

Generation of the Iron Methylene Complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(=\text{CH}_2)]^+\text{X}^-$ through Inner-Sphere vs Outer-Sphere Electron-Transfer Processes and Reactivity toward Sulfur Compounds

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The methylene complexes $[\text{M}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)]^+\text{X}^-$ (**3a**, M = Fe; **3b**, M = Ru) generated *in situ* by protonation of $\text{M}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{OCH}_3$ (**2a**, M = Fe; **2b**, M = Ru; Cp* = η^5 -pentamethylcyclopentadienyl) in the presence of $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SR}$ (**1a**, R = Me; **1b**, R = Ph) yield the binuclear sulfonium compounds $\{[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)](\text{SR})\{[\text{M}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)]\}\text{BF}_4$ (**4a**, M = Fe, R = Me; **4b**, M = Fe, R = Ph; **4c**, M = Ru, R = Me). The iron methylene complex **3a** reacts with dimethyl disulfide and diphenyl disulfide to give $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-RSCH}_2\text{SR})\text{BF}_4$ (**6a**, R = Me; **6b**, R = Ph) in 60–80% yields. The X-ray crystal structure of **6b** shows that it crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 24.564(9)$ Å, $b = 11.210(4)$ Å, $c = 20.595(6)$ Å, $\beta = 104.27(4)^\circ$, and $Z = 8$. The structure was solved and refined (4404 reflections) to the final residual values $R = 0.46$ and $R_w = 0.43$. The methylene complex **3a** is also generated from **1a** and **1b** by ferrocenium oxidation under CO atmosphere. The metallathiacyclopropane complexes $\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})$ (**7a**, R = Me; **7b**, R = Ph), prepared by irradiation of **1a** or **1b** in the near-UV region, are isolated as pure single diastereoisomers. These complexes give the same products as **1a** and **1b** give upon ferrocenium oxidation. A cyclic voltammetry study indicates that the 17-electron Fe(III) metallacyclic compounds $[\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})]^+$ and the 19-electron $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^2\text{-CH}_2\text{SR})]^+$ should be intermediates in the generation of methylene complex **3a** and the subsequent formation of complexes **4** and **6** during the one-electron-oxidation pathway. Treatment of **1a** with $[\text{Ph}_3\text{C}][\text{PF}_6]$ affords the trityl adduct $[\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{S}(\text{CH}_3)(\text{CPh}_3)][\text{PF}_6]$ (**9a**). Complex **9a** thermally reacts *in situ* to form the methylene complex **3a**, trapped as phenylcyclopropane in the presence of styrene, or it reacts with **1b** to give **4b** isolated in 55% yield. A mechanism is proposed and the dichotomy observed for the ferrocenium and trityl oxidation of the thioalkoxyalkyl complexes **1a** and **1b** is discussed in terms of inner-sphere versus outer-sphere electron transfer.

The inner-sphere versus outer-sphere character of electron-transfer reactions has attracted active attention.¹ The dichotomy between these two pathways has been considered as the extremes of the same mechanism according to the degree of "concertedness of bond formation with electron transfer and bond breaking".² In the case of the stepwise reaction, the electron-transfer step is of the outer-sphere type and described by the Marcus model³ whereas a new model has been developed to describe the concerted pathway of the inner-sphere type.⁴ Important investigations have been devoted to the kinetic and electrochemical aspects of this fundamental problem, and *ab initio* calculations were recently reported.¹

The first goal of the work reported here was to investigate from an experimental point of view the behavior of the organometallic electron donors $\text{FeCp}^*(\text{CO})_2\text{CH}_2\text{SR}$ (Cp* = η^5 -pentamethylcyclopentadienyl; R = CH₃, **1a**; R = Ph, **1b**) toward an outer-sphere (ferrocenium salt) and a potential inner-sphere (trityl cation) acceptor. The second objective was to probe the formation of the methylene cation $[\text{FeCp}^*(\text{CO})_2(=\text{CH}_2)]^+$ through an unambiguous ET pathway. Indeed, carbene species constitute a class of compounds which play a key role in a wide variety of catalytic processes such as alkene metathesis and Fischer-Tropsch syntheses or stoichiometric reactions such as the cyclopropanation of alkenes. The patterns of reactivity involve either electrophilic or nucleophilic properties of the carbene ligands, but their role in ET reactions has not yet been clearly established.⁵ However, there is great interest in transition-metal chemistry derivatives because of their conceptual relationship to catalytic active metal

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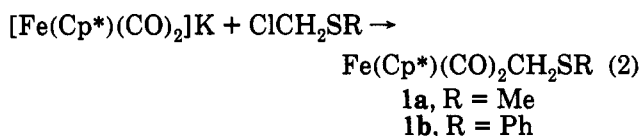
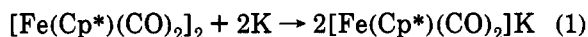
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surfaces and the related ET pathways.⁶ As a prelude, we describe in the first section of the paper the synthesis of the electron-transfer-reaction products through ionic pathways involving the same transient methylene intermediate. A small portion of this work has been communicated.⁷

Results and Discussion

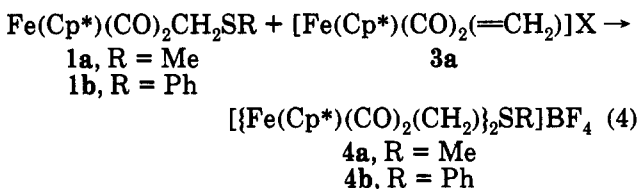
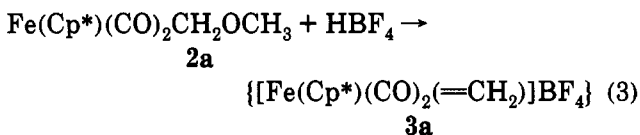
1. Methyleneiron Complex Addition to α -Thioether Ligands: Synthesis of the Binuclear Sulfonium Salts.

The preparation of the thioalkoxyalkyl complexes $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SR}$ (**1a**, R = Me; **1b**, R = Ph) is conveniently achieved by the reaction of the *in situ* generated ferrate $[\text{Fe}(\text{Cp}^*)(\text{CO})_2]\text{K}$ with the corresponding chloromethyl thioether. The thioalkyl derivatives are obtained after chromatography over neutral alumina in 80% yield (eqs 1 and 2). The IR spectra (CH_2Cl_2 , pentane) each display



a set of two carbonyl stretching bands at 1933, 1992 and 1935, 1995 cm^{-1} for **1a** and **1b**, respectively.

Treatment of the (alkylthio)methyl complexes **1a** and **1b** with 1 equiv of the methylene complex $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(=\text{CH}_2)]\text{X}$ (**3a**, generated *in situ* by reaction of the alkoxymethyl derivative $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{OCH}_3$ (**2a**)⁸⁻¹⁰ with $(\text{CH}_3)_3\text{SiOSO}_2\text{CF}_3$ or HBF_4) affords the binuclear sulfonium compounds $[\{\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)\}_2\text{SR}]\text{X}$ (**4a**, R = Me; **4b**, R = Ph; X = OSO_2CF_3 or BF_4) as tetrafluoroborate or triflate salts recovered in 70% yield after recrystallization (eqs 3 and 4).



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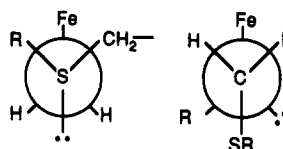
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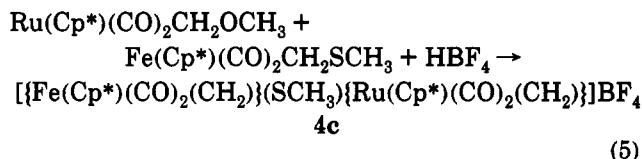
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Chart I. Representation of **4** and **6** in Newman Projections along the C-S Bond Axis



Similarly, the heterobimetallic sulfonium compound **4c** was obtained by addition of 1 equiv of HBF_4 to a 1/1 mixture of **1a** and $\text{Ru}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{OCH}_3$ (**2c**, eq 5).¹⁰



Interestingly, these reactions show that the iron methylene complex **3a** can be used as a convenient organometallic synthon, despite its very high thermal instability.¹¹

The ^1H and ^{13}C NMR spectra of the heterobinuclear complex **4c** exhibit four different resonances for the M- CH_2 methylene protons and four distinct signals for the carbonyl ligands, as expected because of the chirality at the sulfur center. The ^1H NMR spectra of the symmetric homobinuclear sulfonium complexes **4a** and **4b** exhibit two doublets at δ 1.97, 2.16 ($^2J_{\text{HH}} = 9.9$ Hz) and 2.29, 2.39 ($^2J_{\text{HH}} = 9.7$ Hz), respectively, attributed to the chemically nonequivalent Fe-CH and Fe-CH' methylene protons as depicted on Chart I. Note that the two terminal carbonyl groups are diastereotopic and resonate as two singlets at δ 216.9 and 217.3 (**4a**) or δ 215.5 and 216.0 (**4b**). These features are a consequence of the irreversible character of the reaction described by eq 4, which contrasts with the previous observations reported for the reaction between metal complexes of sulfur-containing ligands and the rhenium methylene complex $[(\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2)]\text{PF}_6$.¹² In the latter case, a rapid equilibrium on the NMR time scale between the methylene complex, the dialkyl sulfur, and the sulfonium organometallic derivative was probed by ^1H NMR spectroscopy. Moreover, addition of free trimethylphosphine to a CH_2Cl_2 solution of **4a** or **4b** confirms that the C-S bond is not cleaved even on a greater time scale. Indeed, no reaction occurs and the phosphonium adduct $[(\text{Cp}^*)\text{Fe}(\text{CO})_2(\text{CH}_2\text{PMe}_3)]\text{PF}_6$ is not detected. The methylene complex **3a** is certainly a better electrophile than the rhenium one, and the sulfonium adduct is much more stable in the $[\text{Fe}(\text{Cp}^*)(\text{CO})_2]$ series. The binuclear sulfonium complexes **4a** and **4b** are also much more stable than the iron sulfonium salts $[\text{FeCp}(\text{CO})_2\text{CH}_2\text{S}(\text{CH}_3)_2]\text{X}$. It has been shown that these compounds thermally decompose to the highly reactive methylene complex $[\text{FeCp}(\text{CO})_2(=\text{CH}_2)]\text{X}^{\text{9b,13}}$ and as a consequence are effective reagents for the cyclopropanation of alkenes.¹⁴

However, the addition of an excess of trimethylamine *N*-oxide to a CH_2Cl_2 solution of the bimetallic sulfonium

