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ISOCYANIDE AND HETEROALLENE BRIDGED METAL COMPLEXES

VII *. FURTHER REACTIONS OF $[Fe(\eta\text{-}C_5H_5)(CO)_2CS_2]^-$ WITH METAL COMPOUNDS

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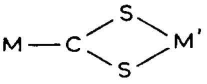
Summary

Displacement by $[FpCS_2]^-$ ($Fp = Fe(\eta\text{-}C_5H_5)(CO)_2$) of the halide in $EClMe_3$ (E = Si, Sn) and $Ru(\eta\text{-}C_5H_5)(I)(CO)_2$ affords the new ferriodithiocarboxylato complexes $Me_3ES(S)CFp$ (**2a**, **2b**) and $(\eta\text{-}C_5H_5)(CO)_2RuS(S)CFp$ (**6**). The latter and its congeners $FpC(S)SML_n$ ($ML_n = Re(CO)_5$, Fp) are alkylated at the thione-S to give the salt-like compounds $[FpC(SR)SML_n]CF_3SO_3$ (R = Me, Et) (**7**) in high yield. FpC(S)SMe acts as a strong S donor ligand towards the neutral metal carbonyl fragments $M(CO)_5$ (M = Cr, Mo, W) and $Mn(\eta\text{-}C_5H_4X)(CO)_2$ (X = H, Me) but with $Co_2(CO)_8$, only the cluster $MeSCCo_3(CO)_9$ (**14**) is obtained.

Successive combination of the three components basic metal, CS_2 and Lewis-acidic metal has provided a series of stable di- and less stable tri-nuclear complexes with carbon disulfide bridges of the type **1** [1–3].



(1)

In addition a few CS_2 complexes with $\mu_2:\eta(C,S)$ and $\mu_3:\eta(C,S,S')$ bonding modes, mainly involving the Fp system **, have been reported [4–9]. Some addi-

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* For the previous paper in this series see ref. 23.

** $Fp = Fe(\eta\text{-}C_5H_5)(CO)_2$.

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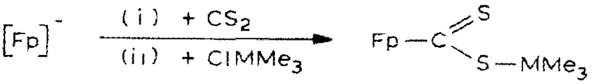
tional examples as well as reactions of FpC(S)SMe with metal carbonyls, are described below.

1. Reactions of $[FpCS_2]^-$ with metal compounds

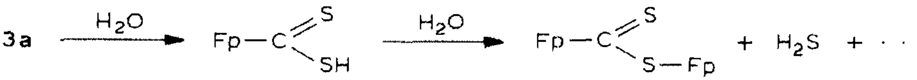
In a search for a storeable equivalent of the $[FpCS_2]^-$ anion we synthesized the trimethyl-silyl and -stannyl esters of the ferriodithiocarbonic acid **2** according to eq. 1.



(1)

(**2a** M = Si,
2b, M = Sn)

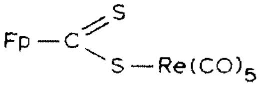
However, these compounds turned out to be thermally labile and very sensitive to moisture, which brings out decomposition which finally gives the known complex **4** (eq. 2).



(3) (4) (2)

The suggested intermediate **3** has been prepared in our group by the direct approach $\{Fp^-/CS_2/H^+\}$ [10].

Only two metal complexes containing monodentate ferriodithiocarboxylato ligands (viz. **4**, **5**) have been previously reported [3,5,7]. Addition of $Ru(\eta\text{-}C_5H_5)I(CO)_2$ to $[FpCS_2]^-$ has now given the ruthenium analogue of **4**, viz. **6**, which like **5** is more labile than the homodinuclear **4**, and so must be isolated rapidly to prevent its decomposition in solution; as for **5** this decomposition may involve initial loss of CO [3].



