Metal Perfluoro-alkane- and -arene-thiolates. Part III.[1] Cyclopentadienylcobalt Derivatives †

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The products of the reactions between $[(cp)Co(CO)_2]$ and RS·SR (R = CF_3 or C_6F_5) depend upon the conditions used. $[\{(cp)CoSR\}_2]$ (R = CF_3 or C_6F_5), $[(cp)Co(CO)(SC_6F_5)_2]$, and $[(cp)Co_2(SC_6F_5)_3]$ are described.

We have described previously reactions leading to a range of metal trifluoromethane- and pentafluorobenzene-thiolates[1,2] and, in particular, have given details of the reaction between octacarbonyldicobalt and bis(trifluoromethyl) disulphide which yields the non-sulphur-containing complex $[Co_3(CO)_9CF]$ and also $[\{Co_2(CO)_5S\}_n]$. Bis(pentafluorophenyl) disulphide has been reported to react directly with octacarbonyldicobalt to give a product which retains the S–S bond.[3] In general, thiolate derivatives of cobalt are polymeric showing considerable complexity although it has been pointed out[3] that the presence of strongly electronegative substituents on the sulphur should reduce the tendency to polymerisation. We report here on the reactions between disulphides with strongly electronegative substituents and some carbonylcyclopentadienylcobalt species.

The products of the reactions between dicarbonyl

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† No reprints available.

[1] Part II, J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1973, 1957.

[2] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1972, 107.

[3] G. Bor and G. Natile, *J. Organometallic Chem.*, 1971, **26**, C33.

cyclopentadienylcobalt and bis(pentafluorophenyl) disulphide depend upon the reaction conditions. In the absence of solvent a 1 : 1 molar ratio of the reactants gives the dark green air-sensitive solid [{(cp)Co(SC_6F_5)}$_2$] (I), the reaction occurring at room temperature. In pentane solution there is no reaction up to 263 K but above this temperature and on irradiation black crystals of [(cp)Co(CO)(SC_6F_5)$_2$] (II) are formed and the solution becomes green because of formation of traces of [{(cp)Co(SC_6F_5)}$_2$]. The thermal reaction in pentane at 293 K gives red and then green solutions but only pure [(cp)Co(CO)(SC_6F_5)$_2$] is deposited. Solutions of [(cp)Co(CO)(SC_6F_5)$_2$] heated above 323 K give [{(cp)Co(SC_6F_5)}$_2$] and a further green complex considered to be [(cp)Co_2(SC_6F_5)$_3$] (III).

The reaction between carbonylcyclopentadienylcobalt and bis(trifluoromethyl) disulphide in the dark gives an ill-defined purple-black solid probably containing a single carbonyl group. The complex could not be fully characterised. The photolytic reaction in pentane gave the air-sensitive green-black solid [{(cp)Co(SCF_3)}$_2$] (IV).

The complexes [{(cp)Co(SR)}$_2$] (I) and (IV) presumably have puckered Co_2S_2 rings with cobalt–cobalt bonding analogous to structures postulated for [{(cp)Co(SMe)}$_2$] [4] and described for [{(cp)Co(PPh_2)}$_2$].[5] The ^{19}F n.m.r. spectra of (I) and (IV) show only single signals. This suggests that the substituents are in the *syn* (equatorial, equatorial) configuration [6] although fluxional behaviour involving inversion at sulphur is a further possibility. Both *syn*- and *anti*-isomers are generally found for [{Fe(CO)$_3$(SR)}$_2$] complexes where *anti* (equatorial, axial) substituents are favoured by bulky substituents on sulphur [7] so that the present n.m.r. spectra might well result from lack of significant steric interaction between the cyclopentadienyl ligand and the organic group R (the complexes are too unstable in solution to allow variable-temperature n.m.r. measurements).

I.r. and n.m.r. spectra

Compound	I.r. spectra/cm^{-1}			N.m.r. spectra	
	Solvent	ν_{CO}	C_6F_5/CF_3 modes	^{19}F (p.p.m.)	^1H (τ)
[{(cp)Co(SC_6F_5)}$_2$] (I)	*a*		1510s, 1486s, 1081m	163·6, 158·0, 129·6	5·15
[(cp)Co(CO)(SC_6F_5)$_2$] (II)	*b*	2079m	1506s, 1476s, 1084m	162·2, 157·0, 128·2	4·7
[(cp)Co_2(SC_6F_5)$_3$] (III)	*c*		1512s, 1476s, 1085m	153·3	5·5
[{(cp)CoSCF_3}$_2$] (IV)			1138m, 1131m, 1099m, 1089s	33·1	5·0

[a] Cyclohexane. [b] CCl_4. [c] $CHCl_3$.

The stoicheiometry and method of preparation of [(cp)Co(CO)(SC_6F_5)$_2$] (II) suggest a close similarity to other [(cp)Co(CO)X_2] (X = Cl, Br, I, or R_FI) complexes.[8] The i.r. spectrum is in accord with this and shows a single CO stretching mode at 2079 cm^{-1} and a weak C–H stretching mode at 3120 cm^{-1} characteristic of the π-cyclopentadienyl ligand. The monomeric nature of the complex is confirmed by the molecular weight in chloroform but the mass spectrum shows species derived from [{(cp)Co(SC_6F_5)}$_2$] which is formed by thermal decomposition of (II). The ^{19}F n.m.r. spectrum shows three multiplets of ratio 2 : 1 : 2 as expected for two C_6F_5 groups in identical environments. However, the ^1H spectrum at 307 K shows a flat extremely broad band centred at τ 4·55 and extending over 2·5 τ units whereas at 193 K this band has changed to a sharp singlet at τ 5·5.

