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Preliminary communication

REACTION OF DIMETHYLTHIOCARBAMOYLCHLORIDE WITH $[Cr(CO)_5(thf)]$, AND THE FORMATION OF TRITHIOCARBONATE, DISELENOTHIOCARBONATE AND TRISELENOCARBONATE COMPLEXES OF PENTACARBONYLCHROMIUM(0) FROM ONE OF THE PRODUCTS CONTAINING COORDINATED *N,N*-DIMETHYLTHIOFORMAMIDE

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Summary

Three unexpected products are formed in the title reaction. One of them, $[Cr(CO)_5\{SC(NMe_2)SC(S)NMe_2\}]$, is produced by formal S insertion into a metal—carbene bond. Another product, $[Cr(CO)_5(SCHNMe_2)]$, can be used for the preparation of the thio- and seleno-carbonate complexes. An X-ray crystal structure determination of the third product, $[Cr(CO)_5\{SC(NMe_2)SC(O)NMe_2\}]$, indicates the participation of water (absorbed on commercial SiO_2) in one of the transformations.

The study of thione derivatives of transition metals has provided interesting new reactions and complexes [1—3]. Hitherto, however, no studies involving reactions between Group VI metals in zero oxidation states and carbamoyl derivatives have been described. We now report some of the unusual reactions observed in such a study, and also a new entry into the field of the rare trithiocarbonate [4], diselenothiocarbonate and triselenocarbonate complexes of chromium(0).

Reaction of dimethylthiocarbamoyl chloride with $[Cr(CO)_5(thf)]$ in tetrahydrofuran (thf), followed by column chromatography (undried SiO_2 ; CH_2Cl_2 hexane, 1/1; —10°C), and recrystallization (ether hexane, —30°C) produced the crystalline complexes (1) (yellow, 17%, m.p. 69°C), (2) (orange, 9%, m.p. 99°C) and (3) (orange, 13%, m.p. 86°C) (Scheme 1). Complex 1 was also obtained (53%) by irradiating $[Cr(CO)_6]$ with *N,N*-dimethylthioformamide (Scheme 1). The proposed structures of the new compounds are based on elemental analy-

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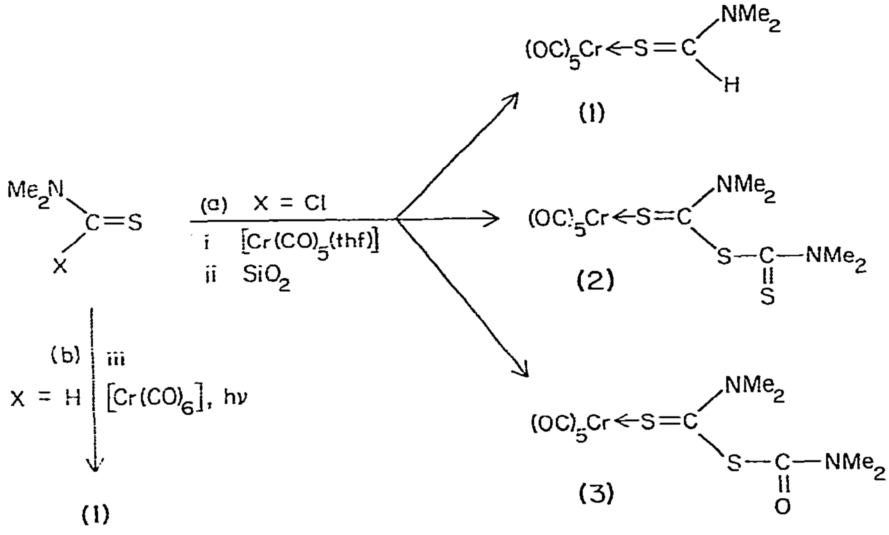
ses, mass spectroscopic molecular mass measurements, spectroscopic (IR, ^{1}H NMR) data, and a single-crystal X-ray diffraction study in the case of compound 3. The yields of the new complexes were not optimised.



SCHEME 1. Reagents: i, [Cr(CO)$_5$(thf)]; ii, SiO$_2$; iii, [Cr(CO)$_6$], *hν*.