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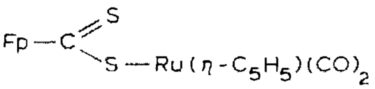
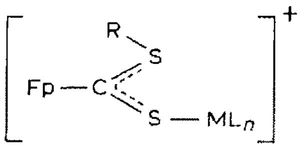


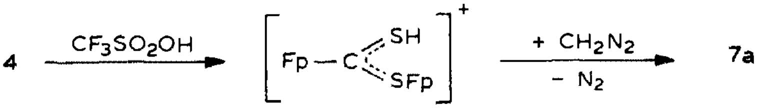
(6)

The thione-sulfur function in ferriodithiocarboxylatometal complexes represents a center of low basicity, which is capable of reacting with electrophiles, such as H^+ [10], Me^+ [3,7], CF_3CO^+ [11] and L_nM^{m+} [8,9]. Thus, complexes **4**, **5** and **6** are readily alkylated by ethyl- or methyl-trifluoromethane sulfonate in CH_2Cl_2 to give the yellow, stable dithiocarbene triflate $(CF_3SO_3^-)$ salts **7a**–**7e** in excellent yield:



(ML_n = Fp; R = Me (**7a**, 86%), R = Et (**7b**, 87%)
ML_n = $Re(CO)_5$, R = Me (**7c**, 78%), R = Et (**7d**, 73%)
ML_n = $Ru(\eta\text{-}C_5H_5)(CO)_2$, R = Me (**7e**, 83%))

The significant increase in yield above that obtained in the previously reported route to [FpC(SMe)SRe(CO)$_5$]PF$_6$ [3] may be largely due to the omission of the anion-exchange step. Complex **7a** was also prepared from [FpC(SH)SFp]SO$_3$CF$_3$ and diazomethane (eq. 3).


(3)

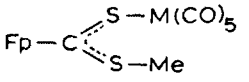
The yield was quantitative, confirming our observations that type 7 complexes do not react with diazomethane [11], and in contrast with recent findings on the reaction of the related thiocarbene [FpC(SMe)H]SO$_3$CF$_3$ with CH$_2$N$_2$ which gives a vinyl sulfide complex [12].

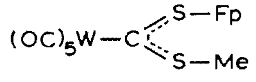
The ^{1}H NMR spectra at room temperature (Table 1) indicate that the complexes **7** either undergo rapid *syn-anti* isomerization or are present as only one conformational isomer, as observed for [FpC(SMe)SRe(CO)$_5$]$^+$ (**7c**) [3]. In the ^{13}C NMR spectra of **7** the carbene carbon resonances appear in the range 313–323 ppm downfield from SiMe$_4$, which agrees well with data for [FpC(SMe)XPh]$^+$ (**8**) (X = S, 309; X = Se, 321 ppm) [13] indicating analogous bonding situations in both dithiocarbene systems. The higher energy barrier to rotation about the $\mathrm{C}{=}\mathrm{SML}_n$ bond compared with that in **8** (coalescence at ≈ 30 °C) or [FpC(SMe)$_2$]$^+$ (coalescence at −2.5 °C) [13], revealed by the ^{1}H NMR spectrum of **7c** may if steric effects are ruled out, be attributed to better $L_nMS \rightarrow$ C(carbene) π-donation with respect to that of XPh or SMe.

Reactions of the most stable metallodithioestermetal **4** with other Lewis acids such as BF$_3$, AlCl$_3$ and HgX$_2$ (X = Cl, Br, I) also proceed with formation of S-adducts as shown by their separation from the reaction solution or by the IR spectra of the solutions; no stable (BF$_3$, AlCl$_3$) or pure (HgX$_2$) products could be isolated, however.

2. Reactions of FpC(S)SMe with metal carbonyls

It is known, that molecules possessing a $>$C=S function can be stabilized by coordination to a pentacarbonylmetal (Group VIA) fragment [14], and the orange complexes **10** obtained by reaction of FpC(S)SMe (**9**) with photo-generated M(CO)$_5$THF (M = Cr, Mo, W) are thermally more stable (dec. 86–120 °C) than the precursor **9** (dec. 72 °C).