Restricted rotation of a substituted cyclopentadienyl ring has been previously observed in [{π-C_5H_4·C(CF_3)$_2$OH}-Ru(PPh_3){C_2(CO_2Me)$_2$H}] because of hydrogen bonding between the hydroxo-group and the ligand C_2(CO_2Me)$_2$H.[9] This has suggested that in (II) steric interaction between the C_6H_5 groups and the cyclopentadienyl ring is sufficient to slow rotation of the cyclopentadienyl ring. At 193 K the pentafluorophenyl groups may be frozen in a configuration pointing away from the cyclopentadienyl ring but at higher temperatures the barrier to free rotation about sulphur may be overcome at the expense of the restriction of free rotation of the cyclopentadienyl ring.

The formulation [(cp)Co_2(SC_6F_5)$_3$] (III) is based on analysis for C, H, Co, F, and S. The spectroscopic data for this complex are inconclusive and a structure cannot be postulated at this stage.

EXPERIMENTAL

The experimental methods employed are similar to those previously described. [(cp)Co(CO)$_2$] Was purchased from Strem Chemicals Inc.

Reactions of (C_6F_5S)$_2$ *and* [(cp)Co(CO)$_2$].—(*a*) Pentane solutions of [(cp)Co(CO)$_2$] and (C_6F_5S)$_2$ (molar ratio 1 : 1) were mixed under nitrogen, transferred to a reaction tube which was sealed, and shaken for three days at 293 K to give black crystals of *carbonyl(π-cyclopentadienyl)bis(pentafluorobenzenethiolato)cobalt* (75%) recrystallised from methylene chloride–hexane [Found: C, 39·5; H, 1·0; Co, 11·0; F, 33·2; S, 12·5%; *M* (by osmometry in $CHCl_3$), 495. $C_{18}H_5CoF_{10}OS_2$ requires C, 39·3; H, 0·9; Co, 10·7; F, 34·5; S, 11·6%; *M*, 550].

(*b*) The solution prepared as above was allowed to warm over a period of three days from 195 K. No reaction was observed up to 263 K when crystals of (II) are formed (63% yield after three days at 263 K). Solvent was removed from the green solution and traces of (C_6F_5S)$_2$ removed by sublimation. Recrystallisation of the residue from pentane gave small quantities of green *cyclopenta-*

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dienyl(pentafluorobenzenethiolato)cobalt dimer (I) [Found: C, 40·0; H, 1·2; Co, 17·7; F, 30·6; S, 9·7%; *M* (mass spec.), 646. $C_{11}H_5CoF_5S$ requires C, 40·9; H, 1·5; Co, 18·3; F, 29·4; S, 9·9%; *M*, 646].

(*c*) A pentane solution was irradiated in a Pyrex reaction vessel. Large crystals of $[\{(cp)CoSC_6F_5\}_2]$ (4%) and $[(cp)Co(CO)(SC_6F_5)_2]$ (36%) formed on the sides of the vessel adjacent to the u.v. source and smaller quantities of the monomer crystallised on other parts of the reactor. The products were separated as above.

(*d*) Addition of $(C_6F_5S)_2$ to $[(cp)Co(CO)_2]$ in the absence of solvent led to rapid evolution of carbon monoxide. The flask was evacuated and heated at 313 K for 24 h to give $[\{(cp)CoSC_6F_5\}_2]$ in 32% yield.

Thermal Decarboxylation of $[(cp)Co(CO)(SC_6F_5)_2]$. The complex was dissolved in pentane and heated in a sealed flask at 363 K for 40 h. The pentane-soluble residue contained small amounts of $[\{(cp)CoSC_6F_5\}_2]$. The insoluble residues were extracted with methylene chloride, hexane was added, and solvent removed to give dark green $[(cp)Co_2(SC_6F_5)_2]$ (III) (34%) (Found: C, 35·3; H, 1·0; Co, 14·0; F, 34·5; S, 11·0. $C_{23}H_5Co_2F_{15}S_3$ requires C, 35·4; H, 0·6; Co, 15·1; F, 36·5; S, 12·5%).

Reactions of $(CF_3S)_2$ *and* $[(cp)Co(CO)_2]$.—Thermal reactions were carried out similarly to those described above for $(C_6F_5S)_2$ but the products could not be identified because of instability and low yield of products.

Irradiation of a pentane solution of the reactants for 50 h gave a green solution from which green air-sensitive *cyclopentadienyl(trifluoromethanethiolato)cobalt dimer* was obtained by sublimation at 353 K after removal of solvent [Found: C, 31·6; H, 1·9; Co, 25·6; F, 26·0; S, 14·3%; *M* (mass spec.), 450. $C_6H_5CoF_3S$ requires C, 32·0; H, 2·2; Co, 26·2; F, 25·3; S, 14·2%; *M*, 450].

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