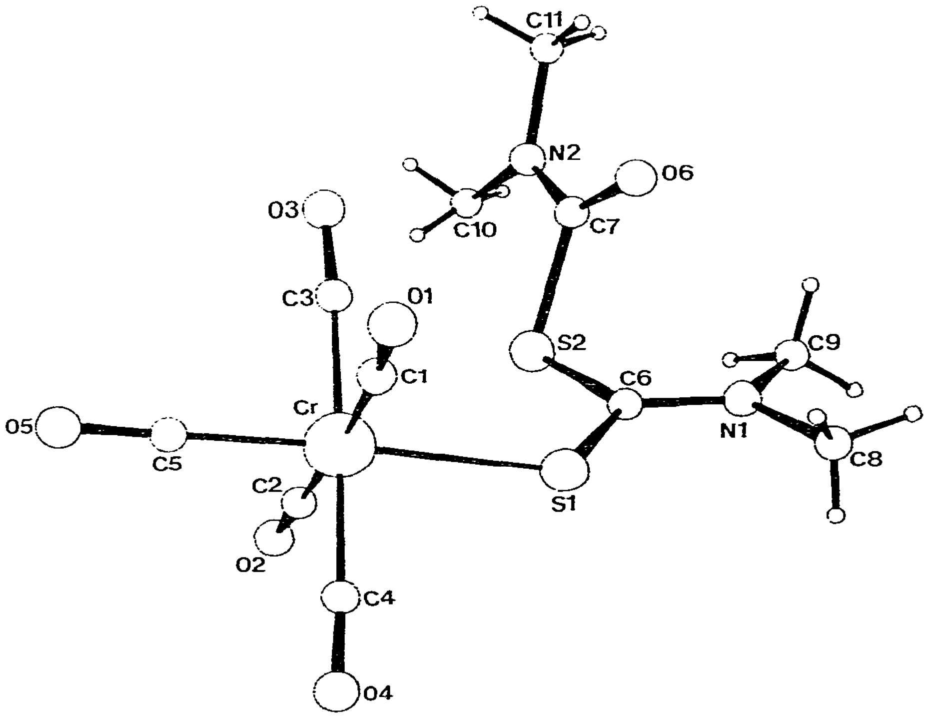


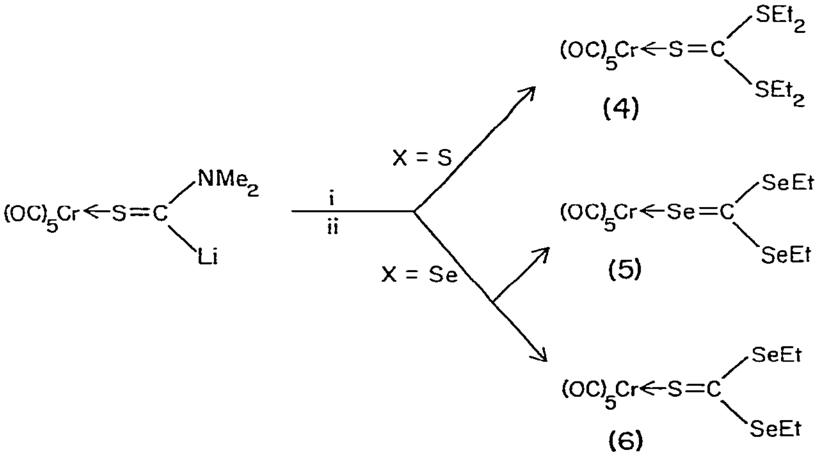
Fig. 1. The structure of [Cr(CO)$_5${SC(NMe$_2$)SC(O)NMe$_2$}] (3). Selected bond lengths (Å); Cr—S(1) 2.449(1), S(1)—C(6) 1.686(3), C(6)—S(2) 1.773(3), Cr—C(1) 1.902(3), Cr—C(2) 1.902(3), Cr—C(3) 1.919(3), Cr—C(4) 1.886(3), Cr—C(5) 1.844(4).

Crystal data: $C_{11}H_{12}CrN_2O_6S_2$ (3), $M = 384.31$, triclinic, a 13.76(2), b 9.15(1), c 6.75(1) Å, α 85.0(1), β 95.7(1), γ 105.7(1)°; D_m 1.57 g cm^{-3}; $Z = 2$; μ(Mo-K_α) 9.15 cm^{-1}; 2256 independent reflections with $\theta < 23$, 33 unobserved. The atomic coordinates for this work are available on request from the authors (G.J.K.).