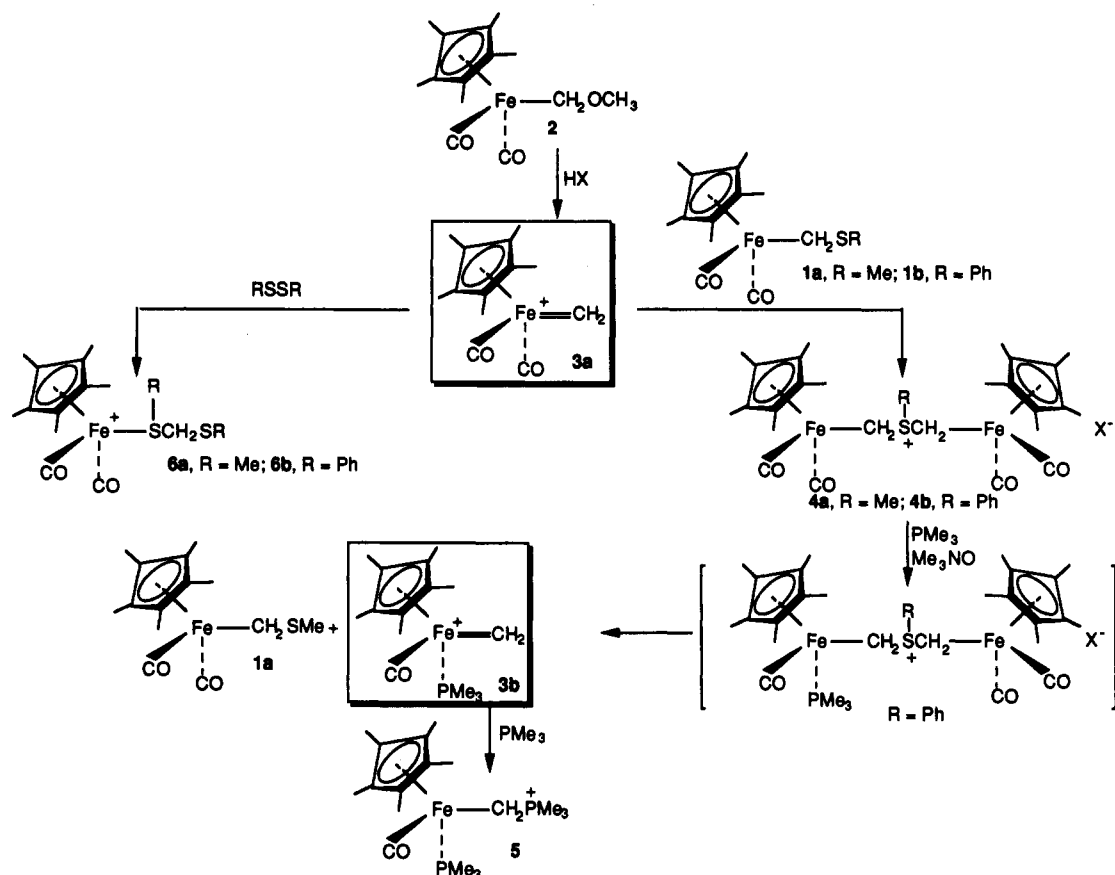
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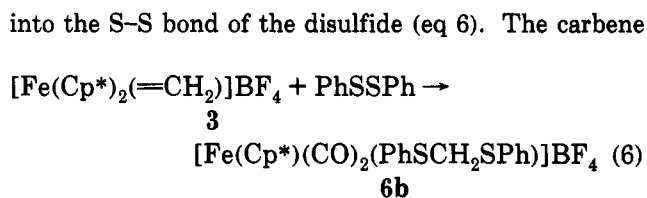
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Scheme I. Reactivity of the Iron Methylene 3a and 3b Generated through an Ionic Pathway



compound 4a or 4b followed by addition of PMe_3 affords the methylene phosphonium complex $[\text{Fe}(\text{Cp}^*)(\text{CO})(\text{PMe}_3)(\text{CH}_2\text{PMe}_3)]\text{BF}_4$ (5) and the thioether complex 1a or 1b (Scheme I). We assume that the nucleophilic displacement of a carbonyl ligand at one of the iron centers¹⁵ is followed by the coordination of the phosphine at the vacant site, giving rise to the unstable intermediate $[\{\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)\}\{\text{Fe}(\text{Cp}^*)(\text{CO})(\text{PMe}_3)(\text{CH}_2)\}\text{SR}]\text{BF}_4$. In the latter species, the sulfur-carbon bond dissociation occurs at the more electron-rich center, giving rise to the (alkylthio)methyl complex 1a or 1b and the transient iron methylene compound $[\text{Fe}(\text{Cp}^*)(\text{CO})(\text{PMe}_3)(=\text{CH}_2)]^+$. The new phosphonium adduct 5 (80% yield) is obtained as a result of the *in situ* attack of PMe_3 on the electrophilic methylene ligand, as previously observed.¹⁶ The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of compound 5 displays two doublets, $\delta -0.24$ and -0.26 , attributed to the diastereotopic methylene protons.

2. Methylene Insertion into the S-S Bond: Synthesis of the Bis(alkylthio)methane Complex $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-RSCH}_2\text{SR})\text{X}]$ (R = CH₃, 6a; R = Ph, 6b; X = BF₄, PF₆). Reaction of the methylene complex 3a, generated as above in the presence of diphenyl disulfide, gives the new complex $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-PhSCH}_2\text{SPh})]\text{BF}_4$ (6b, 80% isolated) after workup and crystallization from a CH_2Cl_2 /diethyl ether mixture. Formally, compound 6b results from the insertion of the $:\text{CH}_2$ methylene fragment



and carbenoidal reagents are known to insert into the sulfur-sulfur bond of the disulfide, and sometimes insertion of more than one CH_2 occurs.¹⁷ Ample precedent is available for displacement of a labile ligand by PhSSPh at an iron center. Reaction 6 is very specific, and the formation of the dimeric species $[\text{FeCp}^*(\text{CO})_2(\mu\text{-PhSSPh})\text{FeCp}^*(\text{CO})_2](\text{BF}_4)_2$ is not observed.¹⁸ The replacement of diphenyl disulfide by dimethyl disulfide produces 6a as the major product of the reaction (60% yield), but attempts at purifying the product were unsuccessful.

On the other hand, ferrocenium hexafluorophosphate oxidation of the dimer $[\text{Fe}(\text{Cp}^*)(\text{CO})_2]_2$ in the presence of an excess of bis(methylthio)methane or bis(phenylthio)methane affords after 3 days the complexes 6a and 6b, isolated as pure samples in 80 and 60% yields, respectively. The procedure involving the iron methylene intermediate appears to be more convenient to prepare 6b, whereas the oxidation of the dimer is more efficient in the case of 6a.

Yellow crystals were grown by slow diffusion of pentane into a CH_2Cl_2 solution of complex 6b as its hexafluoro-

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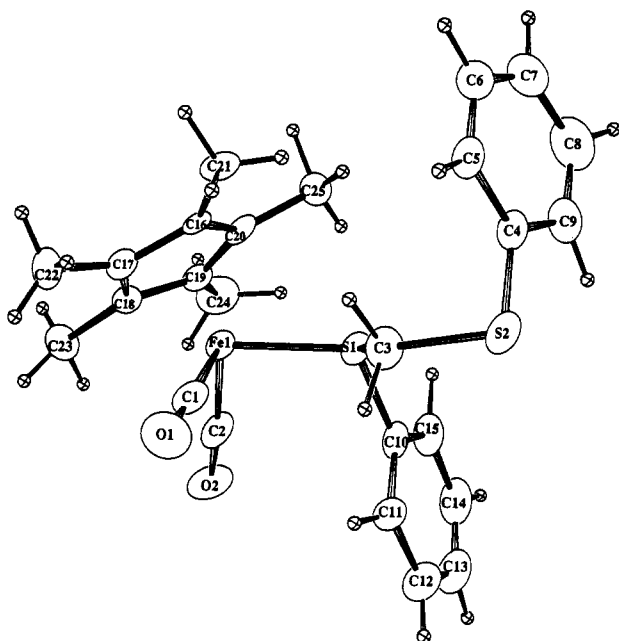


Figure 1. ORTEP representation of $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-PhSCH}_2\text{SPh})]\text{PF}_6$ (**6b**). Atoms are represented by thermal ellipsoids at the 50% probability level.

Table I. Experimental Crystallographic Data for **6b**

formula	$\text{C}_{25}\text{H}_{27}\text{FeF}_6\text{O}_2\text{S}_2\text{P}$
fw	624.43
cryst system	monoclinic
space group	$P2_1/c$
a , Å	24.564(9)
b , Å	11.211(4)
c , Å	20.595(6)
β , deg	104.27(4)
V , Å ³	5496(4)
Z	8
d_{calc} , Mg m ⁻³	1.509
cryst size, mm	$0.15 \times 0.18 \times 0.22$
$2\theta_{\text{max}}$, deg	50
hkl range	$h = 0, 10; k = 0, 22; l = -20, 20$
diffractometer	CAD4 Enraf-Nonius
λ (Mo K α), Å	0.710 69
monochromator	graphite crystal
T , K	120
$F(000)$	2560
abs coeff (μ), cm ⁻¹	8.11
scan type	$\omega/2\theta = 1$
t_{max} , s	60
no. of reflns read	7999
no. of unique reflns	4404 [$I > 2\sigma(I)$]
R_{int} ^a	0.023
R , R_w	0.046, 0.043
S_w	2.5
$\Delta\rho_{\text{max}}$, e Å ⁻³	0.43, 1.84

$$^a w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}.$$

phosphate salt, and a single-crystal X-ray structure was determined (Figure 1), revealing a monoclinic cell with a $P2_1/c$ space group and 8 molecules in the asymmetric unit. The X-ray data were collected as outlined in Table I, and the refinement gave the structure shown in Figure 1. The result of the study is a structure of a racemic mixture with the two enantiomeric molecules in two slightly different conformations. For one of them the atomic coordinates and selected bond distances and angles are listed in Tables II–IV (for the other one see the supplementary material). The molecule presents the classical pseudooctahedral geometry invariably observed for three-legged piano-stool complexes.¹⁹ The Cp* ring occupies three ligand sites and

Table II. Positional Parameters and Their Estimated Standard Deviations for **6b**^a

