = CH_3$, X = BF_4).[5a] Although this preparation was quite efficient with respect to yields of product obtained, it was somewhat cumbersome and required the use of trimethyloxonium tetrafluoroborate. This latter reagent requires special handling procedures and is somewhat inconvenient to prepare,[10] although it may be obtained commerically at a rather high price. Therefore, we sought to develop a much more practical procedure for obtaining these useful sulfonium salts. On the basis of previous experience, we realized that the salts needed to contain weakly coordinating or noncoordinating counterions which would not interfere with the subsequent reactions of the iron reagents with alkenes. The fluorosulfonate salt, which would be available

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(9) (a) Okaya, Y. In "Computing in crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: The Netherlands, 1978; pp 153–165. (b) Frenz, B. A. *Ibid.* pp 64–71.

(10) (a) Meerwein, H. "Organic Syntheses", Wiley: New York, 1973: Collect. Vol. V, pp 1096–1098. (b) Curphey, T. J. *Ibid.* **1971**, *51*, 142–147.

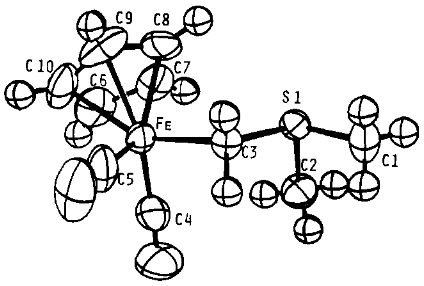


Figure 1. ORTEP drawing of the cation of $(\eta^5\text{-}C_5H_5)(Fe(CO)_2CH_2S(CH_3)_2{}^+$ FSO_3^- (**4**) with the crystallographic numbering scheme. The atoms are represented by % probability ellipsoids.

through use of methyl fluorosulfonate (Magic Methyl), appeared to be a reasonable choice. Our further efforts have now resulted in the streamlined preparation of the fluorosulfonate **4** (eq 1). The

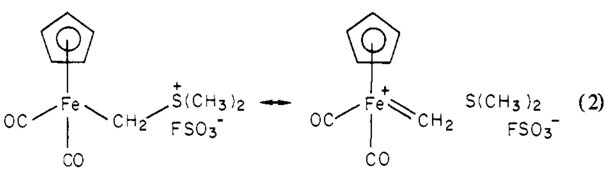
$$0.5[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow[(2)\ ClCH_2SCH_3]{(1)\ Na/Hg,\ THF} (\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SCH_3 \xrightarrow[THF]{FSO_3CH_3} \underset{\mathbf{4}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2S(CH_3)_2{}^+FSO_3^-} \quad (1)$$

commerically available or easily prepared $[(\eta_5\text{-}C_5H_5)Fe(CO)_2]_2$[7] is converted to the corresponding sodium ferrate by reaction with sodium amalgam, and without any apparent need for separation from the remaining mercury, the solution of the ferrate is allowed to react with chloromethyl methyl sulfide. The resulting solution of the sulfide $(\eta^5\text{-}C_5H_5)fe(CO)_2CH_2SCH_3$[8] is filtered. Reaction of the filtrate with methyl fluorosulfonate [**Caution**: Methyl fluorosulfonate is a toxic, volatile liquid which should be used with proper ventilation.[11]] results in immediate precipitation of crystalline **4** which may then be isolated by suction filtration in the air. This procedure is readily adaptable to large-scale preparations of the desired product. Subsequent reaction of **4** with cyclooctene to give bicyclo[6.1.0]nonane indicates that this salt is nearly comparable in reactivity to the previously reported tetrafluoroborate.[5a]

The structure of **4** was determined by single-crystal X-ray diffraction. The solution of the structure by a combination of Patterson and difference Fourier peak searching techniques was very straightforward except that the fluorine and oxygen substituents of the fluorosulfonate anion could not be distinguished from one another. The geometry of the cation of **4** is shown in Figure 1, and the observed bond distances and angles are listed in Table III.

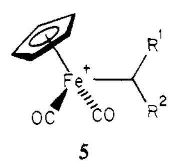
Discussion

A principal reason for studying the structure of **4** was to determine whether any of the structural parameters of this compound are indicative of its reactivity patterns and specifically its possible role as a precursor of a cationic carbene complex of type **1**. One conceivable explanation for the reactivity of **4** would be the contribution of **4′** to the overall structure of the reagent (eq 2).

