Synthesis and *X*-Ray Structure of *cis*-[(Ethoxy)-1,3-dithianylidene-(hydroxy)methylcarbene-*C*,*S*]tetracarbonylchromium(0). The Formation of a Complex with Carbonyl Insertion

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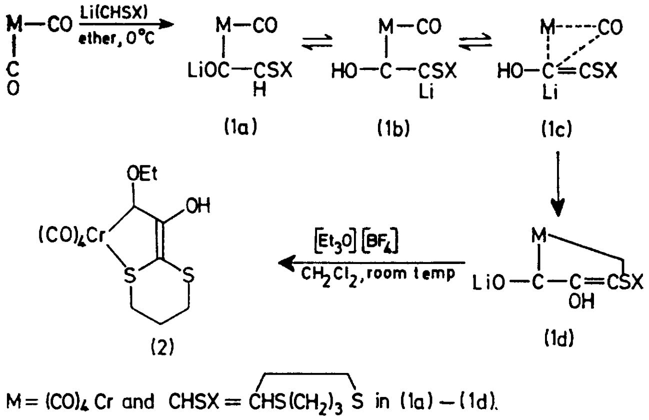
Summary The reaction of $\mathrm{Li[\overline{CHS(CH_2)_3S}]}$ with $\mathrm{[Cr(CO)_6]}$ and subsequent alkylation produces the novel carbonyl-inserted carbene-thio-tetracarbonyl-complex, *cis*-$\mathrm{[\underline{CrC(OEt)\{C(OH)\overline{CS}}\overline{(CH_2)_3S}\}(CO)_4]}$.

Treatment of $\mathrm{[Cr(CO)_6]}$ with LiR (R = an organic group) usually affords the compounds $\mathrm{[(CO)_5CrC(OLi)R]}$ which can be further alkylated according to established procedures.[1] In view of the interest in so-called insertion reactions shown by different organometallic transition metal complexes,[2] we report a new carbene-complex formation reaction for the synthesis of the title compound (**2**) during which proton migration (α to the carbene carbon atom[3]) and carbonyl insertion take place. The insertion probably involves the migration of a carbene ligand to a co-ordinated carbon monoxide ligand in the *cis*-position and the occupation of the vacant co-ordination site by an available sulphur-donor atom.



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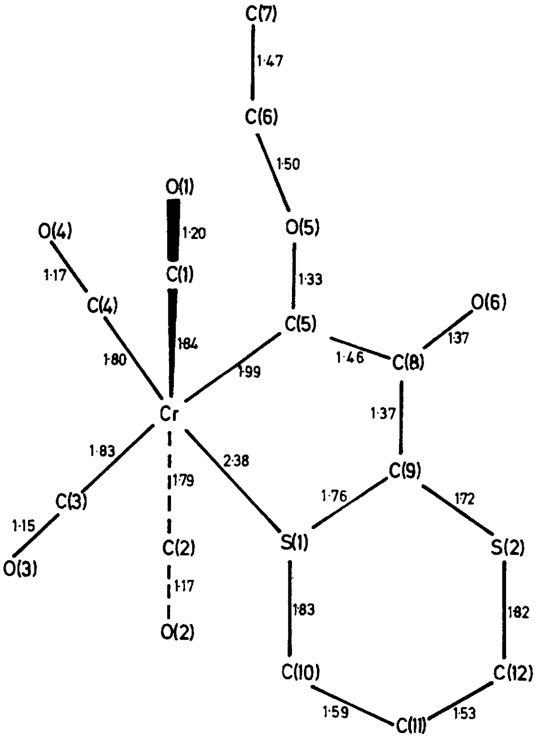

FIGURE. Molecular structure of *cis*-$\mathrm{[CrC(OEt)\{C(OH)CS(CH_2)_3S\}(CO)_4]}$. Average e.s.d.'s = 0·02 Å.