atom	x	y	z	B , Å ²
Fe1	0.38707(3)	0.19723(8)	0.13217(4)	1.62(2)
S1	0.36393(6)	0.2930(2)	0.21803(7)	1.98(3)
S2	0.26769(7)	0.3901(2)	0.26702(8)	2.91(4)
P1	0.86207(7)	-0.2607(2)	-0.04212(9)	2.78(4)
F1	0.8299(2)	-0.3688(5)	-0.0175(3)	5.8(1)
F2	0.8761(2)	-0.2033(5)	0.0310(2)	5.4(1)
F3	0.8059(2)	-0.1862(5)	-0.0623(4)	8.3(2)
F4	0.1046(2)	0.1548(4)	0.0658(2)	4.4(1)
F5	0.8489(2)	-0.3182(4)	-0.1149(2)	5.1(1)
F6	0.9182(2)	-0.3381(4)	-0.0214(2)	3.9(1)
O1	0.2923(2)	0.0310(5)	0.1032(2)	3.7(1)
O2	0.4623(2)	0.0200(5)	0.2116(2)	4.1(1)
C1	0.3280(3)	0.0986(6)	0.1148(3)	2.4(1)
C2	0.4321(3)	0.0912(7)	0.1828(3)	2.7(2)
C3	0.2877(2)	0.2062(7)	0.7066(3)	2.4(1)
C4	0.7120(2)	0.0290(7)	0.2583(3)	2.4(1)
C5	0.7312(3)	0.0746(7)	0.3234(3)	2.8(2)
C6	0.7143(3)	0.1811(7)	0.3426(3)	3.1(2)
C7	0.6771(3)	0.2524(7)	0.2954(4)	4.1(2)
C8	0.6592(3)	0.2123(8)	0.2306(4)	3.9(2)
C9	0.6755(3)	0.1022(7)	0.2118(3)	3.1(2)
C10	0.3885(2)	0.2132(6)	0.2948(3)	2.0(1)
C11	0.3635(3)	0.1118(6)	0.3111(3)	2.3(1)
C12	0.3858(3)	0.0539(7)	0.3715(3)	3.3(2)
C13	0.4340(3)	0.0972(8)	0.4142(3)	3.8(2)
C14	0.4595(3)	0.1959(8)	0.3976(3)	3.8(2)
C15	0.4370(3)	0.2574(7)	0.3384(3)	3.0(2)
C16	0.3635(2)	0.3277(6)	0.0566(2)	1.5(1)
C17	0.3767(2)	0.2204(6)	0.0274(3)	2.1(1)
C18	0.4342(2)	0.1909(6)	0.0605(3)	2.0(1)
C19	0.4558(2)	0.2836(6)	0.1070(3)	1.8(1)
C20	0.4130(2)	0.3709(6)	0.1035(3)	1.8(1)
C21	0.3094(3)	0.3950(6)	0.0333(3)	2.3(1)
C22	0.3399(3)	0.1515(7)	-0.0287(3)	3.1(2)
C23	0.4671(3)	0.0874(7)	0.0430(3)	3.0(2)
C24	0.5156(3)	0.2929(7)	0.1476(3)	3.0(2)
C25	0.4191(2)	0.4857(6)	0.1398(3)	2.4(1)
H3A	0.274(3)	0.321(6)	0.162(3)	4.0*
H3B	0.282(3)	0.219(6)	0.218(3)	4.0*
H5	0.244(3)	0.521(6)	0.148(3)	4.0*
H6	0.274(3)	0.715(6)	0.118(3)	4.0*
H7	0.336(3)	0.830(6)	0.191(3)	4.0*
H8	0.363(3)	0.768(6)	0.295(3)	4.0*
H9	0.338(3)	0.563(6)	0.329(3)	4.0*
H11	0.339(3)	0.081(6)	0.282(3)	4.0*
H12	0.370(3)	-0.011(6)	0.378(3)	4.0*
H13	0.450(3)	0.065(6)	0.452(3)	4.0*
H14	0.489(3)	0.230(6)	0.424(3)	4.0*
H15	0.456(3)	0.330(6)	0.328(3)	4.0*
H21A	0.309(3)	0.436(6)	-0.009(3)	4.0*
H21B	0.305(3)	0.455(6)	0.065(3)	4.0*
H21C	0.279(3)	0.342(6)	0.030(3)	4.0*
H22A	0.350(3)	0.068(6)	-0.031(3)	4.0*
H22B	0.341(3)	0.203(6)	-0.071(3)	4.0*
H22C	0.303(3)	0.152(6)	-0.025(3)	4.0*
H23A	0.449(3)	0.013(6)	0.031(3)	4.0*
H23B	0.501(3)	0.062(6)	0.088(3)	4.0*
H23C	0.486(3)	0.117(6)	0.013(3)	4.0*
H24A	0.529(3)	0.206(6)	0.160(3)	4.0*
H24B	0.538(3)	0.333(6)	0.123(3)	4.0*
H24C	0.519(3)	0.342(6)	0.188(3)	4.0*
H25A	0.443(3)	0.480(6)	0.179(3)	4.0*
H25B	0.431(3)	0.548(6)	0.113(3)	4.0*
H25C	0.383(3)	0.514(6)	0.146(3)	4.0*

^a Asterisks indicate that atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

the two carbonyls, and the sulfur atom is positioned in the other three sites. The bond distances and angles involving the carbonyl ligands are comparable to values

Table III. Selected Bond Distances (Å) for $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-PhSCH}_2\text{SPh})]\text{PF}_6$ (**6b**)^a

Fe-C1	1.789(8)	C1-O1	1.139(9)
Fe-C2	1.776(8)	C2-O2	1.150(9)
Fe-S1	2.258(2)	S1-C10	1.788(7)
S1-C3	1.829(7)	C'-Fe	1.741
C9-S2	1.754(8)		

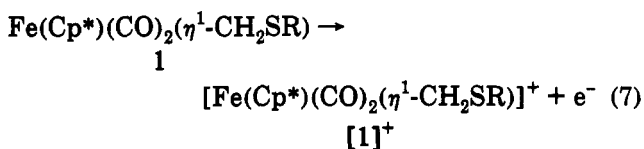
^a C' = centroid of Cp*.**Table IV.** Selected Bond Angles (deg) for $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-PhSCH}_2\text{SPh})]\text{PF}_6$ (**6b**)

C'-Fe-S1	119.8	S1-Fe-C1	95.8(2)
C'-Fe-C1	123.8	S1-Fe-C2	95.7(2)
C'-Fe-C2	121.3	Fe-S1-C3	110.4(3)
Fe-S1-C10	111.1	C3-S1-C10	103.2(3)

reported for related systems.^{16d,20} The coordination of the bis(phenylthio)methane to the iron center produces a lengthening of the bonds between the chiral sulfur atom and both the methylene carbon atom and the ipso-carbon atom of the phenyl ring. The sulfur atom coordinated to the iron center is distinctly pyramidal with C-S bond lengths of 1.829(7) and 1.788(7) Å; the Fe-S-C and C-S-C bond angles (110.4(3), 111.1(2), 103.2(3)°) total 324.7°. In typical organic sulfonium salts, C-S bond lengths of 1.78–1.84 Å and C-S-C bond angles of 100–108° are found.²¹

The ¹H NMR spectrum of **6b** (CDCl₃) displays a multiplet (10H) centered at δ 7.43 for the phenyl resonances and two singlets at δ 4.30 (2H) and 1.66 (15H), corresponding to the CH₂ and Cp* proton resonances, respectively. The chemical equivalency of the two diastereotopic hydrogen atoms of the methylene fragment is explained by a fluxional behavior at the chiral sulfur atom on the NMR time scale (Chart I). As a consequence of the rapid inversion at the sulfur center, the two CO ligands appear as a singlet at δ 210.3 in the ¹³C NMR spectrum. At -80 °C, the methylene protons appear as an AB quartet at δ 4.16 with a *J*_{HH} of 14 Hz. Coalescence of these signals is observed at -30 °C, and at higher temperature (20 °C) the singlet becomes sharp. The calculated Δ*G*[‡] value for the inversion barrier of the configuration at the sulfur atom is 11.2 kcal mol⁻¹ (46.7 kJ mol⁻¹). This value is lower than those previously reported for organic sulfonium salts. Indeed, classical kinetic methods have found typical sulfonium inversion barriers in the range 25–29 kcal mol⁻¹.²²

3. Methylene Generation through an Outer-Sphere ET Process: Oxidation of $[\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SR}]$ with $[\text{FeCp}_2][\text{PF}_6]$. The initial scans in the cyclic voltammograms (CVs) of complexes **1a** and **1b** from -1.0 to +1.5 V (vs SCE) are characterized by irreversible oxidation waves at the platinum electrode in dichloromethane (eq 7).



The oxidation peak potentials are 0.70 V for **1a** and 0.75 V for **1b**. The addition of 2/3 equiv of $[\text{FeCp}_2][\text{PF}_6]$ to a solution of **1a** or **1b** in CH₂Cl₂ or CHCl₃ at -80 °C resulted

(20) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

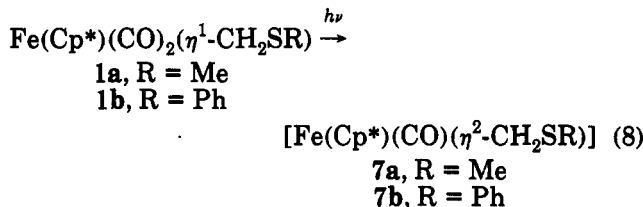
(21) Perozzi, C. J. M. In *The Chemistry of the Sulphonium Group*; Stirling, J. M., Patai, S., Eds.; John Wiley & Sons: New York, 1981; Part 1, pp 15–77.

(22) (a) Darwish, D.; Tomilson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5938. (b) *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience: New York, 1971; Vol. 6, p 89.

in a color change from dark blue to green, and after workup no traces of Cp*-containing product were detected by ¹H NMR. In connection with the exceptional lability of a CO ligand in a 17-electron complex, it can be assumed that the first step in the decomposition of the 17-electron [1]⁺ would be the displacement of a CO ligand by the sulfur atom of the (methylthio)alkyl group. An important question is whether the reaction proceeds through an associative mechanism involving a 19-electron complex as a transition state or an intermediate. As previously noted, this seems likely to depend on the specific case, and our system could favor the intramolecular formation of 19-electron species.²³

The ferrocenium oxidation of **1b** was repeated under a carbon monoxide atmosphere. The bis(phenylthio)methane complex **6b** was selectively precipitated from the reaction medium by addition of diethyl ether and isolated after filtration as a pure microcrystalline complex in 43% yield. Then addition of pentane to the mother liquor afforded a new solid sample identified as the bimetallic sulfonium salt **4b**, isolated in 41% weighted yield. It was established that the optimal stoichiometric ratio between the ferrocenium salt and the starting (methylthio)alkyl complex is 0.66 to bring the reaction to completion and to obtain the best yield. The use of more than 2/3 equiv of oxidizing reagent precluded the isolation of pure **4b** and **6b** due to the presence of unreacted ferrocenium salt.

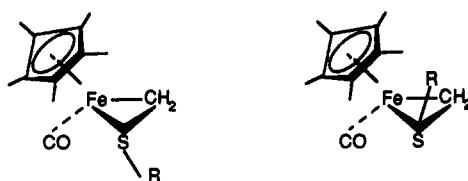
In order to check the assumption of the coordination of the sulfur atom in the oxidation process, the η²-alkyl thioether complexes $\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})$ (eq 6; R = Me, **7a**; R = Ph, **7b**) were prepared.



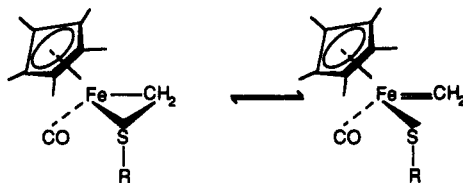
Photolysis of a pentane solution of the (alkylthio)methyl complex $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SR}$ (**1a** or **1b**) in a glass vessel produces a brownish solution that, after removal of the solvent, gives the metallathiacyclopropane $\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})$ (eq 8; R = Me, **7a**; R = Ph, **7b**). The IR spectra of **7a** and **7b** exhibit a single stretching band in the carbonyl region at 1903 and 1913 cm⁻¹, respectively. The ¹H NMR spectrum of a crude sample of **7a** shows two singlets at δ 1.04 and 1.68, corresponding to the coordinated SMe group and Cp*, respectively. The two diastereotopic methylene protons resonate as two doublets both at 20 °C and at -80 °C (δ(20 °C) 1.74 and 2.19). In the case of **7b**, a similar

(23) (a) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1986**, *5*, 926. (b) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49. (c) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802. (d) Symons, M. C. R.; Bratt, S. W. *J. Chem. Soc., Dalton Trans.* **1979**, 1739. Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437. (e) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (f) Fawcett, J. P.; Jackson, R. A.; Poš, A. *J. Chem. Soc., Chem. Commun.* **1975**, 733. (g) Therien, M. J.; Ni, C. L.; Anson, F.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037. (h) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087. (i) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (j) Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265. (k) Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. *J. Am. Chem. Soc.* **1982**, *104*, 5633. (l) Ohst, H. H.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1986**, 121. (m) Ohst, H. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2897. (n) Lhadi, E. K.; Patin, H.; Darchen, A. *Organometallics* **1984**, *3*, 1128. (o) For relevant reviews, see: *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 22.

