Notes

Preparation of Some Metallodithiocarboxylato- and Metallodithiocarbene-metal Complexes

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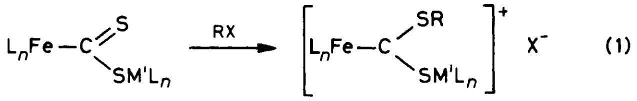
The reaction between the carbon disulphide adduct of dicarbonyl(cyclopentadienyl)iron, $[(cp)(CO)_2FeCS_2]^-$ (cp = η^5-C_5H_5), and $[M(CO)_5Br]$ (M = Mn or Re) produces in good yield the heterodinuclear complexes $[(cp)(CO)_2FeCS_2M(CO)_4]$ in which the CS_2 group acts as a bridge in the unit FeC(=S)SM. Depending on the reaction conditions, both the chelato-complex $[(cp)(CO)_2FeC(=S)SRe(CO)_4]$ and the unidentate $[(cp)(CO)_2$-$FeC(=S)SRe(CO)_5]$ derivative are obtained. Alkylation of the thione sulphur atom in the unit FeC(=S)SRe produces the dithiocarbene $[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5]^+$ in good yield. The reaction of this metallodithiocarbenemetal complex with methylamine yields $[(cp)(CO)_2FeC(=S)(SCH_3)]$ and $[Re(CO)_4(NH_2CH_3)$-$(CONHCH_3)]$. The compounds $[(cp)(CO)_2FeC(=S)(SCH_3)]$ and $[Re(CO)_5Br]$ were formed from the reaction of $[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5]^+$ with LiBr.

SINCE the synthesis of the first complex containing the carbon disulphide group as a bridge between two metal atoms, $K_6[(CN)_5CoCS_2Co(CN)_5]$,[1] several CS_2-bridging derivatives have been synthesized either from η-CS_2 adducts and labile tetrahydrofuran (thf) derivatives or from the electron-rich carbon disulphide adduct of dicarbonyl(η-cyclopentadienyl)iron and halogeno-complexes of transition metals.[2] Apart from the facile preparation of $[(cp)(CO)_2FeCS_2]^-$ (cp = η^5-cyclopentadienyl),[3] only the two heterodinuclear derivatives, $[(cp)(CO)_2FeCS_2Pt(PPh_3)_2]^+$ and $[\{(cp)(CO)_2FeCS_2\}_2Pt]$,[4] formulated as metallodithiocarboxylatometal complexes, have been obtained by the latter method and attempts to prepare other compounds having the same interesting kind of linkage have proved unsuccessful.[5]

The isolation of $[\{(cp)(CO)_2Fe\}_2CS_2]$,[5] the only known unidentate ferriodithiocarboxylato-complex, and the ease with which the thione sulphur atom in dithioester complexes is alkylated [6] led us to attempt the preparation of dithiocarbene compounds as illustrated in equation (1).[7]



In this paper we describe the synthesis of $[(cp)(CO)_2$-$FeC(=S)SM(CO)_4]$ (M = Mn or Re) and the characterization of $[(cp)(CO)_2FeC(=S)SRe(CO)_5]$, together with some results on the reactivity of $[(cp)(CO)_2FeC(SCH_3)$-$SRe(CO)_5]^+$ towards nucleophiles.

RESULTS AND DISCUSSION

The $[(cp)(CO)_2FeCS_2]^-$ adduct, readily available through the reaction of $[Fe(cp)(CO)_2]^-$ with carbon disulphide, reacts with $[Mn(CO)_5Br]$ to yield the corresponding ferriodithiocarboxylato-complex $[(cp)(CO)_2$-$FeC(=S)SMn(CO)_4]$ (1a) (45%, yield). Extensive formation of $[\{Fe(cp)(CO)_2\}_2]$ and $[Mn_2(CO)_{10}]$ occurs in this reaction, as reported by Ellis *et al.*,[5] and we find that the amount of these dimeric species increases with reaction time; best results are obtained using thf solutions at room temperature and short reaction times (40 min). Under these experimental conditions small amounts of $[(cp)(CO)_2FeMn(CO)_5]$ [8] (5—10%) are also obtained.