(10a, M = Cr;
10b, M = Mo;
10c, M = W)


(11)

Complex **11** which is a "coordination isomer" of **10c** has recently been obtained by treatment of W(CO)$_5$CS with (i) SMe$^-$ and (ii) Fp$^+$ [15]. Like **4** and **5** [8,9], **9** reacts with other 16-electron metal fragments such as Mn(η-C$_5$H$_4$X)(CO)$_2$ to form the red-brown derivatives FpC(SMe)SMn(η-C$_5$H$_4$X)(CO)$_2$ (**12a**, X = H; **12b**, X = Me). All members of the two series of adducts (**10**, **12**) are air stable as solids but

TABLE 1

SELECTED IR [a] (cm^{-1}) AND ^{1}H NMR (ppm) DATA

	ν(CO) [CH$_2$Cl$_2$]	ν(CS) [KBr]	Chemical shift δ
[FpC(SCH$_3$)SFp]SO$_3$CF$_3$ (**7a**)	2047sh,2041vs,2003vs	925s,812m,755m, 710w	5.51,5.43(s,C$_5$H$_5$),3.35(s,CH$_3$) [b]
[FpC(SC$_2$H$_5$)SFp]SO$_3$CF$_3$ (**7b**)	2047sh,2042vs,2002vs	927s,830m,750m, 715w	5.58, 5.51(s,C$_5$H$_5$),4.00(q,CH$_2$),1.58(t,CH$_3$) [b]
[FpC(SCH$_3$)SRe(CO)$_5$]SO$_3$CF$_3$ (**7c**)	2142m,2085w,2039vs,2008s	927s,825m,749m	5.57(s,C$_5$H$_5$),3.49(s,CH$_3$) [b]
[FpC(SC$_2$H$_5$)SRe(CO)$_5$]SO$_3$CF$_3$ (**7d**)	2142m,2085w,2040s,2010s	925s,830m,750m	5.53(s,C$_5$H$_5$),4.02(q,CH$_2$)1.55(t,CH$_3$) [b]
[FpC(SCH$_3$)SRu(CO)$_2$(η-C$_5$H$_5$)]SO$_3$CF$_3$ (**7e**)	2050vs,2044sh,2002vs	924s,815m,752m, 709w	5.67, 5.28(s,C$_5$H$_5$),3.30(s,CH$_3$) [c]
[FpC(SH)SFp]SO$_3$CF$_3$	2048sh,2042vs,2005vs	915s,780m,760m, 720w;2498m ν(SH)	5.55,5.63(s,C$_5$H$_5$) [b]
FpC(SCH$_3$)SCr(CO)$_5$ [d] (**10a**)	*2057m*,2035vs,1991vs, *1980sh,1930vs,1901sh*	927ms,798m,748m	5.09(s,C$_5$H$_5$),2.90(s,CH$_3$) [c]
FpC(SCH$_3$)SMo(CO)$_5$ [d] (**10b**)	*2061m*,2035vs,1993vs, *1928vs,1897sh*	925s,798m [e]	5.12(s,C$_5$H$_5$),2.91(s,CH$_3$) [c]
FpC(SCH$_3$)SW(CO)$_5$ [d] (**10c**)	*2061m*,2031vs,1997vs, *1978sh,1927vs,1896sh*	923s,803m [e]	5.20(s,C$_5$H$_5$),2.93(s,CH$_3$) [c]
FpC(SCH$_3$)SMn(CO)$_2$(η-C$_5$H$_5$) [d] (**12a**)	2031s,1983s,*1923s,1863s* [f]	930s,803m [e]	5.01,4.53(s,C$_5$H$_5$),2.81(s,CH$_3$) [c]
FpC(SCH$_3$)SMn(CO)$_2$(η-C$_5$H$_4$CH$_3$) [d] (**12b**)	2030s,1982s,*1919s,1857s* [f]	923s,808m [e]	5.02(s,C$_5$H$_5$),4.40(C$_5$H$_4$),2.83,1.87(s,CH$_3$) [c]