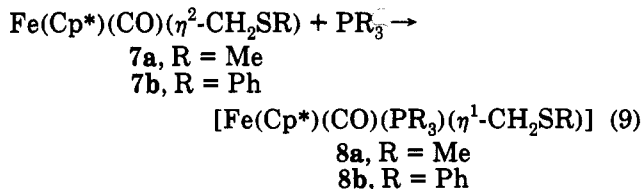
Chart II



Scheme II



pattern is observed. This feature evidenced that the displacement of a carbonyl group by the sulfur atom which occurs with simultaneous formation of chiral centers both at the iron and at the sulfur atoms leads to the observation of a single diastereoisomer (Chart II). In the Cp series, the same reaction has been reported and the two diastereoisomers were observed in a 85/15 ratio.²⁴ The η^2 -coordinated (alkylthio)methyl ligand was the subject of other studies,²⁵ and an X-ray crystal structure has been determined in the case of the molybdenum compound $\text{MoCp}(\text{CO})_2(\eta^2\text{-CH}_2\text{SCH}_3)$.^{25c} This latter complex presents a *trans* geometry of the Cp and CH_3 groups with respect to the plane of the three-membered ring, and the same geometry can be supposed for **7a** and **7b**. However one can wonder if the formation of a single diastereomer is kinetic or thermodynamic in origin. On the basis of the temperature-dependent ^1H NMR spectra of $\text{Cp}(\text{CO})\text{Fe}[\eta^2\text{-C}(\text{SMe})(\text{SMe})_2]$, Angelici has shown this complex to be in a rapid equilibrium with the carbene mercaptide form (Scheme II).²⁶ It cannot be excluded that the kinetic isomers of the complexes **7a** and **7b** isomerized to the thermodynamic more stable isomer via a transition state or an intermediate of this type. In the case of the Cp* series, the carbene mercaptide form should be favored relative to the Cp series, where the two diastereoisomers are both observed.²³ However, the reactivity of complexes **7a** and **7b** is not characteristic of a metal-carbene derivative.²⁶ Indeed, the metallathiacyclopropane complexes $\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})$ react with the tertiary phosphines to give quantitatively the thioether compounds $\text{Fe}(\text{Cp}^*)(\text{CO})(\text{PR}_3)\text{CH}_2\text{SR}$ (eq 9; R = CH_3 , **8a**; R = Ph, **8b**), which are chiral at iron.



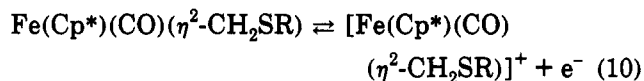
The heteroatom-containing metallacyclopropane complexes constitute a class of organometallic compounds which has been the subject of several studies, and in part

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(25) (a) Hofmann, L.; Werner, H. *J. Organomet. Chem.* 1983, 255, C41. (b) Yoshida, G.; Kurosawa, H.; Okarawa, R. *Chem. Lett.* 1977, 1387. (c) Gil, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* 1969, 91, 3751. (d) King, R. B.; Bisnette, M. B. *Inorg. Chem.* 1965, 4, 486.

(26) Angelici, R. J.; Glavee, G. N. *J. Am. Chem. Soc.* 1989, 111, 3598.

this interest comes from the carbenic character of the metal-carbon bond.²⁵⁻²⁷ However, their redox properties were not the subject of investigations. The initial scans in the cyclic voltammograms of complexes **7a** and **7b** from -1.0 to $+1.5$ V (vs SCE) are characterized by a reversible oxidation process at the platinum electrode in dichloromethane with the (i_p^a/i_p^c) current ratio of unity at a 0.1 V s^{-1} scan rate (eq 10). The reversible oxidation potentials



(E_0) are 0.18 V for **7a** and 0.19 V for **7b**, and the anodic and cathodic peak separations ($E_p^c - E_p^a$) are 0.09 V for **7b** and 0.15 V for **7a** in dichloromethane at a 0.1 V s^{-1} scan rate. The substitution of a CO group in **1a** and **1b** by the sulfur atom of the (alkylthio)methyl group causes a cathodic shift of the oxidation potential of about 0.6 V.

The addition of 0.66 equiv of $[\text{FeCp}_2][\text{PF}_6]$ to a solution of **7a** or **7b** in CH_2Cl_2 at -80 $^\circ\text{C}$ results in a rapid color change from dark brown to green, and after workup no traces of Cp*-containing product are recovered. On the other hand, the ferrocenium oxidation of **7b** under carbon monoxide atmosphere is much cleaner and allows the recovery as pure compounds of the bimetallic sulfonium salt **4b** in 41% yield and the bis(phenylthio)methane complex **6b** in 43% yield. It is noteworthy that the same compounds **4b** and **6b** are obtained with approximately the same yields from the ferrocenium salt oxidation of **1b** and **7b** under a carbon monoxide atmosphere. Moreover, the ferrocenium oxidation of **7a** under CO atmosphere gives a mixture of organometallic compounds in which complexes **4a** and **6a** are identified by ^1H NMR spectroscopy in a $1/1$ molar ratio with an overall yield of 50% .

A more detailed study of the cyclic voltammograms of complexes **1a** and **1b** from -0.2 to $+1$ V (vs SCE) provides the key to a better understanding of the reaction mechanism. The initial scan displays only anodic waves at 0.78 and 0.74 V, as shown in Figure 2 (wave A), for complexes **1a** and **1b**, respectively. In the reverse sweep, cathodic waves B are observed at 0.11 and 0.07 V for **1a** and **1b**, respectively. These waves are associated with anodic ones (labeled C) at 0.22 and 0.13 V, respectively, observed in the second oxidation sweep. Waves B and C correspond to the reversible redox couple $[\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})]^{0/+}$ and indicate that the 17-electron Fe(III) $(\eta^2\text{-CH}_2\text{SR})$ complex $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-CH}_2\text{SR})]^+$ should be the common intermediate in the ferrocenium oxidation of both compounds **1a** and **1b** and the metallacyclic complexes **7a** and **7b**. Whereas the Fe(II)/Fe(III) couples of **7a** and **7b** appear to be stable at the platinum electrode for scan rates as low as 0.050 V s^{-1} , the 17-electron species thermally react in solution. The thermal decomposition observed in the absence of carbon monoxide takes place at the radical cation $[\mathbf{7}]^+$, which, probably through iron-carbon or iron-sulfur bond breaking, gives a very unstable electron-deficient species as the origin of the decomposition process.

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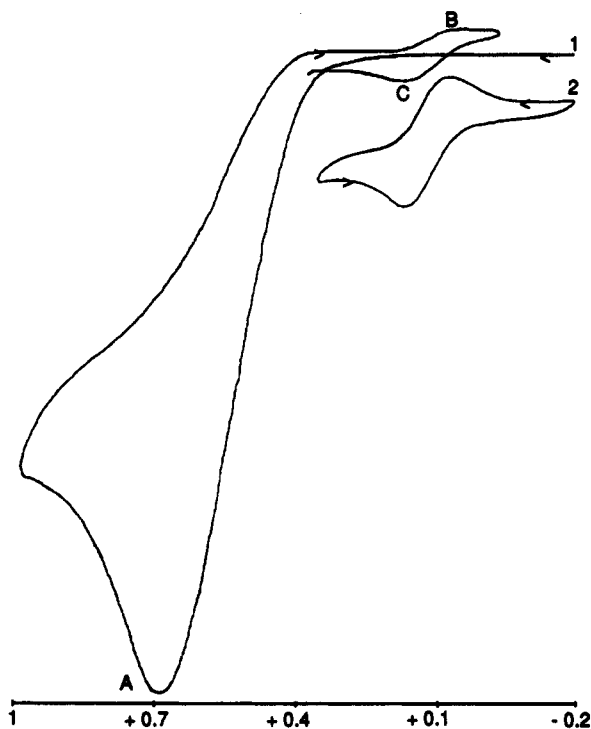
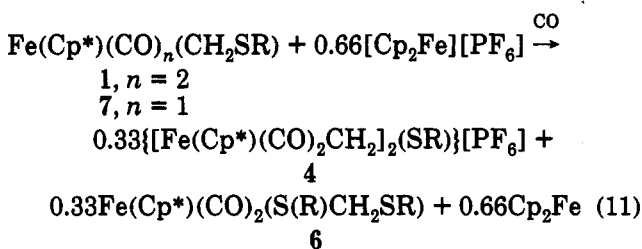


Figure 2. Cyclic voltammograms at 20 °C for (1) $\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-CH}_2\text{SPh})$ (**1b**) and (2) $\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SPh})$ (**7b**). Experimental conditions: $[\text{nBu}_4\text{NPF}_6] = 0.1 \text{ M}$; CH_2Cl_2 ; potentials relative to SCE; scan rate = 100 mV/s.

Moreover, direct homolytic scission of the alkyl-metal bond can be an important decomposition pathway in the absence of a closed valence shell,²⁸ and this supports a Fe-C bond cleavage hypothesis. Under CO atmosphere, it can be assumed that CO reversibly reacts with the 17-electron species $[7]^+$ via a 19-electron intermediate, as previously established for the ligand substitution reactions,²³ forming $[1]^+$ (Scheme III).

The stoichiometry of the reaction between the starting material and the isolated products shows that the thio complexes **1** and **7** react with $2/3$ equiv of ferrocenium salt to afford roughly 0.33 mol of the binuclear complexes **4** and 0.33 mol of the sulfur complexes **6**, as depicted in eq 11. Such a stoichiometry suggests that the reaction should



proceed through the dimerization of the 17-electron radical cation $[1]^+$ by a ligand-ligand coupling with formation of a S-S bond (Scheme III).³¹ It has been shown that diamagnetic iron(II) S-S-bonded species are formed in solution by dimerization of cationic iron(III) thiolate complexes,²⁹ and the behavior of these compounds in solution strongly suggested the existence of an equilibrium between a paramagnetic monomer and diamagnetic dimer.^{18,30} The transient 18-electron methylene complex

3a could result from the decomposition of this bimetallic intermediate with simultaneous formation of the disulfide adducts $\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2\text{S}(\text{R})\text{SR})$, which further reorganize into compounds **6** by insertion of the methylene fragment into the S-S bond. The formation of the binuclear sulfonium salt **4b** takes place via the reaction of **3a** with the starting thioalkyl compound **1b**.

The formation of compounds **4** and **6** upon oxidation of $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{S}$ is strongly dependent on both the concentration of the reagents and the temperature. A higher dilution of the starting material or working at a temperature above -40 °C does not result in the observation of the final products **4** and **6** but gives unidentified byproducts. This indicates that the reaction should proceed by a bimetallic pathway, and the conditions must be suitable to produce the intermediate, namely the 17-electron complex $[1]^+$, in a sufficient concentration to effect its dimerization.³¹ The proposed mechanism also agrees well with the observation that the addition of PhSSPh to the reaction medium does not change the 4/6 ratio.