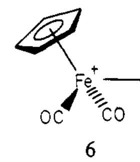


4 **4′**

According to calculations performed by Hoffmann and co-workers on this system,[4n] a reasonably significant π-bonding interaction is possible between a rehybridized donor orbital on iron and the empty p orbital of the carbene ligand. An obvious parameter to examine in **4** is the Fe–C bond length for which a possible shortening may be expected in comparison with iron alkyls in which only Fe–C σ bonding is likely. Another point of interest is the CH_2–S bond of the methylide portion of the structure of **4** which may be expected to be somewhat lengthened. A tendency toward planarity of the Fe–CH_2 system would be another possible indication of carbene-like character of the complex. Finally, Hoffmann's theoretical studies of **1** (vide supra) predict that in the actual carbene complex, the geometry shown in **5** should be favored over **6**, the two structures differing by a 90° rotation about the Fe–C bond.[4n] This point has been studied in experimental work of others.[4s,t,x]

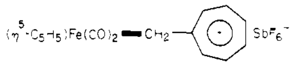
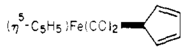
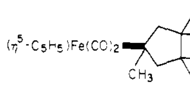
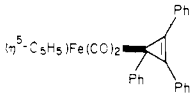
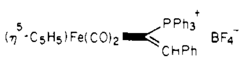
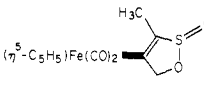
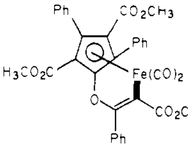
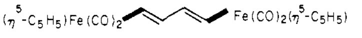
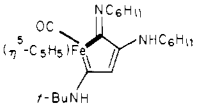
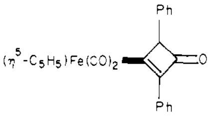


5



6

Table IV. Selected Fe–C Bond Lengths from Previous X-ray Crystallographic Studies

entry	compound	Fe–C σ bond length (Å)[a]	R	ref
1		2.16 (5)	0.123	12
2		2.11 (2)	0.141	13
3	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$—$CH_2CO_2$-menthyl	2.11 (1)	0.084	14
4		2.098 (2)	0.0391	15
5	$(\eta^5\text{-}C_5H_5)Fe(CO)_2$—$(CH_2)_n$—$Fe(\eta^5\text{-}C_5H_5)(CO)_2$, $n = 3$	2.08 (1)	0.051	16
6	$n = 4$	2.08 (1)	0.059	16
7		2.08 (1)	0.097	17
8	$(\eta^5\text{-}C_5H_5)Fe(CO)_2$—$CH_2CO_2H$	2.06 (2)	0.132	18
9		2.025 (6)	0.076	19
10	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$—$CH_2O$-mentyl	2.001 (8)	0.062	20
11		1.996 (8)	0.0580	21
12		1.99 (2)	0.139	22
13		1.987 (3)	0.0548	23
14		1.960 (3)	0.0505	24
15		1.935 (6)	0.068	25
16	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$—$CO_2$-menthyl	1.825 (6)	0.066	26

[a] These values refer to the lengths of the heavily shaded Fe–C bonds.

Upon examination of the actual X-ray structural data for **4**, the most obvious parameter relative to the preceding discussion

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[11] For a descritpion of toxic effects of methyl fluorosulfonate and a suggested treatment for inhalation of this volatile reagent, see: *Chem. Eng. News* **1978**, 56.

is the Fe–C3 bond length of 2.036 (3) Å (see Table III). From earlier X-ray data of others (Table IV), a typical Fe–C(sp^3) bond length would be expected to be within the range of approximately 2.08–2.10 Å (entries 2–7) whereas Fe–C(sp^2) values are most typically in the range of 1.98–2.00 Å (see especially entries 11–13), although these latter values are quite sensitive to the exact nature of the organic group. Therefore, the bond in **4** is slightly shorter than normal for Fe–C(sp^3) bonds and is actually intermediate between the typical Fe–C(sp^3) and Fe–C(sp^2) values. However, in the case of **4**, the value is not as short as those for previously studied cases of actual carbene complexes. For these compounds, the Fe=C bond lengths lie within the range of approximately 1.91–2.00 Å according to X-ray studies.[4t,24,27,28] The bond length of 2.001 (8) Å in the case of an ether derivative (Table IV, entry 10) may be somewhat surprising in view of the poorer leaving-group ability of the alkoxide substituent in contrast to the neutral dimethyl sulfide which serves as the leaving group in **4**. However, the replacement of a carbonyl ligand by the better electron-donating phosphine in entry 10 would be expected to result in greater stabilization of the cationic carbene form of the complex.[4s]