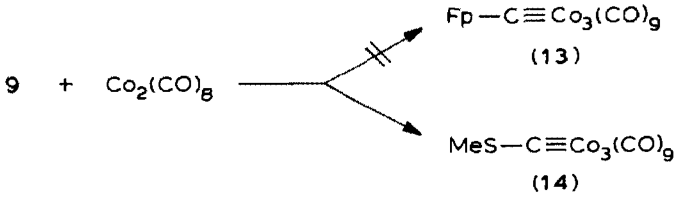
[a] ν(CF$_3$), ν(SO$_3$) for cationic complexes at 1270vs, 1225m, 1150s, 1030s, 633s. [b] In acetone-d_6. [c] In CDCl$_3$. [d] Bands due to M(CO)$_5$ or Mn(CO)$_2$(η-C$_5$H$_4$X) are in italics. [e] Nujol mull. [f] Cyclohexane solvent.

completely decompose in solution at room temperature within one day to form **9** and $M(CO)_6$ or $Mn(\eta\text{-}C_5H_4X)(CO)_3$, respectively. This instability resembles that of the analogous μ_3-CS_2 derivatives $FpC(SFp)SM(CO)_5$, which also decompose in solution without desulfurization [9].

Spectroscopic data (IR, ^1H NMR) for the heterodinuclear methyldithiocarboxylato-bridged complexes **10** and **12** are given in Table 1. The stretching vibrations of the iron-bonded carbonyl groups are slightly shifted to higher wavenumbers compared with those of the precursor **9** reflecting an increased positive charge on the iron atom. Consistently, the $\nu(CO)$ band positions and intensity pattern of the $M(CO)_5$ and $Mn(\eta\text{-}C_5H_4X)(CO)_2$ parts correspond well to those of other $>C{=}S{-}ML_n$ species [9,14,17–19], in which a considerable amount of electron density is forced upon the metal. The existence of a strong $S \rightarrow ML_n$ interaction in type **10** and **12** complexes is further borne out by the $\nu(CS)$ IR-frequencies and $\Delta\nu(CS)$ values ($\Delta\nu(CS) = \nu_{as}(CS_2) - \nu_s(CS_2)$) [16] (Table 1), which are remarkably similar to those of dithiocarbene complexes, e.g. $[FpC(SMe)_2]^+$, again emphasizing the close relationship between metallated and alkylated systems.

To examine its potentially bidentate nature, **9** was also treated with $Mo(CO)_4(\eta^4\text{-}C_7H_8)$. Again, however the pentacarbonyl species **10b** was isolated as the only product, indicating the inability of the SMe group to take part in metal complexation.

It had been shown, that dithioesters RC(S)SR′ react with dicobalt octacarbonyl with formation of cluster compounds of the type $Co_3(CO)_9{\equiv}CR$ [20]; by analogy, **9** should give the carbido cluster **13**.



The analytical and spectroscopic data for the resulting black-violet product indicate, however, that instead of FpC, the MeSC fragment is located on top of the cobalt triangle. Other alkyl derivatives of **14** were previously prepared by Seyferth et al. [21], though in lower yield and by a different route.

Experimental

All manipulations were carried out using standard Schlenk techniques under pure dinitrogen. Solvents were dried by standard methods, and degassed and distilled before use; spectroscopic measurements used the following instrumentation: IR: Zeiss IMR-25 or Perkin–Elmer 257 spectrophotometers, ^{13}C NMR: Varian XL 100, ^1H NMR: JEOL JNM-PMX-60, MS: Varian MAT 212 (70 eV). Melting points were determined with a Büchi or a Kofler hot stage microscope and are uncorrected.