4. Methylene Generation through an Inner-Sphere ET Process: Oxidation of $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SR}$ with $[\text{Ph}_3\text{C}][\text{PF}_6]$. The reaction of the (methylthio)methyl complex **1a** with 1 equiv of $[\text{Ph}_3\text{C}][\text{PF}_6]$ proceeds in an unusual fashion. Indeed, treatment of **1a** with $[\text{Ph}_3\text{C}][\text{PF}_6]$ at -80 °C in CH_2Cl_2 or in CHCl_3 affords a yellow air-sensitive salt, isolated in 95 % yield after crystallization and identified as the sulfonium adduct $[\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{S}(\text{CH}_3)(\text{CPh}_3)]\text{PF}_6$ (**9a**, Scheme III).³² The IR spectrum (Nujol) of **9a** is similar to that of **1a** and displays two carbonyl stretching bands at 1949 and 2009 cm^{-1} . The ¹H NMR spectrum (CD_2Cl_2) exhibits an AB quartet for the two chemically nonequivalent α -methylene protons due to the chirality at the sulfur atom. Note that the two CO ligands are diastereotopic.

It is noteworthy that direct thiomethoxide abstraction or hydride abstraction does not occur, contrasting the reaction of the trityl salt with that of the related alkoxymethyl complex $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{OCH}_3$ (**3**),¹⁰ since the tritylsulfonium compound **9a** is quantitatively obtained. The driving force for the sulfonium formation is the nucleophilicity at the sulfur atom, and the presence of the electron-rich C_5Me_5 ligand appears to be essential in the formation of **9a**. Indeed, the reaction of the trityl salt with the C_5H_5 analogue of **1a** gives the (phenylthio)carbene complex $[\text{Fe}(\text{Cp})(\text{CO})_2(=\text{CHSPh})]\text{PF}_6$.³³ While the C-alkylation of a vinylrhenium complex by the trityl cation has been reported,³⁴ the formation of a trityl adduct like **9a** is unusual.^{35,36}

The reversibility of the trityl adduct formation was probed by the reaction of **9a** with 1 equiv of PMe_3 in

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(32) The classical hydride abstraction reaction generally observed with the trityl reagent can also be observed as a secondary process by working in CH_2Cl_2 : Thépot, J.-Y. Work in progress and ref 7.

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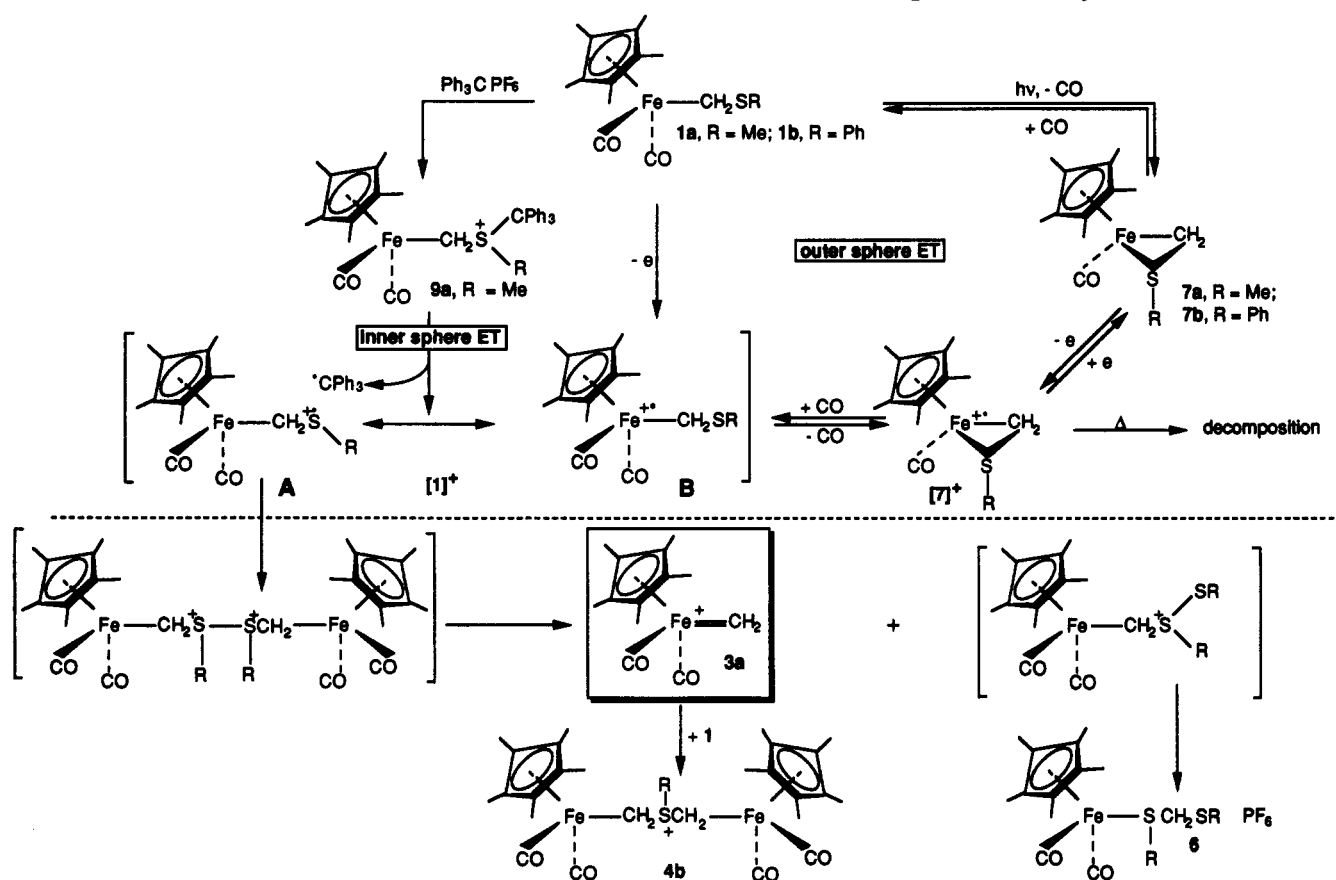
(34) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

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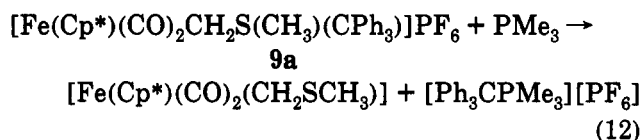
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Scheme III. Generation of the Iron Methylene 3 through ET Pathways



CH_2Cl_2 . At -40°C , the reaction immediately occurred and a white solid precipitated. This solid was isolated (95% yield) and identified as $[\text{Me}_3\text{PCPh}_3][\text{PF}_6]$ by comparison of its ^1H NMR properties with those of an authentic sample (eq 12). From the solution, the (alkylthio)methyl complex 1a was quantitatively recovered.



On the other hand, Helquist and co-workers have reported syntheses of iron sulfonium salts, and they have shown these compounds to be effective reagents for the cyclopropanation of alkenes.¹⁴ Even though 9a is also a poor cyclopropanating reagent, it exhibits a chemical reactivity widely different from that described for $[\text{CpFe}(\text{CO})_2\text{S}^+(\text{CH}_3)_2]\text{BF}_4$ (10).¹⁴ Whereas the sulfonium salt 10 reacts with alkenes in refluxing 1,4-dioxane (102°C), the trityl adduct 9a slowly reacts in a dichloromethane solution of styrene above -40°C , completion of the reaction being reached below 20°C with formation of phenylcyclopropane in 5–10% yield. More interestingly, although dimethyl sulfide was formed in the thermal decomposition process of 10, triphenylmethyl methyl sulfide, found to be as stable under the reaction conditions, was not detected. The ^1H NMR analysis of the crude product showed that

triphenylmethane Ph_3CH was quantitatively formed. These data are consistent not with the heterolytic cleavage of $\text{Ph}_3\text{C-S-CH}_3$ from complex 9a but rather with a homolytic reaction affording both the organometallic radical $[\text{FeCp}^*(\text{CO})_2\text{CH}_2\text{SMe}]^{\bullet+}$ and the trityl radical $\text{Ph}_3\text{C}^\bullet$, which captures a hydrogen atom from the solvent to give triphenylmethane. This assumption is strongly supported by the three following experiments.

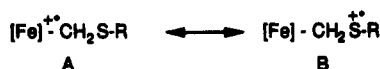
The thermal decomposition of 9a was followed by ESR spectroscopy. The trityl adduct was dissolved in a 1/1 mixture of $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$ at -80°C , and the solution was placed in a 2-mm quartz tube. The resulting sample was ESR silent. After it was warmed to room temperature and immediately frozen with liquid nitrogen, its ESR spectrum was recorded at 77 K. The spectrum exhibited an intense signal with three g tensor components ($g_1 = 2.2096$; $g_2 = 2.0604$; $g_3 = 2.0038$). These three well-separated features were those expected for an iron(III) 17-electron organometallic species having octahedral symmetry³⁷ and probed the formation of $[1]^+$ upon the thermal decomposition reaction of 9a. Moreover, the final spectrum recorded at 293 K showed that the iron radical disappeared and was replaced by an intense signal centered on $g = 1.999$ with a 16-line fine structure characteristic of $\text{Ph}_3\text{C}^\bullet$.³⁸

Treatment of a -40°C dichloromethane solution of the trityl adduct 9a with 1 equiv of complex 1a or 1b gives upon warming the bimetallic sulfonium salt 4a or 4b, isolated after selective precipitation with diethyl ether in

(36) (a) Agbossou, S. K.; Bodner, G. S.; Patton, A. T.; Gladysz, J. A. *Organometallics* 1990, 9, 1184. (b) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* 1990, 9, 1191. (c) Astruc, D.; Mandon, D.; Madonik, A.; Michaud, P.; Ardoin, N.; Varret, F. *Organometallics* 1990, 9, 2155.

(37) (a) Roger, C.; Hamon, P.; Toupet, L.; Rabaà, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* 1991, 10, 1045. (b) Guerschais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* 1986, 663.
(38) Mandon, D.; Astruc, D. *Organometallics* 1989, 8, 2372.

Scheme IV



a pure form in 40–54% yield. ^1H NMR analysis of the residue reveals the presence of **6a** (10% yield) in both cases.

On the other hand, the (phenylthio)methyl complex **1b** reacts with 0.5 equiv of $[\text{Ph}_3\text{C}][\text{PF}_6]$ in chloroform at -40°C to give complexes **4b** and **6b**, obtained after workup in 59 and 39% yields, respectively. The reaction of the trityl salt with $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SPh}$ (**1b**) has been monitored by variable-temperature ^1H NMR. Below -40°C , the starting material is observed and no reaction occurs. Above this temperature, the reaction begins and the slow and spectroscopically quantitative conversion of **1b** into the reaction products **4b** and **6b** is observed, along with the formation of Ph_3CH . On this basis, the trityl salt is assumed to give the adduct **9b** from the thioether complex **1b**. Whereas the trityl adduct **9a** is sufficiently stable to be isolated and characterized, the phenyl analogue **9b** is too unstable to be spectroscopically observed.