Similarly, $[Re(CO)_5Br]$ gives, after separation by column chromatography, $[\{Fe(cp)(CO)_2\}_2]$, a very small amount of $[Re_2(CO)_{10}]$, and a fraction which shows nine ν(CO) absorptions in the i.r. and two cyclopentadienyl signals at τ 5.02 and 5.12 in the ^1H n.m.r. spectrum. By heating a sample of this mixture in a sealed n.m.r. tube in $CDCl_3$ at 60 °C the disappearance of the signal at τ 5.12 is observed, and its i.r. spectrum shows a set of ν(CO) absorptions identical to that of (1a) (Table). The fraction resulting from the chromatography is then heated in boiling hexane for 10 min and, on cooling, the yellow air-stable crystalline complex $[(cp)(CO)_2Fe$-$C(=S)SRe(CO)_4]$ (1b) is obtained (50% yield).

These results are consistent with an initial formation of the unidentate ferriodithiocarboxylato-complex $[(cp)$-$(CO)_2FeC(=S)SRe(CO)_5]$ (2) followed by the displacement of a carbonyl group co-ordinated to the rhenium atom which produces the chelato-complex (1b). In fact, if $[(cp)(CO)_2FeCS_2]^-$ and $[Re(CO)_5Br]$ are allowed to react at -78 °C, complex (2), contaminated with small amounts of (1b) [*ca.* 10% from the intensity ratio of the two ^1H n.m.r. cyclopentadienyl signals at τ 5.12 (2) and 5.02 (1b)], is obtained.

The $[(cp)(CO)_2FeC(=S)SM(CO)_4]$ derivatives react with PPh_3 to produce, in an almost quantitative yield, $[(cp)(CO)_2FeC(=S)SM(CO)_3(PPh_3)]$ [M = Mn (3a), Re (3b)] complexes which have been fully characterized by means of spectroscopic and analytical data. The i.r.

Spectroscopic data for new compounds

Compound	I.r. bands[a] (cm^{-1}) ν(CO)	ν(CS)[c]	^{1}H n.m.r. (τ)[b]
(1a) $[(cp)(CO)_2FeC(=\overline{S)SM}n(CO)_4]$	2 085w, 2 045m, 2 001s, 1 995s, 1 961s	921m, 870m	5.10 (s)
(1b) $[(cp)(CO)_2FeC(=\overline{S)SR}e(CO)_4]$	2 100m, 2 043m, 2 002 (sh), 1 998s, 1 986s, 1 951s	920m, 870m	5.02 (s)
(2) $[(cp)(CO)_2FeC(=S)SRe(CO)_5]$	2 130m, 2 070w, 2 030s, 1 995s	998s, 920m	5.12 (s)
(4) $[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5][PF_6]$	2 142m, 2 085w, 2 040s, 2 010s[d]		4.43 (s, 5 H),[e] 6.51 (s, 3 H)
(3a) $[(cp)(CO)_2FeC(=\overline{S)SM}n(CO)_3(PPh_3)]$	2 040m, 2 012s, 1 990m, 1 938s, 1 906s	934m, 870m	2.37 (m, 18 H), 5.37 (s, 5 H)
(3b) $[(cp)(CO)_2FeC(=\overline{S)SR}e(CO)_3(PPh_3)]$	2 040m, 2 015s, 1 990m, 1 928s, 1 900s	930m, 872m	
$[(cp)(CO)_2FeMn(CO)_5]$[f]	2 082w, 2 018w, 1 995s, 1 988m, 1 978m, 1 947w		4.85 (s)

[a] In n-hexane. [b] In $CDCl_3$, τ in p.p.m., $SiMe_4$ as internal standard. [c] Nujol mull. [d] In CH_2Cl_2. [e] In [$^2H_6$]acetone. [f] See ref. 8.

spectra of complexes of type (1) and (3) present a remarkably constant band pattern in the C–S stretching region which seems to be characteristic of the $FeC(=\overline{S)SM}$ group.

The complex $[(cp)(CO)_2FeC(=S)SRe(CO)_5]$ is readily methylated with methyl trifluoromethanesulphonate to give $[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5]^+$ which after anion exchange produces the PF_6^- salt (4) in almost quantitative yield. Since (1b) does not react with $CH_3SO_3CF_3$ under these conditions, (2) can be used as it is obtained directly from its preparation at −78 °C.

