Synthesis and *X*-Ray Structure of *fac*-{[1,3-Dithian-2-ylidene(ethoxy)methyl-(ethoxy)carbene-*C*,*S*]t-butyl isocyanide}tricarbonylchromium(0). One of a New Class of Metallocyclic Complexes obtained by the Generation of Anions α to Co-ordinated Sulphur Atoms

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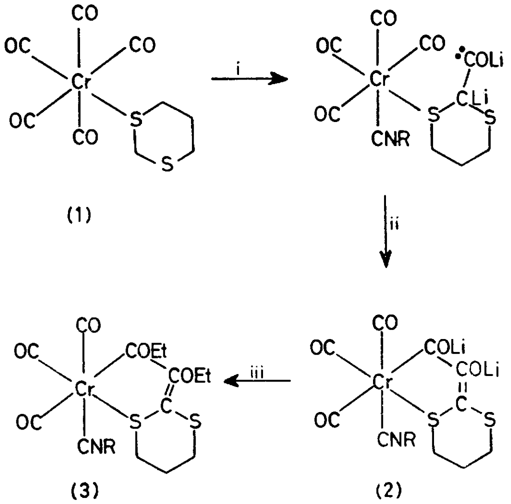
Summary Reaction of $[\mathrm{Cr\{S(CH_2)_3SCH_2\}(CO)_5}]$ (**1**) with BuLi in the presence of t-butyl isocyanide, gives, *via* double carbonylation, the compound *fac*-$[\mathrm{CrC(OLi)\{C(OLi)CS[CH_2]_3S\}(Bu^tNC)(CO)_3}]$ (**2**), which can be alkylated to yield the title compound, (**3**).

During a preliminary study of the reactivity of the complexes *cis*-$[\mathrm{MC(OEt)\{C(OR^1)C(R^2)SR^3\}(CO)_4}]$[1] [M = Cr, W; $\mathrm{R^1 = H, Et}$; $\mathrm{R^2 = Ph}$; $\mathrm{R^3 = Me, Ph}$; $\mathrm{R^2R^3 = S(CH_2)_3}$], we have observed that treatment with HBr furnishes the thio-pentacarbonyl complexes, $[\mathrm{M\{S(CH_2R^2)R^3\}(CO)_5}]$ by a route which probably involves consecutive decarbonylation of the bidentate thio-carbene ligand. We now report on the formation of the *fac*-chelate (**3**) obtained after metallation of one of the thio complexes (**1**) with the strong base BuLi (pentane, −20 °C), in the presence of $\mathrm{Bu^tNC}$, followed by alkylation with $[\mathrm{Et_3O}][\mathrm{BF_4}]$ ($\mathrm{CH_2Cl_2}$, −20 °C).

Total elemental analysis ($C_{18}H_{25}CrO_5NS_2$) and spectroscopy (i.r.: ν_{N-C} 2125 cm^{-1}; ν_{CO} 1948, 1892, and 1858 cm^{-1}; mass spectrum: *m/e* 451) indicated the composition and $ML^1L^2L^3(CO)_3$ structure of the main product (**3**), obtained as dark purple crystals from ether–hexane (−30 °C), after column chromatography (CH_2Cl_2–hexane 1 : 1, −20 °C) of the final mixture. The structure was finally established as a *fac* trisubstituted carbonyl complex by three dimensional *X*-ray analysis, based on a total of 2650 independent reflections (Phillips PW 1100 diffractometer, Mo-K_α radiation). Data were collected to $\theta \leqslant 22°$. Reflections (552) for which $I \leqslant 1{\cdot}65\,\sigma\,(I)$ were regarded as 'unobserved' for the structure solution. *Crystal data*: triclinic, space group $P\bar{1}$, $a = 12{\cdot}33(1)$, $b = 9{\cdot}61(1)$, $c = 9{\cdot}64(1)$ Å; $\alpha = 105{\cdot}6(1)$, $\beta = 95{\cdot}0(1)$, $\gamma = 94{\cdot}9(1)°$; $Z = 2$; $D_m = 1{\cdot}37$ g cm^{-3}, $D_c = 1{\cdot}38$ g cm^{-3}. 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, led to an *R*-value of 0·040.†

The Cr–C (isonitrile) bond distance [2·00(1) Å] is significantly longer than the Cr–C (carbonyl) distances [mean 1·84(1) Å][2] and is about equal to the Cr–C (carbene) bond length [2·02(1) Å]. Aside from the replacement of one CO group by CNBu^t and a hydrogen atom by an Et group, the structure is essentially identical with that of *cis*-$[CrC(OEt)\{C(OH)CS[CH_2]_3S\}(CO)_4]$ as previously reported.[1]

Unique features of the proposed mechanism (Scheme) for the formation of the chiral complex (**3**) are the easy generation of an anion α to the co-ordinated sulphur atom (step i) and the hitherto unknown consecutive double (*cis–cis*) carbonylation[3] (steps i and ii) *via* nucleophilic attack of a carbene carbon atom on a co-ordinated carbonyl group (step ii). The formation of the unstable carbene in step i might be compared with the unstable derivative $Me_3SiC(O)Li$, which results from the reaction of Me_3SiLi with unco-ordinated CO.[4]



R = Bu^t

Scheme. Reagents: i and ii, RNC, BuLi, pentane, −20 °C; iii, $[Et_3O][BF_4]$, CH_2Cl_2, −20 °C.

Analogous reactions were found with tungsten as the central atom and also with other Lewis bases, *i.e.* PR_3, $P(OR)_3$ (R = Me, Ph), $AsPh_3$ and SPh_2. In the absence of such a base, the vacated co-ordination site (step i), is occupied by a carbonyl group from the mixture itself. This leads to another method for the preparation of *cis*-$[(MC(OEt)\{C(OEt)C(R^2)SR^3\}(CO)_4]$ $[R^2R^3 = S(CH_2)_3]$.[1]

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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