The formation of the two iron complexes **4b** and **6b** in the same ratio from **1b** when it was reacted either with ferrocenium or with the trityl salt is particularly significant and strongly suggests that the same mechanism should be involved in the product-forming step in these two reactions. These results clearly establish that the one-electron oxidation of the (α -thioether)iron complexes **1a** and **1b** produces the methylene complex **3a**. Moreover, a CO atmosphere is required for the ferrocenium oxidation, whereas the reaction with the trityl reagent can be carried out under argon. This finding reveals a dichotomy in the initial one-electron-transfer process. As shown above, the trityl salt gives an adduct, and the one-electron oxidation of the transition-metal species occurs in a second step with the homolytic S–CPh₃ bond cleavage. As a result of a bond breaking being involved in the formation of the 17-electron organometallic complex, the oxidation reaction can be regarded as an inner-sphere electron-transfer process. Formally, in this reaction the oxidation occurs at the thioalkyl ligand (A, Schemes III and IV) whereas the ferrocenium oxidation occurs at the metal center giving the 17-electron species (B, Schemes III and IV). Because the two species A and B can be considered as the two valence tautomers of the single species $[1]^+$, we believe that they could explain the role of carbon monoxide. As evidenced by the cyclic voltammetric data, the CO displacement by the sulfur atom quickly occurs at the 17-electron iron species B and produces the metallacyclic compound $[7]^+$ with CO loss. In the case of the oxidation with the trityl salt via a trityl adduct, one can suppose that the oxidation occurs at the sulfur atom rather than at the metal center, favoring ligand–ligand coupling between two radical species. The formation of compounds **4** and **6** then occurs as in the case of the ferrocenium oxidation.

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were predried and distilled over sodium benzophenone ketyl prior to use. Dichloromethane and chloroform were refluxed over P_2O_5 and distilled over Na_2CO_3 . Pentamethylcyclopentadiene was prepared according to the

published procedure,³⁰ and other chemicals were used as received. All the manipulations were carried out under an argon atmosphere using Schlenk techniques or in a Jacomex 532 drybox filled with nitrogen. Routine NMR spectra were recorded using a Bruker AW 80-MHz spectrometer. High-field NMR experiments were performed on a multinuclear Bruker 300-MHz instrument. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and to H_3PO_4 for ^{31}P NMR spectra. Photolyses were performed with a Hanovia lamp (450 W, 250 nm) equipped with a glass jacket, at room temperature under a stream of argon. Cyclic voltammograms were recorded by using a PAR 362 instrument. Elemental analyses were performed at the Center for Microanalyses of the CNRS, Lyon-Solaise, France.

1. Synthesis of the Thioalkoxyalkyl Complexes $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{SR}$ (1a, R = Me; 1b, R = Ph). To a THF solution of 10 mmol of $(\text{Cp}^*)\text{Fe}(\text{CO})_2\text{K}^+$ (prepared from 5 mmol of $[(\text{Cp}^*)\text{Fe}(\text{CO})_2]_2$ and metallic potassium¹⁰), cooled to -50°C , was added dropwise with stirring the corresponding chloromethyl alkyl sulfide (11 mmol; R = Me, 0.92 mL; R = Ph, 1.47 mL). The solution was allowed to warm to room temperature, and then the solvent was removed under reduced pressure. The residue was extracted with pentane (2×100 mL), and the concentrated extracts were transferred onto a neutral alumina column. Upon elution with pentane, a red band of the $[(\text{Cp}^*)\text{Fe}(\text{CO})_2]_2$ compound was first recovered, and then elution with pentane/diethyl ether (95/5) afforded the yellow thioether complex. The solvent was removed under vacuo and the thioether isolated as a yellow solid (80%; **1a**, 2.45 g; **1b**, 2.95 g).

1a: IR (pentane, ν_{CO} , cm^{-1}) 1952 s, 2000 s; ^1H NMR (25 $^\circ\text{C}$, CD_2Cl_2) 1.71 (s, 15H, C_5Me_5), 1.79 (s, 2H, CH_2), 2.09 (s, 3H, CH_3); ^{13}C NMR (25 $^\circ\text{C}$, CD_2Cl_2) 9.6 (q, $^1J_{\text{CH}}$ 128 Hz, C_5Me_5), 16.2 (t, $^1J_{\text{CH}}$ 143 Hz, CH_2), 25.3 (q, $^1J_{\text{CH}}$ 136 Hz, CH_3), 95.9 (s, C_5Me_5), 218.2 (s, CO). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{SFe}$: C, 54.56; H, 6.54. Found: C, 54.55; H, 6.34.

1b: IR (pentane, ν_{CO} , cm^{-1}) 1957 s, 2010 s; ^1H NMR (25 $^\circ\text{C}$, CDCl_3) 1.83 (s, 15H, C_5Me_5), 2.14 (s, 2H, CH_2), 7.03–7.33 (m, 5H, C_6H_5); ^{13}C NMR (25 $^\circ\text{C}$, CDCl_3) 8.8 (t, CH_2 , $^1J_{\text{CH}}$ 144 Hz), 9.5 (q, C_5Me_5 , $^1J_{\text{CH}}$ 128 Hz), 95.8 (s, C_5Me_5), 123.6 (dd, Ph_{para} , $^1J_{\text{CH}}$ 162 Hz, $^2J_{\text{CH}}$ 7 Hz), 125.0 (dt, Ph_{meta} , $^1J_{\text{CH}}$ 160 Hz, $^2J_{\text{CH}}$ 7 Hz), 128.3 (dt, Ph_{ortho} , $^1J_{\text{CH}}$ 160 Hz, $^2J_{\text{CH}}$ 7 Hz), 146.8 (t, $^2J_{\text{CH}}$ 8 Hz, Ph_{ipso}), 217.6 (s, CO). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{SFe}$: C, 61.63; H, 5.99. Found: C, 61.63; H, 6.16.

2. Synthesis of the Binuclear Sulfonium Salts $[\{\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)_2\text{SR}\}_2\text{X}]$ (4a, R = Me; 4b, R = Ph; X = OSO_2CF_3 or BF_4) and $[\{\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)_2\}(\text{SCH}_3)\{\text{Ru}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2)_2\}]\text{CF}_3\text{SO}_3$ (4c). The β -ether complex $(\text{Cp}^*)\text{Fe}(\text{CO})_2\text{CH}_2\text{OMe}$ (1 mmol, 292 mg) and **1a** (1 mmol, 308 mg) were dissolved in dichloromethane (20 mL), and the solution was cooled to -80°C . The mixture was then treated with 1 equiv of $\text{HBF}_4/\text{Et}_2\text{O}$ (144 μL), and after a few minutes, diethyl ether (30 mL) was added. The solution was filtered to remove the insoluble byproducts. Upon addition of pentane (150 mL), the sulfonium salt precipitated as a yellow crystalline powder. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ /pentane (1/1/5) yielded pure crystals of **4a** as its tetrafluoroborate salt (460 mg, 70%). Similarly **4a** was prepared as its trifluoromethanesulfonate salt (with 1 equiv of $\text{Me}_3\text{SiOSO}_2\text{CF}_3$, 193 μL ; yield 500 mg, 70%). Yield of the tetrafluoroborate salt of **4b** (from **1b**, $(\text{Cp}^*)\text{Fe}(\text{CO})_2\text{CH}_2\text{OMe}$, and $\text{HBF}_4/\text{Et}_2\text{O}$): 460 mg, 75%. Yield of the trifluoromethanesulfonate salt **4c** (from **1a**, $(\text{Cp}^*)\text{Ru}(\text{CO})_2\text{CH}_2\text{OMe}$, and $\text{Me}_3\text{SiOSO}_2\text{CF}_3$): 560 mg, 70%.

4a: IR (CH_2Cl_2 , ν_{CO} , cm^{-1}) 1952 s, 2006 s; ^1H NMR (CD_2Cl_2 , 25 $^\circ\text{C}$) 1.78 (s, 30H, C_5Me_5), 1.97 (d, 2H, $^2J_{\text{HH}}$ 9.9 Hz, CH), 2.16 (d, 2H, $^2J_{\text{HH}}$ 9.9 Hz, CH'), 2.66 (s, 3H, CH_3), 2.67 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2 , 35 $^\circ\text{C}$) 9.6 (q, $^1J_{\text{CH}}$ 128 Hz, C_5Me_5), 28.4 (t, $^1J_{\text{CH}}$ 140 Hz, CH_2), 32.9 (q, $^1J_{\text{CH}}$ 142 Hz, CH_3), 97.7 (s, C_5Me_5), 216.9 (s, CO), 217.3 (s, CO). Anal. Calcd for $\text{C}_{27}\text{H}_{37}\text{O}_4\text{BF}_4\text{SFe}_2$: C, 49.42; H, 5.68. Found: C, 49.28; H, 5.53. Calcd for $\text{C}_{28}\text{H}_{37}\text{O}_7\text{F}_3\text{S}_2\text{Fe}_2$: C, 46.81, H, 5.19. Found: C, 46.68; H, 5.38.

4b: IR (CH_2Cl_2 , ν_{CO} , cm^{-1}) 1954, 2008; ^1H NMR (CD_2Cl_2 , 25 °C) 1.70 (s, 30H, C_5Me_5), 2.29 (d, 2H, $^2J_{\text{HH}}$ 9.7 Hz, CH), 2.39 (d, 2H, $^2J_{\text{HH}}$ 9.7 Hz, CH'), 7.60 (m, 5H, Ph); ^{13}C NMR (CD_2Cl_2 , 25 °C) 9.5 (q, $^1J_{\text{CH}}$ 128 Hz, C_5Me_5), 31.7 (t, $^1J_{\text{CH}}$ 142 Hz, CH_2), 97.9 (s, C_5Me_5), 130.1 (dt, $^1J_{\text{CH}}$ 166 Hz, $^2J_{\text{CH}}$ 8 Hz, Ph_{meta}), 131.4 (dd, $^1J_{\text{CH}}$ 166 Hz, $^2J_{\text{CH}}$ 8 Hz, Ph_{ortho}), 134.6 (dt, $^1J_{\text{CH}}$ 163 Hz, $^2J_{\text{CH}}$ 8 Hz, Ph_{para}), 147.0 (s, Ph_{ipso}), 215.5 (s, CO), 216.0 (s, CO). Anal. Calcd for $\text{C}_{32}\text{H}_{39}\text{O}_4\text{BF}_4\text{SFe}_2$: C, 53.51; H, 5.47. Found: C, 53.29; H, 5.79.

4c: IR (CH_2Cl_2 , ν_{CO} , cm^{-1}) 1957 s, 2012 s; ^1H NMR (CD_2Cl_2 , 25 °C) 1.76 (s, 15H, $\text{C}_5\text{Me}_5\text{Fe}$), 1.90 (s, 15H, $\text{C}_5\text{Me}_5\text{Ru}$), 1.93 (d, 1H, $^2J_{\text{HH}}$ 9.9 Hz, CHFe), 2.13 (d, 1H, $^2J_{\text{HH}}$ 9.9 Hz, CHRu), 2.19 (d, 1H, $^2J_{\text{HH}}$ 10.2 Hz, CHRu), 2.39 (d, 1H, $^2J_{\text{HH}}$ 10.2 Hz, CHRu), 2.66 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2 , 25 °C) 9.5 (q, $^2J_{\text{CH}}$ 128 Hz, $\text{C}_5\text{Me}_5\text{Fe}$), 10.0 (q, $^2J_{\text{CH}}$ 128 Hz, $\text{C}_5\text{Me}_5\text{Ru}$), 21.4 (t, $^2J_{\text{CH}}$ 142 Hz, CH_2Ru), 8.0 (t, $^2J_{\text{CH}}$ 140 Hz, CH_2Fe), 33.0 (q, $^2J_{\text{CH}}$ 142 Hz, CH_3), 97.7 (s, $\text{C}_5\text{Me}_5\text{Fe}$), 101.1 (s, $\text{C}_5\text{Me}_5\text{Ru}$), 202.3 (s, CORu), 202.6 (s, COFe), 216.8 (s, COFe), 217.4 (s, COFe). Anal. Calcd for $\text{C}_{28}\text{H}_{37}\text{O}_7\text{S}_2\text{F}_3\text{FeRu}$: C, 44.04; H, 4.88. Found: C, 44.23; H, 4.81.

