Journal of Organometallic Chemistry, 336 (1987) 349–360
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Reactions of deprotonated sulphur-donor complexes of pentacarbonylchromium(0) with carbon disulphide or carbon diselenide

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(Received May 27th, 1987)

Abstract

The adduct between the α-thio carbanion $[Cr(CO)_5\{\overline{S(CH_2)_3SC}H\}]^-$ and CS_2 was alkylated with $[Et_3O][BF_4]$ to produce the chelate *fac*-$[\underline{Cr(CO)_3}$-$(\{\overline{S[CH_2]_3SC}(C[S]SEt)_2\}]$ (I) by 2,2-dithiocarboxylation. Treated in similar manner $[Cr(CO)_5\{S{=}CNMe_2\}]^-$ afforded a trithiocarbonate complex, $[Cr(CO)_5\{S{=}C(SEt)_2\}]$ (VIII). The β-thio deprotonated complex $[Cr(CO)_5\{S{=}C(SEt)CH_2\}]^-$ also reacted with CS_2, and alkylation afforded the three thione complexes $[Cr(CO)_5\{S{=}C(Me)CH{=}C(SEt)_2\}]$ (X), $[Cr(CO)_5\{S{=}C(SEt)_2\}]$ (VIII), and $[Cr(CO)_5\{S{=}C(SEt)CH{=}C(SEt)_2\}]$ (XII). CSe_2 is less selective in its reactions with all three coordinated carbanions and the diethyltriselenocarbonate complex $[Cr(CO)_5\{Se{=}C(SeEt)_2\}]$ (II) was isolated upon further alkylation. The product from uncoordinated deprotonated 1,3-dithiane and CS_2 was trapped by $[Ti(\eta\text{-}Cp)_2Cl_2]$ (Cp = cyclopentadienyl) to give the four-membered chelate $[Ti(\eta^5\text{-}Cp)_2\{S_2C{=}C(SR^1)SR^2\}]$ ($R^1R^2 = (CH_2)_3$ (III) or $R^1 = R^2 = Ph$ (IV)). During the preparation of the precursor $[Cr(CO)_5\{S{=}CHNMe_2\}]$ (V) from $[Cr(CO)_5\{S{=}C(Cl)NMe_2\}]$ by decomposition on SiO_2, ligand dimerization led to two other thiocarbonyl complexes, viz. $[Cr(CO)_5\{S{=}C(NMe_2)SC(X)NMe_2\}]$ (X = S (VI) or X = O (VII)).

Introduction

Although many transition-metal complexes with sulphur-donor ligands are known, few reactions of the coordinated ligands have been reported [1]. Group 6 metal carbonyl complexes containing thiocarbonyl ligands are still fairly rare. The chro-

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0022-328X/87/$03.50

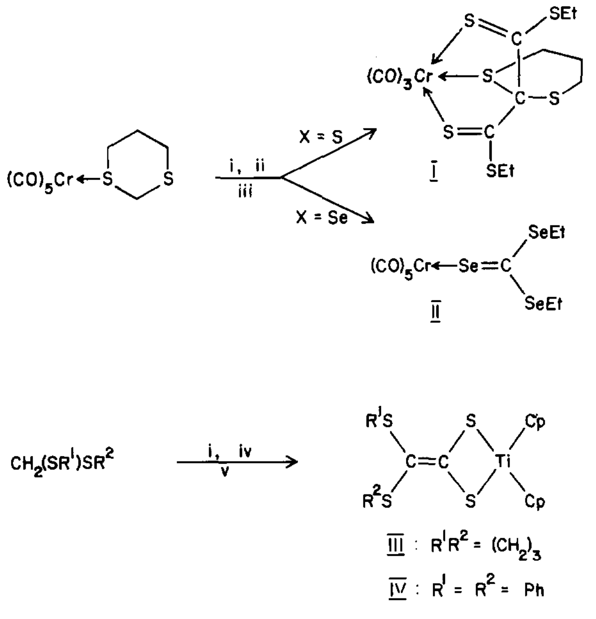
mium complexes $[\mathrm{Cr(CO)_5\{S{=}\overline{CNH(CH_2)_2S}\}}]$ [2], $[\mathrm{Cr(CO)_5\{S{=}\overline{CO(CMe_2)_2O}\}}]$ [3] and $[\mathrm{Cr(CO)_5\{S{=}C(X)Y\}}]$ (X = Y = SPh, OPh, NHPh, Cl and X = SPh or OPh; Y = NHPh or Cl) [4] are formed by substituting the weakly coordinated tetrahydrofuran (THF) in $[\mathrm{Cr(CO)_5(THF)}]$ with the appropriate thione. The thioketone complex $[\mathrm{Cr(CO)_5\{S{=}CMe_2\}}]$ may be made by reaction of $[\mathrm{Cr(CO)_5}]^-$ with $\mathrm{O{=}CMe_2}$ and $\mathrm{H_2S}$ in the presence of silver ions [5]. Recently we reported the formation of the complexes $[\mathrm{Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}}]$ [6] and $[\mathrm{Cr(CO)_5\{S{=}C(Aryl)CH{=}C(Me)NHCHMe_2\}}]$ (Aryl = Ph or $\mathrm{C_6H_4Ph}$) [7] by novel routes.