When $\mathrm{Li[CHS(CH_2)_3S]}$[4] was added to an equimolar amount of $\mathrm{[Cr(CO)_6]}$ in ether at 0 °C and the resulting crude yellow mixture, after removal of the solvent *in vacuo*, was treated with $\mathrm{[Et_3O][BF_4]}$ in $\mathrm{CH_2Cl_2}$ at room temp. the main product (**2**) was obtained in pure form from a silica gel column ($\mathrm{CH_2Cl_2}$–pentane, 1 : 1; −20 °C). After evaporation *in vacuo*, a dark red powder (m.p. 114 °C, decomp.; 65%) was obtained and shown by total microanalysis to have the formula $\mathrm{C_{12}H_{12}CrO_6S_2}$. The structural assignment and formulation of (**2**) were based on spectral evidence.

The mass spectrum showed the consecutive loss of only four carbonyl groups from the molecular ion (*m/e* 368), and the i.r. spectrum (hexane) indicated a *cis*-$\mathrm{M(CO)_4L_2}$ structure. The ^{13}C n.m.r. spectrum [$\mathrm{(CD_3)_2CO}$] indicated the presence of two sp^2-carbon atoms (δ 161·4 and 139·0 p.p.m.) in addition to the carbene carbon (δ 313·3 p.p.m.) and other resonances.

Final confirmation for the structure and stereochemistry of (**2**) was obtained from three-dimensional X-ray analysis based on a total of 1089 independent reflections (Phillips PW 1100 diffractometer, Mo-K_α radiation). Limited by the small size of the crystal (0·04 × 0·06 × 0·12 mm), data were collected to $\theta \leqslant 18°$. Of the intensities measured 754 were considered to be observed with $I/\sigma(I) \geqslant 1{\cdot}65$. *Crystal data:* monoclinic, space group $C2/c$, a = 20·19(2), b = 7·22(1), c = 22·10(2) Å; β = 106·9(5)°; Z = 8; D_m = 1·57, D_c = 1·59 g cm^{-3}. The structure was solved by Patterson methods. A full-matrix least-squares refinement of the trial parameters, with individual anisotropic thermal parameters for the chromium and two sulphur atoms and isotropic thermal parameters for the other non-hydrogen atoms, led to an R-value of 0·070. Unit weights were assigned to all reflections. A more detailed analysis will be carried out when we have obtained larger crystals.

The chromium atom (Figure) is in a slight distorted octahedral environment (angles at Cr 79·3—101·5°) All the atoms, C(5)O(5)C(8)O(6)C(9)S(1)S(2), of the branched bidentate 1,3-dithianylidene(hydroxy)methylcarbene ligand are essentially coplanar with Cr and two carbonyl groups. Some π-character can be ascribed to the C(5)–O(5) [1·33(2) Å] and C(8)–O(6) [1·37(2) Å] bonds. The Cr–S(2) bond length [2·38(2) Å] is significantly shorter than the corresponding value [2·46(1) Å] in $\mathrm{[Cr\{SEt(CH_2Ph)\}(CO)_5]}$[5]. This work is of interest in connection with the synthesis and structure of (3-acetyl-4,5-dihydrofuran-2-yl)tetracarbonylmanganese(I).[6]

In view of the high acidity of a proton α to a carbene-carbon atom[3] [*cf.* (**1a**)], the expected carbocationic character of the latter atom in (**1b**),[1] and previous mechanistic studies for carbonyl insertion[2] which support a nucleophilic attack of a carbanion upon an adjacent carbonyl group [as in the intermediate (**1c**)], complex (**2**) may be formed by the intramolecular migrations in the Scheme.

The enolic hydroxy-group in (**2**) could be alkylated by consecutive treatment with BuLi and $\mathrm{[Et_3O][BF_4]}$, but not by adding only the oxonium salt. When the crude yellow mixture (see above) had been treated with more BuLi and then dissolved in water to decompose excess of BuLi and to hydrolyse all the other C–Li bonds present, subsequent alkylation in $\mathrm{CH_2Cl_2}$ still yielded the compound *cis*-$\mathrm{[CrC(OEt)\{C(OEt)CS(CH_2)_3S\}(CO)_4]}$. This confirmed that the carbene and proton migrations had, at this stage, already taken place as suggested in the proposed mechanism. Also obtained as a byproduct in the reaction was (1,3-dithiane)pentacarbonylchromium(0).[5,7]

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