2,2-Dithiocarboxylation of a Chromium Co-ordinated 1,3 Dithian. *X*-Ray Crystal Structure of *fac*-Tricarbonyl(diethyl 1,3-dithian-2,2-bisdithiocarboxylate)chromium

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Summary Reaction of $[Cr(CO)_5\{\overline{S[CH_2]_3SCH_2}\}]$ with BuLi and CS_2 (−100 °C) followed by alkylation gives the title compound (**1**), the structure of which has been determined by *X*-ray crystallography and in which the two preferentially co-ordinated thioketonic sulphur atoms exercise a considerable *trans* influence compared with the sulphide sulphur donor atom.

THE deprotonation and subsequent double internal carbonylation of complexes of the type $[M(CO)_5\{S(CH_2R^2)R^1\}]$ take place under extremely mild (−80 °C) conditions.[1,2] As part of a study to investigate the possibility of using co-ordinated lithio-thioacetals as precursors for other carbon–carbon bond formations, CS_2, which usually yields 1,1-dithiols with bifunctional CH acids and base,[3] was used as an electrophile with one of the above metallated complexes in which M = Cr and R^1R^2 = $[CH_2]_3S$.

Reaction of $[Cr(CO)_5\{\overline{S[CH_2]_3SCH_2}\}]$ with 1·5 mol. equiv. of BuLi and excess of CS_2 in tetrahydrofuran (thf) (−100 °C) afforded a red–brown salt which was treated with $[OEt_3][BF_4]$ in CH_2Cl_2 (0 °C). Purification of the only coloured product (**1**) was achieved by column chromatography (SiO_2; CH_2Cl_2–hexane, 1:1; −10 °C) and recrystallisation (ether–pentane, −30 °C). The purple crystals obtained, m.p. 150 °C (24%), were suitable for an *X*-ray crystallographic study.

$$[\underline{\overline{Cr(CO)_3PMe\{[CH_2]_2PMe_2}\}\{[CH_2]_2PMe_2}\}]$$

(**2**)

The molecular-ion peak for (**1**) was not observed in the mass spectrum, but a principle-ion peak at *m/e* 380 (*M* − 3CO) indicated that two CS_2 molecules had been taken up, a fact which was also substantiated by elemental analysis and ^1H n.m.r. spectroscopy. The three carbonyl stretching i.r. absorptions (1980vs, 1913s, and 1898s cm^{-1}) were at considerably higher frequency than those in the complex (**2**) (1918s and 1924vs cm^{-1}),[4] in accordance with an unexpectedly low σ(donor)/π(acceptor) ratio for the new tridentate ligand, $S[CH_2]_3SC\{C(S)SEt\}_2$. Two absorption bands at 1260 and 1040 cm^{-1} (KBr) could be ascribed to C=S vibrations. The full molecular structure of (**1**) was established by a single-crystal *X*-ray diffraction study.

Crystal data: $C_{13}H_{16}CrO_3S_6$, M = 464·42, monoclinic, space group $P2_1/n$, a = 13·67(2), b = 10·80(1), c = 13·49(2) Å, β = 105·7(1)°; $D_c = D_m$ = 1·61 g cm^{-3}; Z = 8; μ(Mo-K_α) = 11·72 cm^{-1}; 2509 independent reflections with $\theta < 22°$, 158 unobserved; crystal size 0·1 × 0·15 × 0·1 mm. The structure was solved by Patterson methods. Full-matrix least-squares refinement of the trial parameters, with individual anisotropic thermal parameters for all the atoms except hydrogen and isotropic thermal parameters for hydrogen, converged at R and R_w values of 0·054 and 0·038, respectively.†

$[Cr(CO)_3(CNBu^t)\{C(OEt)C(OEt)CS[CH_2]_3S\}]$

(**3**)

The ligand is bonded to the metal *via* one sulphide [S(1)] and two thione [S(2), S(3)] sulphur atoms (Figure).

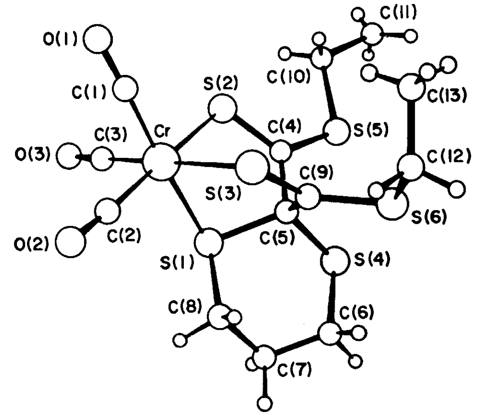
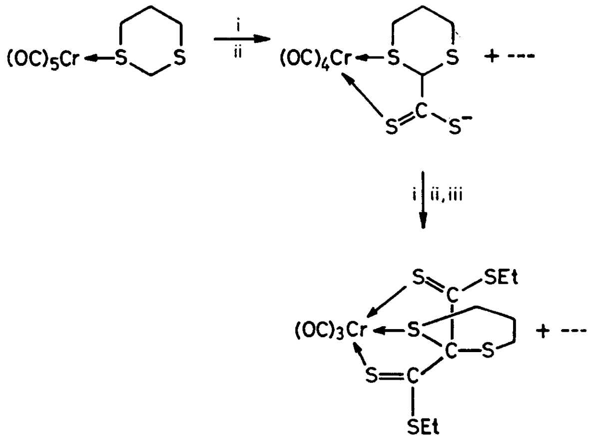


FIGURE. The molecular structure of (**1**) showing the crystallographic numbering scheme.

Although the Cr–S(sulphide) distance, 2·338(2) Å, is somewhat shorter than the same bond length in the complex (**3**), 2·365(2) Å,[5] the *trans* Cr–C [1·824(6) Å] and *trans* C–O [1·182(7) Å] distances are similar to those in (**3**). The Cr–S-(thione) bonds, averaging 2·330 Å, are, however, significantly shorter than the comparable distance in $[Cr(CO)_5(SCMe_2)]$,[6] 2·377 Å, and they exert an unprecedentedly large *trans* influence [in line with the ν(CO) frequencies], leading to the average *trans* bond lengths Cr–C 1·880 and C–O 1·151 Å. It is possible that the considerable charge delocalization over the S=C–SEt moieties [average C(4)–S(5) and C(9)–S(6) bond lengths 1·730 Å compared with C(5)–S(1) 1·864(5) Å] results in less negative charge being effectively transferred to the metal. Cannas *et al.*[7] obtained 1·78 Å for a C(sp^3)–S distance in $[W(CO)_5\{S{=}CNH[CH_2]_2S\}]$, but in this case the presence of a nitrogen atom in the five-membered ligand ring complicates a comparison. It would be interesting to compare the relevant data for compounds such as $[Cr(CO)_5\{SC(SEt)R\}]$ and $[Cr(CO)_5\{SCS[CH_2]_3S\}]$ (which we intend to synthesise) with those available for other pentacarbonyl thio-complexes.



(**1**)

SCHEME. *Reagents:* i, BuLi; ii, CS_2; iii, $[OEt_3][BF_4]$.

The conversion described above can be explained according to the Scheme. The co-ordination of the thione sulphur atom in the first step with expulsion of CO controls the course of the reaction, since the formation of the expected sulphide co-ordinated dianion $\{S[CH_2]_3SC(CSS)\}^{2-}$ during the second proton abstraction is thereby thwarted and the second CS_2 molecule adds on to the same carbon atom as the first one. The substitution of CO and co-ordination of the third sulphur donor atom may also be facilitated by the presence of $[OEt_3][BF_4]$ employed in the alkylation process.[8]

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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