As part of our continuing research on the reactivity of coordinated sulphur-donor ligands [8,9], we now report on the preparation and characterization of new thione and selone complexes of substituted chromium carbonyl. They were synthesized by (a) reaction of $\mathrm{CS_2}$ or $\mathrm{CSe_2}$ with an α-lithiated sulphide complex followed by alkylation of the ionic product, (b) THF substitution in $[\mathrm{Cr(CO)_5(THF)}]$, (c) reaction of $\mathrm{CS_2}$ or $\mathrm{CSe_2}$ with α- or β-deprotonated thione complexes followed by alkylation, and (d) decomposition of $[\mathrm{Cr(CO)_5\{S{=}C(Cl)NMe_2\}}]$ on commercial silica gel. Some of these results have been reported in preliminary communications [10].

Results and discussion

Formation of the new compounds

To avoid the double internal carbonylation which occurs at −60 °C [8], the complex $[\mathrm{Cr(CO)_5\{\overline{S(CH_2)_3SCH_2}\}}]$ was deprotonated with an excess of BuLi at −100 °C and then treated with an excess of $\mathrm{CS_2}$. Alkylation of the product in water with $[\mathrm{Et_3O}][\mathrm{BF_4}]$ produced compound I (Scheme 1). The formation of I is very unusual, since deprotonated difunctional CH acids are normally converted into



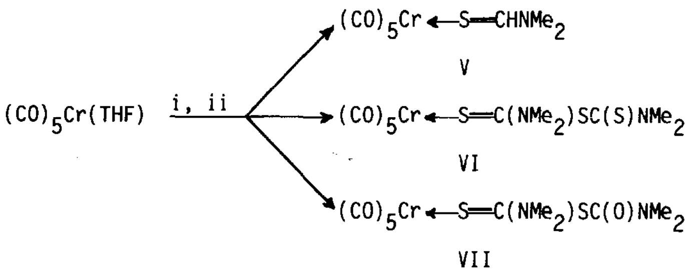
Scheme 1. Reagents: (i) LiBu; (ii) $\mathrm{CX_2}$; (iii) $[\mathrm{Et_3O}][\mathrm{BF_4}]$; (iv) $\mathrm{CS_2}$; (v) $\mathrm{TiCp_2Cl_2}$.

1,1-dithiols or 1,1-dithioethers on treatment with CS_2 followed by protonation or alkylation of the product [11]. When treated in the same manner, uncoordinated 1,3-dithiane gave a series of low-yield products which were not isolated. When deprotonated 1,3-dithiane was treated with an excess of CS_2 in the presence of BuLi and the mixture then added to $[TiCp_2Cl_2]$, a stable purple product (III) (Scheme 1) was formed. Similarly, compound IV, another member of this new class of compounds containing a dithioketene function and a $\overline{C(sp^2)\text{–}S\text{–}Ti^{IV}\text{–}S}$ ring system, was obtained when the procedure was repeated with $PhSCH_2SPh$. From these results we concluded that the unique dithiocarboxylation which occurred during the formation of I, and which was not observed with any other pentacarbonyl thioether complex, is due to the template function of the central chromium atom. We previously speculated that alkene formation during the synthesis of I is probably inhibited and dithiocarboxylation enhanced by bicovalent sulphur coordination after addition of the first CS_2 unit [10a]. No further evidence for such an assumption was found. When, for example, an excess of CS_2 is added to the carbene anion $[Cr(CO)_5\{C(OEt)CH_2\}]^-$ and the adduct then alkylated, the products contain only sulphide sulphur-donor atoms, although intermediate thiocarbonyl coordination is possible [12]. When the reactant CS_2 was replaced by CSe_2, the triselenocarbonate complex $[Cr(CO)_5\{Se{=}C(SeEt)_2\}]$ (II) (Scheme 1) was formed by another pathway. This complex also is formed when carbene anions are treated successively with CSe_2 and $[Et_3O][BF_4]$; a mechanism which accounts for its formation, involving the coupling of two CSe_2 units, which is also applicable to the present reaction and others described later, has been proposed [12].

In principle a trisubstituted sulphur-donor complex belonging to the same class as I could be formed by deprotonation of the complex $[Cr(CO)_5\{S{=}C(SPh)\text{-}\overline{CHS(CH_2)_3S}\}]$ followed by electrophilic addition of one molar equivalent of CS_2 and alkylation of the adduct. During the attempted synthesis of the dithioester precursor from $[Cr(CO)_5\{S{=}C(Cl)SPh\}]$ [4] and $Li\overline{CHS(CH_2)_3S}$, the dark red mixture obtained was subjected to column chromatography at −10 °C. Visible decomposition occurred on silica gel, and gave the orange $[Cr(CO)_5\{S{=}C(SPh)_2\}]$ (46% yield), which is also formed by decomposition of the starting material, $[Cr(CO)_5\{S{=}C(Cl)SPh\}]$, on SiO_2 [4].