3. Attempted Reaction of 4a and 4b with Trimethylphosphine. To a solution of **4a** as its trifluoroborate salt (1 mmol, 656 mg) in 20 mL of CH_2Cl_2 was added trimethylphosphine (10 mmol, 1 mL). The suspension was stirred for 20 h (IR monitoring showed that no reaction occurred). Addition of diethyl ether precipitated the starting material **4a**, which was quantitatively recovered. Starting from **4b** led to similar observations.

4. Synthesis of $[\text{Fe}(\text{Cp}^*)(\text{CO})(\text{PMe}_3)(\text{CH}_2\text{PMe}_3)]\text{BF}_4$ (5**) from **4a** and **4b**.** To a solution of **4a** as its tetrafluoroborate salt (1 mmol, 656 mg) in 20 mL of CH_2Cl_2 were added trimethylamine oxide (5 mmol, 380 mg) and then trimethylphosphine (10 mmol, 1 mL). The suspension was stirred for 20 h (IR monitoring showed the disappearance of sulfonium CO bands and the appearance of three new ones). The mixture was filtered to remove excess Me_3NO ; then diethyl ether was added to precipitate the phosphonium salt **5** as orange crystals. After filtration, the thioether complex **1a** was quantitatively recovered from the supernatant solution. Recrystallization from dichloromethane/diethyl ether (1/5) yielded pure **5** (380 mg, 80%). The same reaction carried out with **4b** yielded **5** (380 mg, 80%) and **1b**.

5: IR (CH_2Cl_2 , ν_{CO} , cm^{-1}) 1893 s; ^1H NMR (CD_2Cl_2 , 25 °C) -0.26 (dd, 1H, $^2J_{\text{HH}}$ 14.4 Hz, $^2J_{\text{PH}}$ 2.7 Hz, CH), -0.24 (d, 1H, $^2J_{\text{HH}}$ 14.4 Hz, CH'), 1.28 (d, 9H, $^2J_{\text{PH}}$ 8.9 Hz, PMe_3), 1.62 (s, 15H, C_5Me_5), 1.64 (d, 9H, $^2J_{\text{PH}}$ 12.8 Hz, P^+Me_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C), -12.8 (dd, $^1J_{\text{PC}}$ 49 Hz, $^2J_{\text{PC}}$ 15 Hz, CH_2), 10.1 (s, C_5Me_5), 14.2 (d, $^1J_{\text{PC}}$ 54 Hz, P^+Me_3), 17.7 (dd, $^1J_{\text{PC}}$ 27 Hz, $^4J_{\text{CH}}$ 4 Hz, PMe_3), 92.5 (s, C_5Me_5), 222.6 (dd, $^2J_{\text{PC}}$ 33 Hz, $^3J_{\text{PC}}$ 8 Hz, CO); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C), 35.99 (s, P^+Me_3), 36.76 (s, PMe_3). Anal. Calcd for $\text{C}_{13}\text{H}_{35}\text{OP}_2\text{BF}_4\text{Fe}$: C, 45.80; H, 7.47. Found: C, 45.64; H, 7.41.

5. Synthesis of $[\text{Fe}(\text{Cp}^*)(\text{CO})_2(\eta^1\text{-RSCH}_2\text{SR})]\text{X}$ ($\text{R} = \text{CH}_3$, **6a; $\text{R} = \text{Ph}$, **6b**).** (A) In a Schlenk tube, the β -ether complex $(\text{Cp}^*)\text{Fe}(\text{CO})_2\text{CH}_2\text{OMe}$ (**2a**, 1.0 mmol, 0.292 g) and CH_3SSCH_3 (1 mmol, 0.094 g) were dissolved in dichloromethane (20 mL) and the solution was cooled to -80 °C. The mixture was then treated with 1 equiv of $\text{HBF}_4/\text{Et}_2\text{O}$ (144 μL). After a few minutes, diethyl ether (150 mL) was added to precipitate **6a** as a yellow powder of the tetrafluoroborate salt. Attempts for recrystallization from dichloromethane/diethyl ether (1/3) did not afford pure **6a**.

In a Schlenk tube, the β -ether complex $(\text{Cp}^*)\text{Fe}(\text{CO})_2\text{CH}_2\text{OMe}$ (**2a**, 1.0 mmol, 0.292 g) and PhSSPh (1 mmol, 0.218 g) were dissolved in dichloromethane (20 mL) and the solution was cooled to -80 °C. The mixture was then treated with 1 equiv of $\text{HBF}_4/\text{Et}_2\text{O}$ (144 μL). After a few minutes, diethyl ether (150 mL) was added to precipitate **6b** as a yellow powder of the tetrafluoroborate salt. Recrystallization from dichloromethane/diethyl ether (1/3) yielded pure **6b** (0.450 g, 80%).

(B) In a Schlenk tube, the bimetallic complex $[(\text{Cp}^*)\text{Fe}(\text{CO})_2]_2$ (0.5 mmol, 0.247 g) and $\text{CH}_3\text{SCH}_2\text{SCH}_3$ (4 mmol, 0.376 g) were dissolved in CH_2Cl_2 , and the solution was then treated with the hexafluorophosphate ferrocenium salt (1 mmol, 0.331 g). After

3 days of stirring, diethyl ether was added to precipitate **6a** as a yellow powder. Recrystallization from dichloromethane/diethyl ether (1/3) yielded pure **6a** as its hexafluorophosphate salt (0.320 g, 80%).

In a Schlenk tube, the bimetallic complex $[(\text{Cp}^*)\text{Fe}(\text{CO})_2]_2$ (0.5 mmol, 0.247 g) and PhSCH_2SPh (4 mmol, 0.932 g) were dissolved in CH_2Cl_2 , and the solution was then treated with the hexafluorophosphate ferrocenium salt (1 mmol, 0.331 g). After 3 days of stirring, diethyl ether was added to precipitate **6b** as a yellow powder of the hexafluorophosphate salt. Recrystallization from dichloromethane/diethyl ether (1/3) yielded pure **6b** (0.350 g, 60%). The yield was lowered by the formation of $[\text{Cp}^*\text{Fe}(\text{CO})_3]\text{PF}_6$ as a byproduct.

6a: IR (CH_2Cl_2 , ν_{CO} , cm^{-1}) 1997, 2041; ^1H NMR (CDCl_3 , 25 °C) 1.88 (s, 15H, C_5Me_5), 2.29 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.68 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C) 9.5 (s, C_5Me_5), 16.3 (s, CH_3), 24.1 (s, CH_3), 49.2 (s, CH_2), 99.9 (s, C_5Me_5), 210.9 (s, CO). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_2\text{S}_2\text{FePF}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 34.30; H, 4.46. Found: C, 34.16; H, 4.30.

6b: IR (CH_2Cl_2 , ν_{CO} , cm^{-1}) 1999, 2043; ^1H NMR (CDCl_3 , 25 °C) 1.66 (s, 15H, C_5Me_5), 4.30 (s, 2H, CH_2), 7.36–7.49 (m, 10H, Ph); ^{13}C NMR (CDCl_3 , 25 °C) 9.2 (q, $^2J_{\text{CH}}$ 129 Hz, C_5Me_5), 52.7 (t, $^1J_{\text{CH}}$ 156 Hz, CH_2), 100.0 (s, C_5Me_5), 129.1 (dd, $^1J_{\text{CH}}$ 161 Hz, $^2J_{\text{CH}}$ 7 Hz, Ph_{ortho}), 129.4 (dt, $^1J_{\text{CH}}$ 162 Hz, $^2J_{\text{CH}}$ 7 Hz, Ph_{para}), 129.8 (dt, $^1J_{\text{CH}}$ 160 Hz, Ph_{ortho}), 130.2 (s, Ph_{ipso}), 130.6 (d, $^1J_{\text{CH}}$ 160 Hz, Ph_{meta}), 130.7 (dd, $^1J_{\text{CH}}$ 161 Hz, $^2J_{\text{CH}}$ 7 Hz, Ph_{ortho}), 131.3 (d, $^1J_{\text{CH}}$ 160 Hz, Ph_{meta}), 131.8 (s, Ph_{ipso}), 132.0 (dt, $^1J_{\text{CH}}$ 164 Hz, $^2J_{\text{CH}}$ 7 Hz, Ph_{para}), 133.3 (d, $^1J_{\text{CH}}$ 157 Hz, Ph_{meta}), 210.3 (s, CO). Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{O}_2\text{S}_2\text{FePF}_6$: C, 48.09; H, 4.36. Found: C, 48.32; H, 4.16. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{O}_2\text{S}_2\text{FeBF}_4$: C, 53.03; H, 4.81. Found: C, 52.79; H, 4.56.

6. Crystal Structure of 6b. Crystals suitable for single-crystal X-ray diffraction studies were obtained from dichloromethane/ether at 5 °C. The data were collected on a CAD-4 Enraf-Nonius automated diffractometer. Tables I–IV give the crystallographic data, data collection parameters, and refinement details. The unit cell parameters were determined by least-squares fitting of a set of 25 high- θ reflections. After Lorentz-polarization corrections, the structure was solved with a Patterson map, which revealed the two iron atoms. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and difference Fourier analyses. After isotropic ($R = 0.090$) and then anisotropic refinements ($R = 0.065$), the hydrogen atoms were located with a difference Fourier map (between 0.62 and 0.24 $\text{e}^{-\text{Å}^{-3}}$). The entire structure was refined by full-matrix least-squares techniques. Atomic scattering factors were taken from ref 40. All calculations were performed on a Digital Micro VAX 3100 computer with the MOIEN package (Enraf-Nonius, 1990).

7. Oxidation of $\text{Fe}(\text{Cp}^*)(\text{CO})_2\text{CH}_2\text{SR}$ with $[\text{FeCp}_2][\text{PF}_6]$. (A) In a Schlenk tube, **1b** (1 mmol, 0.370 g) was dissolved in 20 mL of CH_2Cl_2 , and the solution was cooled to -80 °C. $[\text{Cp}_2\text{Fe}]\text{PF}_6$ (0.66 mmol, 0.218 g) was added, and the resulting solution was allowed to warm to room temperature. After precipitation with diethyl ether, a dark green solid was recovered, and the ^1H NMR spectrum revealed the loss of the Cp^* ligand.

(B) In a Schlenk tube charged with carbon monoxide, **1b** (1 mmol, 0.370 g) was dissolved in 20 mL of CH_2Cl_2 , and the solution was cooled to -80 °C. $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ (0.66 mmol, 218 mg) was then added, and the dark solution was allowed to warm to room temperature. Addition of diethyl ether (20 mL) precipitated the thio complex **6b**, obtained as a pure solid (0.200 g, 43%). Addition of pentane yielded the sulfonium salt **4b** (0.190 g, 41%).