The next structural parameter of concern is the length of the C3–S1 bond between the potential carbene center and the sulfonium group of **4**. Surprisingly, all three of the S–C bond lengths of **4** are approximately 1.78–1.79 Å. For simple organic sulfonium salts, S–CH$_3$ bond lengths vary most commonly in the range of 1.80–1.83 Å, although a value of 1.76 (2) Å has been reported in one case, and S–alkyl (nonmethyl) values generally fall within the range of 1.80–1.84 Å.[29] Therefore, the values for **4** are inconsistent with our original expectations. However, in the case of a previously reported X-ray crystal structure of a sulfonium ylide, a C–S bond length of 1.743 (6) Å between the ylide carbon and the sulfonium group was observed.[29i] Consequently, the slightly low value for the C3–S1 bond in **4** may be a reflection of ylide character. In the case of the menthyl ether shown in entry 10 of Table IV, though, a significant lengthening of the C–O bond to the potential carbene center was reported in conjunction with the aforementioned Fe–C bond shortening as further evidence for carbene-like character of the complex.[20]

For compound **4** the conformation of the methylene group relative to the rest of the ligands of the iron atom is intermediate between that of **5** and **6**. Furthermore, the methylene carbon (C3) possesses a nonplanar, tetrahedral-like configuration, although there is considerable distortion with the Fe–C3–S1 angle opened up to 115.5 (2)°. This enlarged angle may simply result from minimization of steric repulsion between the (η^5-C$_5$H$_5$)Fe(CO)$_2$ and the sulfonium group of **4**. Similar behavior is observed for the compounds in entries 5 and 6 of Table IV for which the Fe–Cα–Cβ bond angles are 113°–115°.[16]

Unfortunately, although a number of sulfonium ylide complexes of other metals have been reported,[8,30,31] very few X-ray crystallographic studies have been performed on these compounds, and the compounds for which detailed structures have been reported are not sufficiently closely related to **4** to permit completely valid comparison of structural parameters. One of these compounds is an oxysulfonium (or sulfoxonium) ylide complex of gold,[31j] and another is a triiodo(dineopentylsulfonium methylide)zincate.[31a] For the latter compound, the bond corresponding to the C3–S1 bond of **4** has a length of 1.76 (6) Å, and the Zn–C–S angle is 111 (3)°. Despite the obvious difference between this zinc compound and **4**, the similarity of these particular parameters for the two compounds is intriguing.

Overall, although one may wish to attribute the somewhat short Fe–C3 bond of **4** to partial carbene character of the complex, the other trends in the structural data are not fully in accord with this explanation. An alternative explanation for our observations is that the slight shortening of the Fe–C3 bond may be attributed to an inductive effect of the positively charged sulfonium group of **4**. A similar effect may be operable in the case of the carboxymethyl derivative shown in Table IV (entry 8) for which the corresponding Fe–C bond length of 2.06 (2) Å may be at least marginally shorter than in the other relevant cases, although the σ and R values for this earlier structure determination are uncomfortably large (see also entries 1 and 3). If this explanation is valid, the perhaps shorter value for **4** would not be unexpected on the basis of the greater inductive effect of the dimethylsulfonium substituent compared to the carboxy group.[32]

A final point pertains to our difficulty in distinguishing the fluorine and oxygen substituents of the fluorosulfonate anion of **4**. This problem is not unusual in that earlier workers have made similar observations with other fluorosulfonate salts and have attributed this behavior to disorder in the arrangement of this ion in the crystal lattice.[33]

Conclusion

We have developed a quite practical, simplified route to the very useful sulfonium complex **4** which should be of considerable

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value to workers wishing to study the reactivity and applications of this class of compounds. However, the details of our X-ray crystallographic structure determination of **4** do not provide a convincing basis for explaining the carbene-like reactivity of this compound. Further investigations are in progrss in our laboratory to probe the mechanistic features of the reactions of **4** and related compounds.