The complex $[Cr(CO)_5\{S{=}C(Cl)NMe_2\}]$, needed to prepare another possible precursor for inducing trisubstitution in the manner described above, has never been isolated. An attempt to make it by reaction of $[Cr(CO)_5(THF)]$ with $S{=}C(Cl)NMe_2$ followed by chromatographic work-up gave instead the three carbamoyl complexes V, VI, and VII as shown in Scheme 2. The formation of VI and VII is complex, and involves C–S coupling of two ligands with formal elimination of chlorine as well as either sulphurization or oxygen oxidation of an intermediately-formed carbene carbon atom. These reactions were not observed when the silica gel was dried for 5 h at 200 °C and saturated with nitrogen before use. Compound V was prepared in much higher yield (53 vs. 17%) by direct replacement of THF in the complex $[Cr(CO)_5(THF)]$ by $S{=}CHNMe_2$. The crystal structure of VII has been reported [10b].

Seebach and co-workers [13] have shown that $S{=}CHNMe_2$ can be deprotonated α to the sulphur atom. Deprotonation of complex V with lithium diisopropylamide (LDA) at − 100 °C, followed by addition of an excess of CS_2 and, then, alkylation with $[Et_3O][BF_4]$ in CH_2Cl_2, produced the trithiocarbonate complex VIII (Scheme

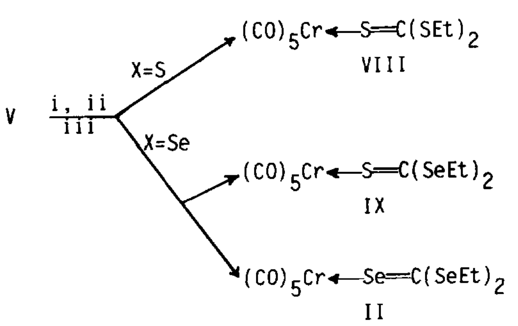


Scheme 2. Reagents: (i) S=C(NMe$_2$)Cl; (ii) SiO$_2$.

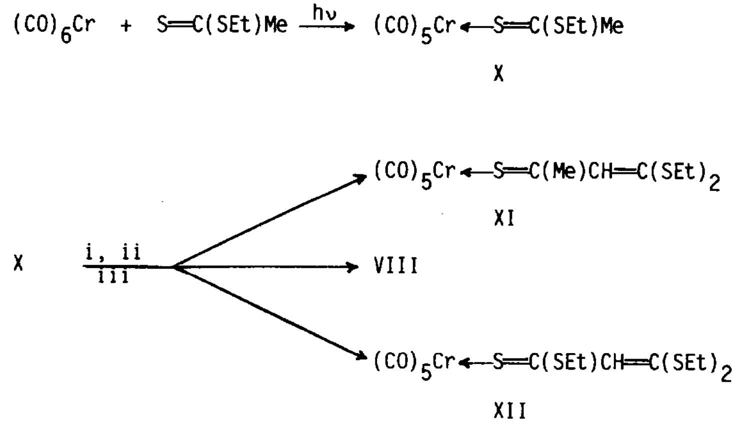
3). A similar sequence starting from CSe$_2$ gave the crystalline S-coordinated diselenothiocarbonate complex IX and the previously mentioned triselenocarbonate compound II. No reaction was observed between the electrophilic reagents Cl$\overline{\mathrm{CHS(CH_2)_3S}}$, MeI or O=CHPh and deprotonated V.

It is known that the ion CS$_3{}^{2-}$ is formed from CS$_2$ in the presence of base [14]. [Mn(CO)$_5$]$^-$ reacts with CS$_2$ in THF to give the manganese trithiocarbonate anion [Mn(CO)$_4$(S$_2$C=S)]$^{2-}$ [15], and Fortune and Manning [16] have reported the formation of [Co(η^5-Cp)(PR$_3$)(CS$_3$)] from [Co(η^5-Cp)(PR$_3$)(CO)] and CS$_2$. As mentioned above, we have proposed an explanation for the formation of triselenocarbonate complexes from coordinated carbanions upon successive treatment with CSe$_2$ and [Et$_3$O][BF$_4$]. This mechanism is also applicable to the formation of the thione VIII observed in the present work. Formation of the very low yield product IX has not previously been observed.

Complexes between dithioesters and metals have been studied extensively [17], but no such complex of chromium(0) is known, and very few reactions of the known complexes have been described. Three different modes of reaction between the deprotonated complex [Cr(CO)$_5${S=C(SEt)Me}] (X) and CS$_2$ which give rise to the intensely coloured compounds XI, VIII and XII, are shown in Scheme 4. Formation of the minor product VIII again probably involves the coupling of two CS$_2$ units, as discussed above. A ketene thioacetal similar to the large ligand in the major product XII is formed when the same sequence of reactions is carried out with the uncoordinated dithioester S=C(Me)SEt [18]. A similar type of reaction also occurs upon treatment of the carbene anion [Cr(CO)$_5${C(OEt)CH$_2$}]$^-$ with CS$_2$ and then [Et$_3$O][BF$_4$] [12].