Preparation of FpC(S)SSiMe₃ (2a)

CS_2 (0.6 cm^3, 10 mmol) was added dropwise by syringe to a solution of $K_xNa_{1-x}[Fp]$ [5] (ca. 8 mmol) in 100 cm^3 THF at −60 °C. After 1 min neat $SiClMe_3$ (1.2 cm^3, 8 mmol) was added and the stirring was continued for 20 min. The mixture was then allowed to warm to 0 °C and the solvent was evaporated. The residue was extracted with light petroleum (150 cm^3) and the filtrated extract was concentrated. Cooling to −40 °C gave red-brown very hygroscopic crystals of **2a** (1.88 g; 72%). M.p.: 45 °C (dec.). Found: C, 40.73; H, 4.80. $C_{11}H_{14}FeO_2S_2Si$ calcd.: C, 40.49; H, 4.32%. MS: $m/e = 326$ $[M]^+$, 298 $[M - CO]^+$, 270 $[M - (CO)_2]^+$, IR(CH_2Cl_2): 2028vs, 1978vs, [ν(CO)]; (KBr): 2950w, 2890w [ν(Me)], 1235m [$\delta(SiMe_3)$], 1010s, 708m-s [ν(CS)], 743w [$\rho(SiMe_3)$], 690m [$\nu_{as}(SiC_3)$] cm^{-1}.

*Preparation of FpC(S)SSnMe₃ (**2b**)*

This compound was prepared by a route analogous to that used for **2a**; CS_2 (0.6 cm^3, 10 mmol), K_xNa_{1-x}[Fp] (ca. 7 mmol), and $SnClMe_3$ (1.59 g, 8.0 mmol) gave brown needles of **2b** (2.94 g, 88%). M.p. 75 °C (dec.). Found: C, 32.27; H, 3.47. $C_{11}H_{14}FeO_2S_2Sn$ calcd.: C, 31.69; H, 3.38%. MS: m/e (^{120}Sn) = 418 $[M]^+$, 403 $[M - Me]^+$, 390 $[M - CO]^+$, 362 $[M - (CO)_2]^+$, IR (CH_2Cl_2): 2020vs, 1978vs [ν(CO)]; (KBr): 2980w, 2910w [ν(Me)], 1183w, 1174w [$\delta(SnMe_3)$], 998vs, 728s [ν(CS)], 770m [$\rho(SnMe_3)$] cm^{-1}.

*Preparation of FpC(S)SRu(η-C_5H_5)$(CO)_2$ · CH_2Cl_2 (**6**)*

To a solution of K_xNa_{1-x}[Fp] (4 mmol) in 50 cm^3 tetrahydrofuran at −60 °C was added CS_2 (0.3 cm^3, 5 mmol), followed by 1.4 g (4 mmol) of Ru(η-C_5H_5)I$(CO)_2$. Stirring was continued for 30 min as the mixture was allowed to warm to room temperature. The solvent was then removed, and the residue extracted with CH_2Cl_2 (50 cm^3). After filtration through Florisil the red solution was concentrated, and the orange product precipitated by addition of n-hexane and cooling to −40 °C. The crude product always contained traces of Fp_2 and FpRu(η-C_5H_5)$(CO)_2$, which were removed by repeated recrystallization from CH_2Cl_2/n-hexane. Yield: 1.41 g (77%). M.p.: 85 °C (dec.). Found: C, 34.18; H, 2.18. $C_{15}H_{10}FeO_4RuS_2 \cdot CH_2Cl_2$ calcd.: C, 34.30; H, 2.16%; mol.wt. (CH_2Cl_2): found 521, calcd.: 560.22. ^1H NMR ($CDCl_3$): δ 5.40(s,Cp), 5.32(s,CH_2Cl_2), 4.88 (s,Cp). IR (CH_2Cl_2): 2035vs, 2023vs, 1987vs, 1975sh [ν(CO)]; (KBr): 1010s, 745m [ν(CS)] cm^{-1}.

*Preparation of [FpC(SR)SML$_n$]SO_3CF_3 (**7a–7e**)*

Stoichiometric amounts of CF_3SO_2OR (R = Me, Et) were added by syringe to a dichloromethane solution of **4**, **5** or **6** at 0 °C. The mixture immediately turned brown, and sometimes a precipitate formed. After 10–20 min of stirring at room temperature the solvent was removed and the residue washed 3 times with Et_2O (10 cm^3). Crystallization from CH_2Cl_2/Et_2O (1/1) at −20 °C afforded yellow crystalline products.