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Supplementary Material Available: Tables of crystal data, scattering factors, bond distances and bond angles, positional and thermal parameters, and calculated and observed structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

Synthesis, Molecular Structure, and Reactions of Bis(tetraphenylphosphonium) Hexakis(μ-thiophenolato)-tetrachlorotetraferrate(II), $(Ph_4P)_2[Fe_4(SPh)_6Cl_4]$. Its Reactions with Dibenzyl Trisulfide and the Synthesis of the $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_4S_4(Cl)_2(SC_6H_5)_2]^{2-}$ "Cubane"-Type Clusters

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Abstract: The reaction between $FeCl_2$, $(C_6H_5)_4PCl$, and KSC_6H_5 in acetonitrile in at 2:1:3 molar ratio or between $[Fe(SC_6H_5)_4]^{2-}$ and FeX_2 (X = Cl, Br) in a 1:2.4 molar ratio affords in excellent yields the new $[Fe_4(SC_6H_5)_6X_4]^{2-}$ clusters. The paramagnetic $[(C_6H_5)_4P]_2[Fe_4(SC_6H_5)_6Cl_4]$ (I) crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The cell dimensions are a = 23.122 (6) Å, b = 13.986 (1) Å, c = 14.189 (4) Å, α = 73.65 (1)°, β = 80.58 (1)°, and γ = 84.91 (1)°. Intensity data were collected with a four-circle computer-controlled diffractometer with use of the θ–2θ step scan technique. All of the nonhydrogen atoms in the anion and the two phosphorus atoms in the cations were refined with anisotropic temperature factors while the carbon atoms in the $(C_6H_5)_4P^+$ cations were refined with isotropic temperature factors. Refinement by full-matrix least squares of 661 parameters on 5514 data gave a final R value of 0.074. The hydrogen atoms were included in the structure factor calculation but were not refined. The overall description of the $Fe_4S_6Cl_4$ core in I is that of a nearly regular Fe_4 tetrahedron inscribed in a slightly irregular octahedron defined by the bridging S atoms in an "adamantane" type of cage. The four chlorine atoms coordinated one on each of the four iron atoms define an outer tetrahedron such that the overall symmetry of the $Fe_4S_6Cl_4$ unit is very nearly T_d. Average values of selected structural parameters and the estimated standard deviations calculated from scatter of values around the mean are Fe–Fe = 3.94 (4) Å, Fe–S = 2.362 (15) Å, Fe–Cl = 2.254 (3) Å, S–S = 3.79 (2) Å, S–Cl = 3.82 (7) Å; Fe–Fe–Fe = 60 (1)°, Fe–S–C = 108.3 (25), Cl–Fe–S = 112 (3), S–Fe–S = 107 (7)°, Fe–S–Fe = 113 (2)°. Distortions in each of the four tetrahedral $ClFe^{II}S_3$ units can be explained in terms of phenyl ring repulsions on the periphery of the Fe_4S_6 cage. The reactions of dibenzyl trisulfide with I in ratios that do not exceed 2, in either CH_3CN or $CH_3CN/HCON(CH_3)_2$ mixtures, afford the new mixed ligand "cubane" $[(C_6H_5)_4P]_2[Fe_4S_4(SC_6H_5)_2Cl_2]$ (II) in very good yields. The chemical and physical properties including electrochemical properties and proton magnetic resonance spectra as well as preliminary X-ray crystallographic results confirm the identity of II. In reactions where the dibenzyl trisulfide to I ratio exceeds 4, the $[Fe_4S_4Cl_4]^{2-}$ (III) "cubane"-type cluster forms and can be isolated in excellent yields when the reagent ratio is 8:1.

Interest in the fundamental coordination chemistry of simple thiolate ligands derives to a great extent from recent advances in the chemistry of metalloproteins. The importance of thiolate coordination in the metal sites of these proteins has been demonstrated in numerous crystallographic studies.[1] Outstanding among the metalloproteins which have been studied in detail are the various types of ferredoxins.[2] In these electron transfer, nonheme iron proteins, thiolato groups of protein-bound cysteinyl residues serve as coordination anchor points for such inorganic cores as Fe_4S_4,[3] Fe_3S_3,[4] or Fe_2S_2[5] and for single Fe(II) or Fe(III)[1a] ions.

Significant recent accomplishments in metal thiolate coordination chemistry include (a) the synthesis and detailed characterization of the $Fe_4S_4(SR)_4$, $Fe_2S_2(SR)_4$, and $Fe(SR)_4$ complexes in various oxidation levels,[6] (b) the synthesis[7] and structural

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