Scheme 3. Reagents: (i) LDA; (ii) CX$_2$ (X = S or Se); (iii) [Et$_3$O][BF$_4$].



Scheme 4. Reagents. (i) LDA; (ii) CS_2; (iii) $[Et_3O][BF_4]$.

Table 1

Physical and analytical data for the chromium(0) and titanium(IV) complexes

Complex	Yield [a] (%)	Colour	M.p. (°C)	Analysis (Found (calc) (%))		
				C	H	Other
I $[Cr(CO)_3\{S[CH_2]_3SC(C[S]SEt)_2\}]$	24	purple	150–151	33.70 (33.60)	3.60 (3.50)	11.25(Cr) (11.20)
II $[Cr(CO)_5(Se{=}C(SeEt)_2\}]$	20 [b] 25 [c] 30 [d]	red	52–53	24.15 (24.05)	1.95 (2.00)	47.90(Se) (47.45)
III $[Ti(\eta^5\text{-}Cp)_2\{S_2C{=}CS(CH_2)_3S]$	52 [e]	purple	[f]	51.70 (51.30)	5.30 (5.45)	
IV $[Ti(\eta^5\text{-}Cp)_2\{S_2C{=}C(SPh)_2\}]$	48 [e]	purple	[f]	60.60 (60.40)	5.30 (5.10)	8.70(Ti) (8.60)
V $[Cr(CO)_5\{S{=}CHNMe_2\}]$	17 [g] 53 [h]	yellow	69–70	34.10 (34.15)	2.50 (2.50)	4.80(N) (4.95)
VI $[Cr(CO)_5\{S{=}C(NMe_2)SC(S)NMe_2\}]$	29	orange	99–100	32.80 (33.00)	3.05 (3.00)	6.85(N) (7.00)
VII $[Cr(CO)_5\{S{=}C(NMe_2)SC(O)NMe_2\}]$	27	yellow	86–87	34.40 (34.40)	3.00 (3.15)	7.25(N) (7.30)
VIII $[Cr(CO)_5\{S{=}C(SEt)_2\}]$	26 [c] 7 [i]	red	44–45	33.60 (33.50)	2.80 (2.80)	26.65(S) (26.85)
IX $[Cr(CO)_5\{S{=}C(SeEt)_2\}]$	3	orange	55–56	26.60 (26.55)	2.30 (2.25)	7.75(S) (7.10)
X $\{Cr(CO)_5\{S{=}C(SEt)Me\}]$	58	orange	oil	35.00 (34.60)	2.80 (2.60)	20.05(S) (20.50)
XI $[Cr(CO)_5\{S{=}C(Me)CH{=}C(SEt)_2\}]$	12	purple	[f]	39.00 (39.20)	3.45 (3.55)	24.40(S) (24.15)
XII $[Cr(CO)_5\{S{=}C(SEt)CH{=}C(SEt)_2\}]$	29	blue	53.54	37.80 (37.90)	3.80 (3.40)	28.65(S) (28.85)

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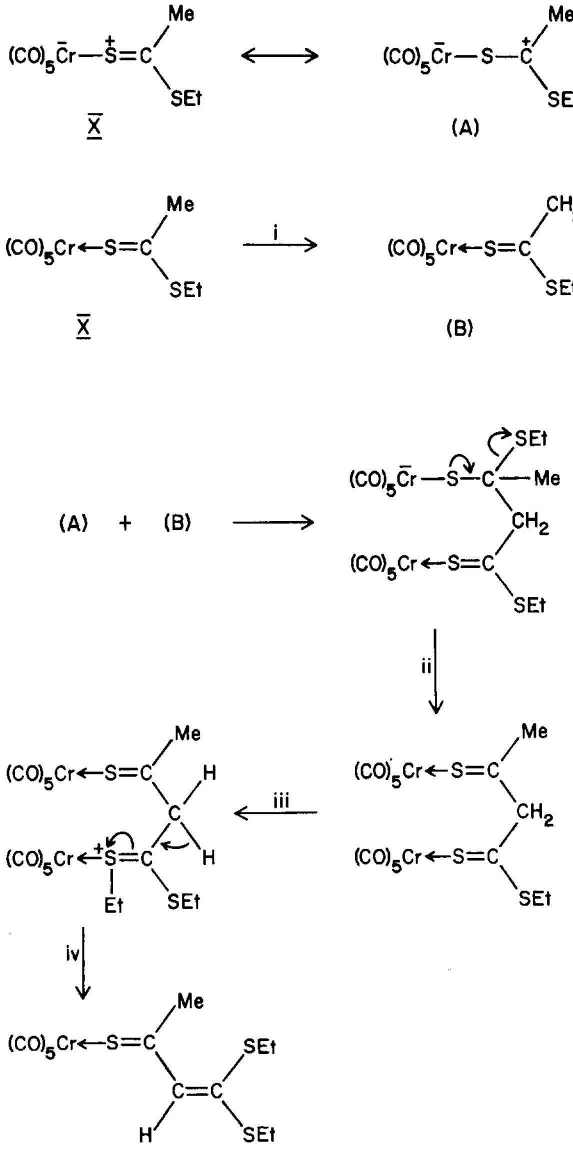
[a] Yields (not optimized) are based on limiting reagent when occurring or else on the starting metal complex. [b] Prepared from $[Cr(CO)_5\{S(CH_2)_3SCHLi\}]$. [c] Prepared from $[Cr(CO)_5(S{=}C(Li)NMe_2\}]$. [d] Prepared from $[Cr(CO)_5\{S{=}C(SEt)CH_2Li\}]$. [e] Crystallized with one molecule THF for analysis. [f] Decomposed slowly. [g] Prepared from $[Cr(CO)_5\{S{=}C(Cl)NMe_2\}]$. [h] Prepared from $[Cr(CO)_5(THF)]$. [i] Prepared from $[Cr(CO)_5\{S{=}C(SEt)CH_2Li\}]$.