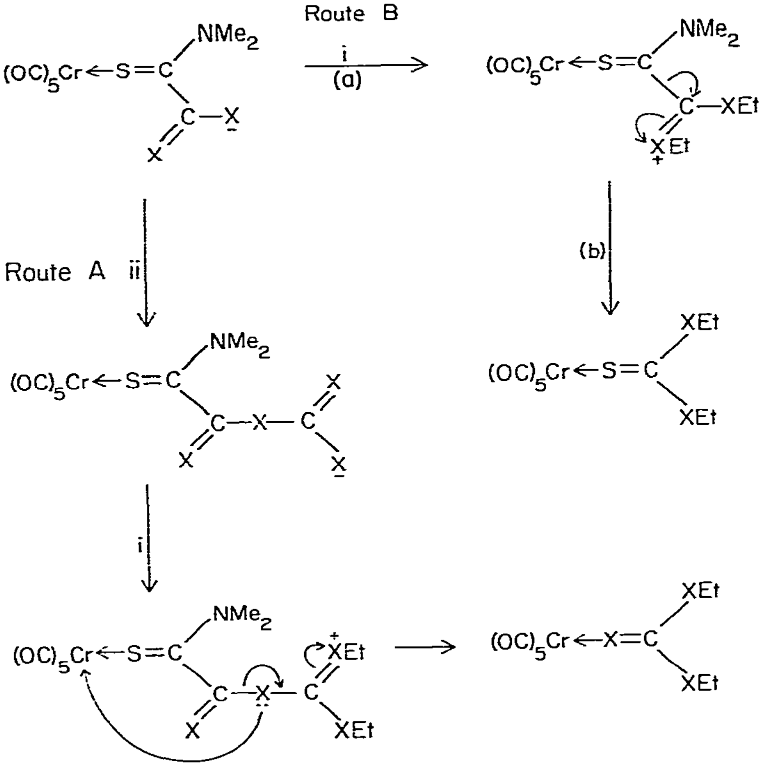
The structure was solved by Patterson methods. Full matrix least squares refinement of the trial parameters, with individual anisotropic thermal parameters for all the atoms except hydrogen, and isotropic thermal parameters for hydrogen, converged at R and R_w values of 0.044 and 0.032, respectively. The structure is shown in Fig. 1 and some bond lengths are given in the caption. The Cr—S bond length (2.449(1) Å) is significantly longer than in some other previously reported thione—chromium(0) linkages, e.g. in a trisubstituted chromium carbonyl complex (average 2.330 Å) [5] and in $[Cr(CO)_5SCMe_2]$ (2.377 Å) [6].

The formation of compound **1** via synthetic route (a) was unexpected. An ionic mechanism, in which chloronium ions replace protons on the (acidic) SiO_2, used for column chromatography, is possible. The formation of compound **2** is comparable to the three-fragment oxidative addition process postulated for the reaction of imidoyl chlorides with chlororhodium complexes [7]. The present reaction however, does not involve chloride coordination to the metal, but is accompanied by a formal sulphur atom insertion into the metal—carbene bond of the intermediately formed complex. The carbamoyl oxygen atom in compound **3** comes from water absorbed on the commerical SiO_2.

Reaction of **1** with lithium diisopropylamide and CS_2 or CSe_2, followed by alkylation with $[OEt_3][BF_4]$, yielded compounds **4** (red needles, 21%, m.p. 44°C), (**5**) (red-purple plates, 5%, m.p. 51°C), and (**6**) (red needles, 2%, m.p. 55°C) respectively, as depicted in Scheme 2. The low yields are due to the formation of several products in each preparation. (The other compounds were present in even lower concentrations and were not isolated.) As a working hypothesis, we suggest that these remarkable transformations are initiated by electrophilic attack of CX_2 (X = S, Se) on coordinated S=C(Li)NMe$_2$ to form



SCHEME 2. Reagents: i, CX_2, ii, $[OEt_3][BF_4]$.



SCHEME 3. Reagents: i, $[OEt_3][BF_4]$; ii, CX_2 (X = S, Se).

$[Cr(CO)_5\{S{=}C(NMe_2)C(X)X\}]^-$ Li^+. The formation of the products can then be further rationalized in terms of two alternative pathways (Scheme 3). Compound 4 can be formed by both routes, whereas route A is the pathway for 5 and route B for 6. Step (b) in Route B is a complicated transformation involving formal extrusion of $CNMe_2^+$. There is still no direct evidence for any of the intermediates. We have established, however, that compounds 4 and 5 are also formed from $[Cr(CO)_5\{SC(SEt)CH_2Li\}]$ and $[Cr(CO)_5\{C(Ph)NHLi\}]$ when they were respectively treated with CS_2 and CSe_2 prior to alkylation with $[Et_3O][BF_4]$. Although it is known that CS_2 reacts with RS^- [8], we have found no precedent for the coupling of two CX_2 molecules in the manner indicated by route A.

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