7a (R = Me, ML_n = Fp). M.p. 140 °C (dec.). Found: C, 33.79; H, 2.07; S, 16.02. $C_{17}H_{13}F_3Fe_2O_7S_3$ calcd.: C, 34.36; H, 2.20; S, 16.19%. Λ_m (acetone): 140 Ω^{-1} mol^{-1} cm^2. ^{13}C NMR (acetone-d_6): δ 29.3 (Me), 88.3, 89.0 (C_5H_5), 211.5, 211.8 (CO), 315.4 (C-carbene).

7b (R = Et, ML_n = Fp). M.p. 137 °C (dec.). Found: C, 35.47; H, 2.64; S, 15.80. $C_{18}H_{15}F_3Fe_2O_7S_3$ calcd.: C, 35.32; H, 2.50; S, 15.82%. Λ_m (acetone): 130 Ω^{-1} mol^{-1} cm^2. ^{13}C NMR (acetone-d_6): δ 13.3 (CH_3), 41.4 (CH_2), 88.4, 89.1 (C_5H_5), 211.6, 211.8 (CO), 315.5 (C-carbene).

7c (R = Me, ML_n = Re$(CO)_5$). M.p. 122°C (dec). Found: C, 24.09; H, 1.24; S, 13.09. $C_{15}H_8F_3FeO_{10}ReS_3$ calcd.: C, 24.23; H, 1.08; S, 12.94%. Λ_m (acetone): 141

Ω^{-1} mol^{-1} cm^2. ^{13}C NMR (acetone-d_6): δ 89.3 (C_5H_5), 211.8 (Fe(CO)$_2$), 187.1 (*cis*-Re(CO)$_4$), 206.8 (*trans*-Re(CO)), 321.4 (C-carbene).

7d (R = Et, ML_n = Re(CO)$_5$). M.p. 116 °C (dec.). Found: C, 25.31; H, 1.40; S, 12.76. $C_{16}H_{10}F_3FeO_{10}ReS_3$ calcd.: C, 25.35; H, 1.32; S, 12.70%. Λ_m (acetone): 132 Ω^{-1} mol^{-1} cm^2. ^{13}C NMR(acetone-d_6) δ 18.3 (CH_3), 35.3 (CH_2), 89.1 (C_5H_5), 211.8 (Fe(CO)$_2$), 187.6(*cis*-Re(CO)$_4$), 206.1 (*trans*-Re(CO)), 323.5 (C-carbene).

7e (R = Me, ML_n = Ru(η-C_5H_5)(CO)$_2$). M.p. 134 °C (dec.). Found: C, 31.68; H, 1.99; S, 15.00; Fe, 8.61. $C_{17}H_{13}F_3FeO_7RuS_3$ calcd.: C, 31.93; H, 2.05; S, 15.04; Fe, 8.73%. Λ_m (acetone, 18 °C): 146 Ω^{-1} mol^{-1} cm^2.

Preparation of [FpC(SMe)SFp]SO$_3$CF$_3$ (7a)

When stoichiometric amounts of CF_3SO_2OH were added dropwise at room temperature to a stirred ether solution of **4**, the yellow [FpC(SH)SFp]SO_3CF_3 separated immediately. After 10 min of stirring the solvent was removed and the resulting dithiocarbene was washed several times with Et_2O (5 cm^3) then dried under vacuum. The solid was then dissolved in CH_2Cl_2 and treated dropwise with anhydrous CH_2N_2/Et_2O until the evolution of N_2 ceased. The resulting orange solution was stirred for 15 min, then the solvent was removed and the residue was washed 3 times with Et_2O (10 cm^3). Crystallization from CH_2Cl_2/Et_2O (1/1) at −20 °C gave the title complex in 85% yield.