Scheme 5. Rationalization of the formation of compound XI. The notations Cr ← S and $\bar{\mathrm{Cr}}$–$\overset{+}{\mathrm{S}}$ are used alternatively for the chromium–sulphur bond. (i) LiBu; (ii) $-\mathrm{SEt}^-$; (iii) $[\mathrm{Et_3O}][\mathrm{BF_4}]$; (iv) $-\mathrm{H}^+$, $-\mathrm{Cr(CO)_5}$.

The formation of the α,β-unsaturated thione complex XI, which may formally be described as involving a CHCSEt insertion into a single C–S bond of the starting compound, probably does not involve interaction with carbon disulphide. The reaction may be accounted for in terms of an initial Claisen-type condensation with SEt as the leaving group, followed by proton loss on alkylation (Scheme 5). When $\mathrm{CSe_2}$ was used instead of $\mathrm{CS_2}$, compound II was isolated in 28% yield.

We have now investigated the reaction of $\mathrm{CX_2}$ (X = S or Se) with five completely different coordinated anions [12]. From the results obtained it follows that $\mathrm{CS_2}$

Table 2

Spectroscopic data for the new compounds

Complex	ν(CO) (cm^{-1})				^{1}H NMR (δ, ppm)
I	1980s	1913s	1898s		1.52 (t, 6H, CH_3), 2.30 (m, 2H, SCH_2CH_2), 2.70–3.30 (m, 10H, SCH_2)
II	2064m	1985w	1947s	1932m(sh)	1.65 (t, 3H, CH_3), 3.57 (q, 2H, CH_2)
V	2061	1974	1930	1908	3.28 (s, 3H, CH_3), 3.38 (s, 3H, CH_3)
VI	2060	1977	1933	1908	3.46 (s, 6H, 2×CH_3), 3.61 (s, 6H, 2×CH_3)
VII	2060	1975	1933	1907	3.05 (s, 6H, $C(O)N(CH_3)_2$), 3.60 (s, 6H, $CN(CH_3)_2$)
VIII	2066	1980	1947	1925	1.42 (t, 6H, CH_3), 3.30 (q, 4H, CH_2)
IX	2063	1984	1949	1932	1.62 (t, 6H, CH_3), 3.53 (q, 4H, CH_2)
X	2070	1987	1949	1920	1.43 (t, 3H, CH_2CH_3), 2.93 (s, 3H, $SCCH_3$), 3.31 (q, 2H, SCH_2)
XI	2060	1981	1940	1927	1.17–1.58 (m, 6H, CH_2CH_3), 2.37 (s, 3H, $SCCH_3$), 2.74–3.51 (m, 4H, SCH_2), 6.54 (s, 1H, =CH)
XII	2065	1987	1945	1920	1.15–1.63 (m, 9H, CH_3), 2.86–3.44 (m, 6H, CH_2), 6.92 (s, 1H, =CH)

[a] Measured in hexane. [b] Measured in CD_3Cl relative to internal $SiMe_4$. [c] Uncoordinated CO: 1688 cm^{-1}.

reacts by various and sometimes complicated pathways, whereas CSe_2 shows practically no selectivity, and the triselenocarbonate complex II is always formed as the major neutral product upon alkylation of the initially formed adduct.

Spectroscopic characterization of the new compounds

All the new compounds described were characterized by elemental analysis and spectroscopy. The relevant data are listed in Tables 1 and 2.

Infrared data confirm the formulation of the tricarbonyl complex I, showing three strong terminal CO stretching bands (2A′ + A″) for the pseudo-C_s local symmetry of the $Cr(CO)_3$ frame at 1980, 1913 and 1898 cm^{-1}. These values are much higher than those for the trisubstituted complex *fac*-$[Cr(CO)_3(CNCMe_3)\{C(OEt)C(OEt)=C(SPh)Ph\}]$ (1958, 1909, and 1860 cm^{-1}) [19] which contains isocyanide, carbene, and sulphide donor groups, and also higher than those (1924 and 1818 cm^{-1}) reported for *fac*-$[Cr(CO)_3PMe\{[CH_2]_2PMe_2\}\{[CH_2]_2PMe_2\}]$ [20]. Clearly an extremely small net transfer of negative charge from the tridentate ligand occurs to the $Cr(CO)_3$ fragment in the new complex. The expected three CH_2CH_3 quartets in the ^{1}H NMR spectrum of compound I overlap with the SCH_2 multiplet resonances of the dithiane ring in the range 2.70–3.30 ppm and, consequently, no assignments are made here. The highest peak in the 60 eV mass spectrum of compound I ($m/z = 380$) corresponds to the $[M - 3CO]^+$ ion. Subsequent stepwise loss of three further CO groups occurs.