The dithiocarbene (4) is stable in the solid state for several months upon exposure to air. It is soluble in acetone but it is insoluble in H_2O and fairly soluble in CH_2Cl_2; solutions of (4) exposed to air decompose completely within one day. Its stability differs from that of the related dithiocarbene complexes $[(cp)(CO)_2FeC(SR)(SR')][PF_6]$, solutions of which are stable for several days.[6]

The i.r. spectrum of the dithiocarbene is composed of four ν(CO) absorptions which are shifted, in accordance with the cationic nature of (4), towards higher wavenumbers with respect to that of its thione precursor (2). In agreement with the proposed structure, the ^{1}H n.m.r. spectrum of (4) in [$^2H_6$]acetone shows two singlets at τ 4.43 (C_5H_5) and 6.51 (CH_3) which are not split upon cooling the solution to −60 °C, indicating the presence of only one isomer.

Because there is only one precedent in the literature for a metallodithiocarbenemetal complex, $[(CO)_5WC(SCH_3)SFe(CO)_2(cp)]$, which has been very recently prepared by the reaction of $[(CO)_5WC(=S)(SCH_3)]^-$ with $[(cp)Fe(CO)_2(thf)]^+$,[9] a reactivity study was undertaken in order to gain further evidence for the proposed structure of (4).

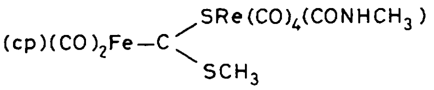
Two major products have been isolated and characterized from the reaction of the dithiocarbene with methylamine, the dithioester $[(cp)(CO)_2FeC(=S)(SCH_3)]$ (5) and the carbamoyl derivative, $[Re(CO)_4(NH_2CH_3)(CONHCH_3)]$ (6), equation (2); whereas complex (5) and $[Re(CO)_5Br]$ are obtained when (4) is allowed to react in acetone at room temperature with LiBr.

$$[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5]^+\ (4) \xrightarrow{3NH_2CH_3} [(cp)(CO)_2FeC(=S)(SCH_3)] + [Re(CO)_4(NH_2CH_3)(CONHCH_3)]\ (6) + NH_3CH_3^+ \quad (2)$$

Although the yields of these reactions are fairly low (30—40%) the results obtained indicate a substantial difference in the reactivity of cationic, $[(cp)(CO)_2FeC(SR)_2]^+$, and neutral, $[(CO)WC(SR)_2]$, dithiocarbene complexes which produce isocyanide derivatives by reacting with primary amines [equation (3)] but do not react with Cl, Br, or I.[6,9]

$$[L_nMC(SR)_2] + NH_2R' \longrightarrow [L_nMCNR'] + 2RSH \quad (3)$$

Since it has been suggested that reactions (3) proceed through a nucleophilic attack at the carbene carbon atom to form an unstable ylide intermediate which then splits off two thiols to form the isocyanide derivatives, the formation of the carbamoyl derivative (6) from reaction (2) may suggest that amine attack does not occur on the p_z orbital of the carbene carbon but rather that reaction takes place at another electrophilic centre, the carbon of the CO group bonded to the rhenium atom, to form an unstable carbamoyl intermediate (7) which reacts further to give the observed products (5) and (6).


$$(cp)(CO)_2Fe{-}C\begin{cases}SRe(CO)_4(CONHCH_3)\\SCH_3\end{cases}$$

(7)

Although these results indicate that the reactivity of (4) is largely controlled by the ease with which the dithioester (5) is released, additional work needs to be done in order to establish a general pattern of the reactivity of these novel dithiocarbene derivatives.

EXPERIMENTAL

General.—All reactions were performed under nitrogen by using standard inert atmosphere techniques. Column chromatography was performed with silica gel of particle size 0.05—0.2 mm.