Preparation of FpC(SMe)SM(CO)$_5$ (10a–10c)

To solutions of M(CO)$_5$THF (M = Cr, Mo, W), prepared by irradiation of M(CO)$_6$ (1.5 mmol) in 250 cm^3 of THF, was added 0.35 g (1.3 mmol) of **9** [22]. The reddish-brown solutions were stirred for 1–2 h at room temperature in the dark. The solvent was then removed, and the residue was dried for 2–5 h under high vacuum. The deep orange solids were dissolved in CH_2Cl_2 and the solutions were filtered through Florisil. After addition of 5 cm^3 n-hexane, the solutions were slowly evaporated to give microcrystalline, orange powders.

10a (M = Cr). Yield: 77%. M.p. 93–98 °C (dec.). Found: C, 36.40; H, 1.88; S, 13.70. $C_{14}H_8CrFeO_7S_2$ calcd.: C, 36.54; H, 1.75; S, 13.98%; mol.wt. (CH_2Cl_2): found 467; calcd. 469.19.

10b (M = Mo). Yield: 48%. M.p. 96–101 °C (dec.). Found: C, 33.12; H, 1.81; S, 12.52. $C_{14}H_8FeMoO_7S_2$ calcd.: C, 33.35; H, 1.60; S, 12.72%.

10c (M = W). Yield: 82%. M.p. 118–122 °C (dec.). Found: C, 28.15; H, 1.51; S, 10.70. $C_{14}H_8FeO_7S_2W$ calcd.: C, 28.40; H, 1.36; S, 10.38%.

Preparation of FpC(SMe)SMn(η-C$_5$H$_4$X)(CO)$_2$ (12a–12b)

To solutions of Mn(η-C_5H_4X)(CO)$_2$THF (X = H, Me), prepared by irradiation of Mn(η-C_5H_4X)(CO)$_3$ (0.5 mmol) in 35 cm^3 of THF, was added **9** [22] (0.08 g, 0.3 mmol). The solution was stirred for 1 h at room temperature, the solvent removed under vacuum, and the residue was chromatographed on an alumina column. Elution with light petroleum/Et_2O (5/1) gave initially two fractions which contained unreacted starting materials. The red-brown solids obtained from the third fractions were crystallized from CH_2Cl_2/hexane at −20 °C to give the title complexes.

12a (X = H). Yield: 43%. M.p. 115–116 °C (dec.). Found: C, 43.21; H, 3.03; S, 14.39. $C_{17}H_{14}FeMnO_4S_2$ calcd.: C, 43.26; H, 2.95; S, 14.44%.

12b (X = Me). Yield: 52%. M.p. 96–97 °C (dec.). Found: C, 44.35; H, 3.39; S, 13.71. $C_{17}H_{15}FeMnO_2S_2$ calcd.: C, 44.56; H, 3.30; S, 13.99%.

Preparation of $MeS\text{-}C{\equiv}Co_3(CO)_9$ ***(14)***

Etheral solutions of 2.15 g (6.3 mmol) of $Co_2(CO)_8$ and 0.56 g (2.1 mmol) of **9** [22] were mixed. After the initial violent gas evolution (CO) had stopped (ca. 1 h), the mixture was evaporated to dryness and the resulting black residue was extracted with n-pentane. The extract was filtered and concentrated, then chromatographed on silica gel (15 × 3 cm). Elution with light petroleum/CH_2Cl_2 (8/1) gave a first fraction containing 0.79 g (77%) of **14**. M.p.: 72 °C (dec.). Found: C, 27.59; H, 0.57. $C_{11}H_3Co_3O_9S$ calcd.: C, 27.07; H, 0.62. MS: $m/e = 488$ $[M]^+$, 460, 432, 404, 376, 348, 320, 292, 264, 236 (basis peak) $[M-(CO)_n, n = 1\text{–}9]^+$. ^1H NMR ($CDCl_3$) δ 2.88 (s,Me). IR (n-pentane): 2102 m-s, 2055 vs, 2038 vs, 2020 m-s, 1985 m [ν(CO)], (KBr): 928 m-s, 700 w [ν(CS)] cm^{-1}.

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