Except for compounds VI and VII, which gave highest peaks corresponding to the rearrangement ion $[Cr(CO)_6]^+$ and the fragment ion $[M - S]^+$, respectively, the pentacarbonyl complexes afforded molecular ions and showed the stepwise loss of all the carbonyl groups in their mass spectra.

The infrared spectra of the thione and selone complexes II and V–XII, exhibit the same intensity pattern in the carbonyl ligand stretching frequency region, i.e. a medium band ($A_1^{(1)}$) at 2060–2070 cm^{-1}, a weak one (B_1) at 1974–1987 cm^{-1}, a

Table 3

Calculated Cotton-Kraihanzel force constants for pentacarbonyl thione complexes [a]

Complex	k_1 [b]	k_2 (N m^{-1})	k_i
$[Cr(CO)_5(CO)]$ [a]	1649	1649	22
$[Cr(CO)_5(PPh_3)]$ [a]	1546	1588	31
$[Cr(CO)_5(SEt_2)]$ [c]	1539	1586	34
$[Cr(CO)_5\{S{=}C(SEt)SCH{=}CH_2\}]$ [d]	1525	1592	30
IX $[Cr(CO)_5\{S{=}C(SeEt)_2\}]$	1524	1590	28
II $[Cr(CO)_5\{Se{=}C(SeEt)_2\}]$	1524	1588	29
XI $[Cr(CO)_5\{S{=}C(Me)CH{=}C(SEt)_2\}]$	1518	1593	29
VIII $[Cr(CO)_5\{S{=}C(SEt)_2\}]$	1513	1590	29
X $[Cr(CO)_5\{S{=}C(SEt)Me\}]$	1505	1594	30
XII $[Cr(CO)_5\{S{=}C(SEt)CH{=}C(SEt)_2\}]$	1505	1587	30
$[Cr(CO)_5\{NH_2(C_6H_{11})\}]$ [e]	1505	1576	32
$[Cr(CO)_5\{S{=}C(Ph)CH{=}C(Me)NHCHMe_2\}]$ [f]	1495	1580	31
V $[Cr(CO)_5\{S{=}CHNMe_2\}]$	1488	1569	32
VI $[Cr(CO)_5\{S{=}C(NMe_2)SC(S)NMe_2\}]$	1487	1572	31
VII $[Cr(CO)_5\{S{=}C(NMe_2)SC(O)NMe_2\}]$	1486	1592	31

[a] Ref. 21. [b] k_1 and k_2 are the stretching parameters for CO *trans* to the thione ligand and to another CO respectively; k_i is the approximate averaged *cis* interaction parameter. [c] ν(CO)s from ref. 23. [d] Ref. 6. [e] W.A.G. Graham, Inorg. Chem., 7 (1968) 315. [f] Ref. 7.

strong absorption (E) at 1930–1949 cm^{-1}, and a medium shoulder ($A_1^{(2)}$) at 1907–1932 cm^{-1}. The uncoordinated carbonyl group of the ligand in compound VII gives a band at 1688 cm^{-1}. The force constants for the C–O bonds in the carbonyl ligands were calculated [21], and are compared with values for known pentacarbonyl complexes in Table 3. These results reveal that all the thione complexes (and the selone complex II) have smaller k_1 values, corresponding to the strengths of the C–O bonds *trans* to the thione ligands, than complexes in which these ligands are replaced by CO, PPh_3 or SEt_2, indicating more negative charge transfer to the metal by the former ligands. The spectrum and force constants for the dithioester complex X, which compare well with those for other pentacarbonyl thione complexes, clearly show that the presence of an S=C–SR function in a thione donor group is not a sufficient criterion for an exceptional *trans* influence such as that exhibited by the ligand in compound I. Of the thiones, the ligands containing the S=C–NMe_2 moiety have the highest σ(donor): π(acceptor) ratios, probably due to the electron donating ability of the amino group.

The expected number of resonances and correct relative intensities were observed in the proton ^1H NMR spectra of the pentacarbonyl thione complexes (Table 2). The methyl protons of the thioformamide ligand in complex V give two signals, at δ 3.28 and 3.38 ppm, indicating hindered rotation around the C(thione)–N bond. With this carbon atom also bound to another heteroatom, as in compounds VI and VII, only singlet resonances for these methyl groups appear (at ca. 6.39 ppm), and they are well separated from the singlets (at δ 3.46 and 3.05 ppm) assigned to the NMe_2 protons of the $SC(S)NMe_2$ and $SC(O)NMe_2$ functions respectively.