8. Synthesis of $\text{Fe}(\text{Cp}^*)(\text{CO})(\eta^2\text{-CH}_2\text{SR})$ ($\text{R} = \text{Me}$, **7a; $\text{R} = \text{Ph}$, **7b**).** Complex **1a** (1 mmol, 0.308 g) was dissolved in pentane (50 mL), and the solution was irradiated through a glass vessel. IR monitoring showed concomitant disappearance of the **1a** CO absorption and appearance of a single band at 1904 cm^{-1} . The solution was passed through a short Celite column (10 cm), and

the solvent was removed *in vacuo* to yield almost quantitatively compound **8a** as a dark brown oil. Similarly, **8b** was obtained from **1b**.

7a: IR (C_6H_{12} , ν_{CO} , cm^{-1}) 1903; 1H NMR (C_6D_6 , 25 °C) 1.04 (s, 3H, CH_3), 1.68 (s, 15H, C_5Me_5), 1.74 (d, 1H, $^2J_{HH}$ 4.5 Hz, CH), 2.19 (d, 1H, $^2J_{HH}$ 4.5 Hz, CH'); ^{13}C NMR (C_6D_6 , 25 °C) 10.6 (q, $^1J_{CH}$ 126 Hz, C_5Me_5), 25.4 (q, $^1J_{CH}$ 141 Hz, $^3J_{CH}$ 5 Hz, CH_3), 31.7 (2d, $^1J_{CH}$ 152 Hz, CH_2), 88.6 (s, C_5Me_5), 219.7 (d, $^3J_{CH}$ 3 Hz, CO).

7b: IR (C_6H_{12} , ν_{CO} , cm^{-1}) 1913; 1H NMR (C_6D_6 , 25 °C) 1.70 (s, 15H, C_5Me_5), 2.49 (d, 1H, $^2J_{HH}$ 4.9 Hz, CH), 2.61 (d, 1H, $^2J_{HH}$ 4.9 Hz, CH'), 6.80–7.31 (m, 5H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6 , 25 °C) 10.2 (s, C_5Me_5), 34.6 (s, CH_2), 88.5 (s, C_5Me_5), 127.9 (s, Ph_{para}), 128.8 (s, Ph_{meta}), 131.2 (s, Ph_{ortho}), 138.4 (s, Ph_{ipso}), 219.4 (s, CO).

9. Synthesis of $Fe(Cp^*)(CO)(PR_3)(\eta^1-CH_2SR)$ ($R = Me$, **8a; $R = Ph$, **8b**).** Complexes **7a** (1 mmol, 0.308 g) and **7b** (1 mmol, 0.370 g) were dissolved in pentane (50 mL), and the solutions were treated with an excess of the phosphine (PMe_3 , 5 mmol, 0.5 mL; PPh_3 , 3 mmol, 0.786 g). After overnight stirring at 20 °C, the solvent was removed and **8a** was recovered as a dark brown oily compound without further purification (0.290 g, 80%). Complex **8b** crystallized upon concentration from the pentane solution as orange crystals (0.300 g, 50%).

8a: IR (C_6H_{12} , ν_{CO} , cm^{-1}) 1906; 1H NMR (C_6D_6 , 25 °C) 1.15 (d, 9H, $^2J_{PH}$ 8.7 Hz, PMe_3), 1.58 (dd, 1H, $^2J_{HH}$ 6.8 Hz, $^3J_{PH}$ 3.8 Hz, CH), 1.65 (s, 15H, C_5Me_5), 3.38 (dd, 1H, $^2J_{HH}$ 6.8 Hz, $^3J_{PH}$ 7.0 Hz, CH'), 2.13 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6 , 25 °C) 10.1 (s, C_5Me_5), 14.3 (d, $^2J_{PC}$ 21 Hz, CH_2), 18.0 (d, $^1J_{PC}$ 26 Hz, PMe_3), 25.6 (s, CH_3), 91.6 (s, C_5Me_5), 222.1 (d, $^2J_{PC}$ 31 Hz, CO); $^{31}P\{^1H\}$ NMR (C_6D_6 , 25 °C) 36.5 (s, PMe_3).

8b: IR (C_6H_{12} , ν_{CO} , cm^{-1}) 1895; 1H NMR (CD_2Cl_2 , 25 °C) 1.45 (s, 15H, C_5Me_5), 1.59 (d, 1H, $^2J_{HH}$ 6.1 Hz, $^3J_{PH}$ 0 Hz, CH), 1.90 (dd, 1H, $^2J_{HH}$ 6.1 Hz, $^3J_{PH}$ 14.0 Hz, CH'), 6.90–7.54 (m, 20H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 25 °C) 9.3 (s, C_5Me_5), 10.4 (d, $^2J_{PC}$ 19.1 Hz, CH_2), 93.1 (s, C_5Me_5), 123.3 (s, Ph_{para}), 125.5 (s, Ph_{ortho}), 128.4 (d, $^2J_{PC}$ 9 Hz, PPh_{3meta} , PPh_{3para}), 129.9 (d, $^2J_{PC}$ 10 Hz, PPh_{3ortho}), 136.3 (d, $^1J_{PC}$ 38 Hz, PPh_{3ipso}), 149.1 (d, Ph_{ipso}), 224.5 (d, $^2J_{PC}$ 31 Hz, CO); ^{31}P NMR (CD_2Cl_2 , 25 °C), 83.6 (s, PPh_3). Anal. Calcd for $C_{36}H_{37}OPSFe$: C, 71.42; H, 6.17. Found: C, 71.72; H, 6.27.

10. Oxidation of $Fe(Cp^*)(CO)(\eta^2-CH_2SR)$ ($R = Me$, **7a; $R = Ph$, **7b**) with $[FeCp_2][PF_6]$.** (A) In a Schlenk tube **7a** (1 mmol, 0.308 g) or **7b** (1 mmol, 0.370 g) was dissolved in 20 mL of CH_2Cl_2 , and the solution was cooled to -80 °C. $[Cp_2Fe]PF_6$ (0.66 mmol, 0.218 g) was added, and the solution was allowed to warm to room temperature. The solvent was removed to dryness, and the solid residue was dissolved in CH_2Cl_2 and precipitated with diethyl ether. A dark green solid was recovered, and the 1H NMR spectrum revealed the loss of the Cp^* ligand.

(B) In a Schlenk tube, charged with carbon monoxide, **7b** (1 mmol, 370 mg) was dissolved in 20 mL of CH_2Cl_2 , and the solution was cooled to -80 °C. $[Cp_2Fe][PF_6]$ (0.66 mmol, 218 mg) was then added, and the dark solution was allowed to warm to room temperature. Addition of diethyl ether (20 mL) precipitated complex **6b** recovered as a pure solid (0.280 g, 43%). Addition of pentane yielded the sulfonium salt **4b** (0.190 g, 41%). Similarly the oxidation of **7a** (1 mmol, 0.308 g) gave a crude product after diethyl ether precipitation. 1H NMR analysis of the mixture revealed the presence of **4a** (50%) and **6a** (5%); all other byproducts were not identified.

11. Synthesis of $[Fe(Cp^*)(CO)_2CH_2S(CH_3)(CPh_3)]PF_6$ (9a**).** Methyl thioether complex **1a** (1 mmol, 0.308 mg) was dissolved in 20 mL of dichloromethane, and the solution was cooled to -80 °C. Upon stirring, $[Ph_3C][PF_6]$ (1 mmol, 0.388 g) was added. The yellow solution was allowed to warm to -40 °C before the sulfonium salt **9a** was precipitated by addition of

diethyl ether. A yellow powder was formed and isolated by removing the solvent through a cannula. After a rapid recrystallization at -40 °C (CH_2Cl_2 /diethyl ether (1/5)), the compound was dried under vacuum (95%, 0.66 g).

9a: IR (Nujol, ν_{CO} , cm^{-1}) 1949 s, 2009 s; 1H NMR (CD_2Cl_2 , -40 °C) 0.53 (d, 1H, $^2J_{HH}$ 9.3 Hz, CH), 1.65 (s, 15H, C_5Me_5), 1.75 (d, 1H, $^2J_{HH}$ 9.3 Hz, CH'), 2.22 (s, 3H, CH_3), 7.47 (m, 15H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , -40 °C) 9.4 (s, C_5Me_5), 13.1 (s, CH_2), 23.2 (2, CH_3), 82.4 (s, CPh_3), 97.9 (s, C_5Me_5), 129.3 (Ph), 129.5 (Ph), 129.7 (Ph), 137.0 (br s, Ph_{ipso}), 215.6 (s, CO), 216.8 (s, CO). Anal. Calcd for $C_{33}H_{35}O_2SFePF_6$: C, 56.91; H, 5.07. Found: C, 56.72; H, 4.90.

12. Reaction of **9a with Trimethylphosphine.** Sulfonium salt **9a** (0.696 g, 1 mmol) was dissolved in cold dichloromethane (40 mL, -40 °C), and trimethylphosphine (1.5 mmol, 150 μ L) was added. A white precipitate was immediately formed and identified, by comparison with an authentic sample, as $[Me_3(Ph_3C)P][PF_6]$ (0.450 g, 95%). From the solution, compound **1a** was quantitatively recovered.

13. Reaction of **9a with Styrene.** Sulfonium salt **9a** (0.070 g, 0.1 mmol) was dissolved in cold dichloromethane (1 mL, -60 °C) before the styrene (45 μ L, 0.4 mmol) was added. The solution was stirred while it was allowed to warm to room temperature. The mixture was analyzed by CPG on an Apiezon L column (150 cm, 120 °C), and identification by comparison with standards showed a 10% yield of phenylcyclopropane.

14. Reaction of **9a with **1a** and **1b**.** The thioether complex **1a** (0.308 g, 1 mmol) and the sulfonium salt **9a** (0.696 g, 1 mmol) were dissolved in cold dichloromethane (-40 °C, 40 mL). The resulting mixture was stirred and allowed to warm to room temperature. Addition of diethyl ether and then pentane yielded a mixture of complexes where **4a** (40%) and **6a** (10%) were identified by NMR spectroscopy and by comparison with authentic samples.

Thioether complex **1b** (0.370 mg, 1 mmol) and sulfonium salt **9a** (0.696 mg, 1 mmol) were dissolved in cold dichloromethane (-40 °C, 40 mL). While the solution was stirred, the temperature was allowed to rise to 20 °C. Addition of diethyl ether and then pentane yielded a mixture of complexes where **4b** (55% spectroscopic yield) and **6a** (10%) were identified by NMR comparison with authentic sample.

15. Oxidation of $Fe(Cp^*)(CO)_2(\eta^1-CH_2SPh)$ (1b**) with $[Ph_3C][PF_6]$.** Complex **1b** (1 mmol, 0.370 g) was dissolved in 20 mL of chloroform and the solution cooled to -40 °C. $[Ph_3C][PF_6]$ (0.66 mmol, 0.256 g) was then added, and the yellow solution was allowed to warm to room temperature in 1 h. Addition of diethyl ether (50 mL) caused the precipitation of the thio complex **6b** as pure microcrystals (0.180 g, 39%). After filtration, pentane was added to the mother liquor (50 mL) and the sulfonium complex **4b** was precipitated and isolated as a pure sample (0.270 g, 59%).

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Supplementary Material Available: Additional structural diagrams and complete tables of atomic coordinates and their estimated standard deviations, bond lengths, bond angles, and general temperature factor expressions for **6b** (18 pages). Ordering information is given on any current masthead page.

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