Infrared spectra were recorded on Perkin-Elmer 257 or 225 spectrometers; ^1H n.m.r. spectra were recorded on a Varian XL 100 spectrometer using $SiMe_4$ as internal standard. Mass spectra were recorded on a JEOL JMS-D 100 spectrometer working at 75 eV.* Conductivity measurements were performed on a LKB 5300 B conductivity bridge. Spectroscopic data are given in the Table.

Syntheses of Complexes.—$[(cp)(CO)_2FeC(=\overline{S)SMn}(CO)_4]$ (1a). A solution of $[Fe(cp)(CO)_2]^-$ (*ca.* 9.0 mmol) in thf (30 cm^3) was added with a syringe to 2 cm^3 of CS_2 at room temperature. After 30 s, solid $[Mn(CO)_5Br]$ (1.85 g, 6 mmol) was added to the resulting solution which contains the adduct $[(cp)(CO)_2FeCS_2]^-$.[3] Stirring was continued for 40 min, then the resulting solution was evaporated to dryness and the residue extracted with light petroleum (b.p. 40—70 °C, 100 cm^3). After filtration the solution was evaporated to dryness and the residue chromatographed on a silica gel column (3 × 40 cm). Elution with light petroleum–benzene (2 : 1) gave four fractions in the following sequence: (*a*) $[Mn_2(CO)_{10}]$, (*b*) $[(cp)(CO)_2FeMn(CO)_5]$, (*c*) $[(cp)(CO)_2FeC(=\overline{S)SMn}(CO)_4]$, (*d*) $[\{Fe(cp)(CO)_2\}_2]$. The third yellow fraction (*c*) containing (1a) was evaporated to give a yellow solid, which was crystallized from a minimum amount of gently heated hexane, on cooling at −10 °C. Yellow crystals of (1a) (1.15 g, 2.73 mmol, 46%) were obtained; m.p. 128—129 °C (decomp.) (Found: C, 34.4; H, 1.4; O, 22.6; S, 14.95. Calc. for $C_{12}H_5FeMnO_6S_2$: C, 34.3; H, 1.2; O, 22.85; S, 15.25%). Mass spectrum: *m/e* 420 (M^+); 392, 364, 336, 308, 280, 252 (base peak) $[M - (CO)_n, n = 1—6]$.

$[(cp)(CO)_2FeC(=\overline{S)SRe}(CO)_4]$ (1b). This complex was prepared by a route analogous to that used for (1a), starting with a solution of $[Fe(cp)(CO)_2]^-$ (*ca.* 4.5 mmol) in thf (15 cm^3), CS_2 (1.5 cm^3), and $[Re(CO)_5Br]$ (1.25 g, 3.0 mmol) in thf (15 cm^3). This solution was evaporated to dryness after being stirred for approximately 30 min. The resulting residue was then chromatographed on a silica gel column (3 × 40 cm^3) and elution with benzene–light petroleum (1 : 1) gave a first fraction which contained very small amounts of $[Re_2(CO)_{10}]$, a diffuse yellow fraction, and a third fraction which contained $[\{Fe(cp)(CO)_2\}_2]$. The yellow residue obtained from the second fraction was heated in refluxing n-hexane (20 cm^3); on cooling the solution to −10 °C, yellow crystals of (1b) (0.79 g, 1.44 mmol, 48%) were obtained; m.p. 155 °C (decomp.) (Found: C, 26.25; H, 1.05; O, 17.5; S, 11.45; Calc. for $C_{12}H_5FeO_6ReS_2$: C, 26.15; H, 0.9; O, 17.4 ; S, 11.65%). Mass spectrum: *m/e* 553 (M^+); 525, 497, 469, 441, 413, 384 (base peak) $[M - (CO)_n, n = 1—6]$.