Structural characteristics of I

The X-ray structure of *fac*-tricarbonyl(diethyl-1,3-dithiane-2,2-bisdithiocarboxylate)chromium(0), which has been communicated previously [10a], shows the following important features for the octahedrally coordinated chromium complex: (i) a unique tridentate ligand which binds through one sulphide and two thione sulphur atoms; (ii) three very short Cr–S distances, which vary between 2.322(2) and 2.338(2) Å; (iii) relatively long Cr–C distances (av. 1.880 Å) *trans* to the C=S donor groups; and (iv) significant distortion of the S–C–S part of the dithiane ring, resulting, for example, in a C–S distance 0.038 Å shorter than another C–$\mathrm{S(CH_2)_3S}$ separation in this ring.

Very few trisubstituted sulphur-donor complexes of group 6 carbonyl complexes are known, and none of those reported contains coordinated thione-type sulphur atoms [22]. The present tridentate ligand forms one six-membered and two five-membered chelate rings with chromium. We have previously reported a value of 2.458(2) Å for the Cr–S bond length in the monosubstituted sulphide complex $\mathrm{[Cr(CO)_5(S(Et)CH_2Ph)]}$ [23] and values of 2.449(1) and 2.466(1) Å for the thiocarbamoyl derivative VII [10b] and for the unsaturated thioketone $\mathrm{[Cr(CO)_5\{S{=}C(C_6H_4Ph\text{-}\mathit{o})CH{=}C(Me)NHCHMe_2\}]}$ [7], respectively. The Cr–S distance contracts to 2.384(4) Å in a disubstituted complex, and to 2.365(2) Å in a trisubstituted carbonyl complex containing sulphide, carbene, and isonitrile donor groups [24]. All the chromium–sulphur distances in the present complex are still significantly shorter than these.

The very low σ(donor)/π(acceptor) bonding ratio of the ligand in I, reflected by the position of the CO frequencies in its infrared spectrum, is in full accord with the relatively long Cr–C bond lengths and especially those *trans* to the bicovalent sulphur atoms (av. 1.880 Å). Comparable values thus far reported for thione (carbonyl) complexes lie between 1.81 and 1.84 Å. Also, the C–O distance *trans* to the sulphide donor atom (1.182(7) Å) is markedly longer than the 1.151 Å (average) C–O separation *trans* to the thione donor groups.

Experimental

The general procedures and apparatus were the same as described in recent publications from this laboratory [7,8,12]. The silica gel (60 mesh, particle size 0.063–0.200 mm; Merck) for column chromatography (−10 °C) was not dried before use but only deoxygenated under vacuum and saturated with dry nitrogen. Physical and analytical data are presented in Tables 1 and 2. Although air and moisture sensitive, all the new compounds are thermally stable for some days in solution, and for months in the solid state.

Preparations: $[\mathrm{Cr(CO)_3\{\overline{S[CH_2]_3SC}(C[S]SEt)_2\}}]$ *(I)*

A solution of $[\mathrm{Cr(CO)_5(\overline{S(CH_2)_3SCH_2}\}}]$ [8] (3.1 g, 10 mmol) in 50 cm^3 THF was treated with 1.5 mol equiv. of LiBu (1.8 mol dm^{-3}, 27 cm^3) in hexane at −100 °C. As soon as the solution turned brown, an excess of $\mathrm{CS_2}$ (3.0 cm^3, 50 mmol) was added and the mixture left to attain room temperature. After removal of solvent under reduced pressure, the residue was dissolved in nitrogen-saturated water and alkylated with $\mathrm{[Et_3O][BF_4]}$ (pH 5). An ether extract of the product was dried over sodium sulphate and washed through $\mathrm{SiO_2}$. Column chromatography with hexane/$\mathrm{CH_2Cl_2}$ (1/1) as eluant afforded a solid purple compound which was recrystallized from diethyl ether/hexane (−30 °C) to give 1.2 g analytically pure crystals of compound I.

$[Cr(CO)_5\{Se{=}C(SeEt)_2\}]$ (II)

The procedure described above was used but with CSe_2 (Strem) in place of CS_2. After recrystallization 1.0 g of II was obtained in crystalline form.

$[Ti(\eta^5\text{-}Cp)_2\{S_2C{=}C(SR^1)SR^2\}]$ ($R^1R^2 = (CH_2)_3$ (III); $R^1 = R^2 = Ph$ (IV))

Both compounds were prepared similarly and only the preparation of III is given in detail. A solution of 1,3-dithiane (0.60 g, 5.0 mmol) in 20 cm^3 THF was deprotonated with an equimolar amount of LiBu (1.8 mol dm^{-3}, 2.7 cm^3) in hexane, CS_2 (0.3 cm^3, 5 mmol) was added, the solution stirred for 10 min, and the addition of LiBu and CS_2 was then repeated. After 11 h $[Ti(\eta\text{-}Cp)_2Cl_2]$ (1.2 g, 5.0 mmol) was added in portions during 30 min. The solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2, the solution filtered, and then transferred to a SiO_2-packed column. After elution of all low-yield products and starting material with hexane/CH_2Cl_2 (1/1), the major product still absorbed at the top of the column, was transferred to a glass frit and washed through with CH_2Cl_2. The solution was evaporated and the residue recrystallized from CH_2Cl_2 hexane to afford microcrystals (0.97 g) of the product, which were used for spectroscopic measurements. Analytically pure crystals were obtained by another recrystallization (at −30 °C) from THF/hexane. The recrystallization of IV was carried out at 0 °C.

$[Cr(CO)_5\{S{=}CHNMe_2\}]$ (V), $[Cr(CO)_5\{S{=}C(NMe_2)SC(S)NMe_2\}]$ (VI), and $[Cr(CO)_5\{S{=}C(NMe_2)SC(O)NMe_2\}]$ (VII)

Chromium hexacarbonyl (2.2 g, 10 mmol) in 100 cm^3 THF was irradiated with ultraviolet light for 2.5 h. A solution of dimethylthiocarbamoyl chloride (1.2 g, 10 mmol; Aldrich) in THF (50 cm^3) was added during 10 min with stirring to the orange solution, which turned yellow. The solvent was removed under reduced pressure, and the residue subjected to column chromatography. It turned dark yellow on the SiO_2. Unchanged $[Cr(CO)_6]$ was eluted with hexane and a light yellow zone with hexane/CH_2Cl_2 (10/1). An orange fraction was subsequently eluted with hexane/CH_2Cl_2 (2/1) and finally, with a 1/1 solvent mixture, a dark-yellow band was eluted. After removal of solvent, the three residues were separately dissolved in ether, hexane was added to each solution, and the products V (0.48 g), VI (0.36 g), and VII (0.48 g) crystallized out at −30 °C. Compound V was also prepared by ultraviolet irradiation of $[Cr(CO)_6]$ (2.2 g, 10 mmol) and dimethylthioformamide (0.86 cm^3, 10 mmol; Aldrich) in 100 cm^3 THF for 9 h. Column chromatography (hexane/CH_2Cl_2, 10/1) and recrystallization from diethyl ether/pentane (−30 °C) afforded yellow needles of the product (1.5 g).

$[Cr(CO)_5\{S{=}C(SEt)_2\}]$ (VIII), $[Cr(CO)_5\{S{=}C(SeEt)_2\}]$ (IX), and $[Cr(CO)_5\{Se{=}C(SeEt)_2\}]$ (II)

Diisopropylamine (0.70 cm^3, 5.0 mmol) in 15 cm^3 THF was treated at −78 °C with BuLi (1.8 mol dm^{-3}, 2.7 cm^3). After being stirred for 10 min the mixture was cooled to −100 °C and treated first with 1.41 g (5 mmol) V in 4 cm^3 THF. About 5 min later, CS_2 (0.42 cm^3, 7.0 mmol) was added, to give a dark brown solution. Removal of solvent under reduced pressure, alkylation with $[Et_3O][BF_4]$ at 0 °C in CH_2Cl_2, and column chromatography with hexane/CH_2Cl_2 (10/1) as eluant yielded a red powder, which was recrystallized from CH_2Cl_2/pentane (−30 °C) to give 0.33 g red needles of VIII. A similar procedure starting with 6.5 mmol diisopropylamine, an equimolar amount of V, and with 0.42 cm^3 (6.5 mmol) CSe_2 in place of CS_2, furnished two solid products after column chromatography (hexane/diethyl ether, 10/1). Recrystallization from diethyl ether/hexane (-30 ° C) gave 0.07 g orange needles of the less polar IX and red plates (0.40 g) of the more polar product II.

[Cr(CO)$_5${S=C(Me)SEt}] (X), [Cr(CO)$_5${S=C(Me)CH=C(SEt)$_2$}] (XI), [Cr(CO)$_5${S=C(SEt)$_2$}] (VIII), [Cr(CO)$_5${S=C(SEt)CH=C(SEt)$_2$}] (XII), and [Cr(CO)$_5${SeC(SeEt)$_2$}] (II)

Photochemical reaction of $[Cr(CO)_6]$ (2.2 g, 10 mmol) and dithioethyl acetate (0.80 cm^3, 10 mmol) produced a dark-red solution in THF. After irradiation (2.5 h) the product was purified by column chromatography (hexane/diethyl ether, 10/1). The red oil obtained after removal of solvent was precipitated three times from pentane (-30 ° C), the crystals were then washed at -80 ° C with the same solvent, and the solution obtained was evaporated in vacuo to give 1.8 g of the viscous product X in analytically pure form. Compound X (1.6 g, 5 mmol) was deprotonated with LDA (10 mmol) and converted into neutral products with CS_2 (10 mmol) and $[Et_3O][BF_4]$, as described above for V. The mixture of products obtained was separated by column chromatography with hexane/methylene chloride (3/1) as eluant. The first orange fraction contained starting material X, the second red-purple fraction afforded after recrystallization (ether/pentane, -30 ° C) fine crystals (0.24 g) of XI, the third fraction 0.14 g crystals of VIII, and the last, blue, fraction produced 0.65 g blue needles of XII. A similar procedure but with CSe_2 in place of CS_2, yielded 0.75 g of crystalline II.

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