$[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5][PF_6]$ (4). A solution of $[Fe(cp)(CO)_2]^-$ (*ca.* 4.5 mmol) in thf (30 cm^3) was added to CS_2 (1.5 cm^3) at −78 °C. After 30 s a solution of $[Re(CO)_5Br]$ (1.25 g, 3.0 mmol) in thf (15 cm^3) was added and the stirring was continued for 40 min. The reaction mixture was then allowed to warm to room temperature, the solvent evaporated, and the residue extracted with light petroleum (40—70 °C, 200 cm^3). After evaporation of the solvent the crude $[(cp)(CO)_2FeC(=S)SRe(CO)_5]$ was dissolved in CH_2Cl_2 (20 cm^3) and $CH_3SO_3CF_3$ (0.44 cm^3, 4 mmol) was added with stirring. After one hour the solvent was evaporated and the red oily residue dissolved in acetone. To this solution, NH_4PF_6 (0.500 g, 3.1 mmol) was added and the crude complex (4) precipitated by adding Et_2O. The yellow solid was then dissolved in CH_2Cl_2 (200 cm^3) and filtered. Addition of light petroleum followed by crystallization from acetone–Et_2O (1 : 3) gave yellow microcrystalline (4) (0.872 g, 1.18 mmol, 39%) (Found: C, 22.6; H, 1.2; S, 8.8. Calc. for $C_{14}H_8F_6FeO_7PReS_2$: C, 22.75; H, 1.1; S, 8.65%); Λ_M (acetone) = 141 Ω^{-1} cm^2 mol^{-1}.

$[(cp)(CO)_2FeC(=\overline{S)SM}(CO)_3(PPh_3)]$ [M = Mn (3a), M = Re (3b)]. A solution of CH_2Cl_2 (30 cm^3) containing $[(cp)(CO)_2FeM(CO)_4]$ (0.5 mmol) and a two-fold excess of PPh_3 was stirred for 3 d (M = Mn), or refluxed for 4 d (M = Re). The resulting solutions were then evaporated to dryness and the residue washed with light petroleum. Crystallization from CH_2Cl_2–hexane (1 : 2) afforded the title complexes as yellow crystals: (3a) (85% yield), m.p. 186 °C (decomp.) (Found: C, 54.5; H, 3.3; O, 12.1; S, 9.2. Calc. for $C_{29}H_{20}FeMnO_5PS_2$: C, 53.25; H, 3.1; O, 12.25; S, 9.8%); (3b) (79% yield), m.p. 220 °C (decomp.) (Found: C, 44.5; H, 2.85. Calc. for $C_{29}H_{20}FeO_5PReS_2$: C, 44.35; H, 2.55%).

Reaction of $[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5][PF_6]$ (4) *with* CH_3NH_2.—Methylamine was bubbled through a suspension of complex (4) (0.205 g, 0.28 mmol) in Et_2O (30 cm^3) for one hour. Immediately, the solution turned clear and a white precipitate appeared. The red-orange solution was filtered and evaporated to dryness. The residue was partially extracted with pentane and then with warm hexane. The pentane extracts were evaporated to dryness leaving 0.035 g (46%) of the dark yellow complex $[(cp)(CO)_2FeC(=S)(SCH_3)]$ (5),[3] m.p. 70 °C. I.r. (hexane): 2 040 and 1 990 cm^{-1}; ^1H n.m.r. ($CDCl_3$): τ 7.36 (s, CH_3), 5.06 (s, C_5H_5); mass spectrum: *m/e* 268 (M^+). The hexane extracts gave after evaporation of the solvent 0.037 g (34%) of *cis*-$[Re(CO)_4(NH_2CH_3)(CONHCH_3)]$ (6).[10] I.r. (CCl_4): 2 085, 1 990, and 1 935 cm^{-1}. Another unidentified product was formed in this reaction and all the attempted purifications failed.

Reaction of $[(cp)(CO)_2FeC(SCH_3)SRe(CO)_5][PF_6]$ (4) *with* LiBr.—A solution of complex (4) (0.250 g, 0.34 mmol) in acetone (30 cm^3) and a five-fold excess of LiBr was allowed to stir for 3 h. The solution was evaporated to dryness and the solid partially extracted with pentane. The resulting solution gave after evaporation of the solvent 0.040 g (44%) of $[(cp)(CO)_2FeC(=S)(SCH_3)]$ (5), whereas the residue, insoluble in pentane, was chromatographed on a silica gel column. Elution with hexane–CH_2Cl_2 (3 : 2) gave more complex (5), $[Re(CO)_5Br]$ (0.045 g, 32.6%), and very small amounts of a third product which rapidly decomposes in solution.

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* Throughout this paper: 1 eV = 1.602×10^{-19} J.

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