Studies of Chelation. Part III.† Complexes of Chromium and Molybdenum Tetra- and Penta-carbonyls with *S*-Substituted 1,2-Dimercaptoethane Compounds. Electronic Influences on Chelate-ring Formation

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Complexes in the classes $[M(CO)_5L]$, $[\{(OC)_5M\}_2L]$, and $[M(CO)_4L]$ {M = Cr or Mo; L = $RSCH_2CH_2SR$, R = p-XC_6H_4 [X = NO_2 (nte), Cl(cte), H(pte), Me(tte), OMe(mte), and NMe_2(dte)] and CMe_3(bte)} have been prepared and characterised by i.r., mass, u.v.–visible, and n.m.r. spectroscopy and by analysis. The rate of chelate-ring formation increases with electron donation to the nucleophile and is subject to steric retardation, indicating an important associative contribution to the process. Comparison with analogous tertiary phosphine complexes shows that the stability and reactivity of the complexes is influenced both by the metal atom and the ligand-donor atom in a previously unrecognised manner. The aryl dithioether ligand is displaced from $[M(CO)_5L]$ complexes by ditertiary phosphines under mild conditions.

ALTHOUGH there is widespread and increasing interest in phosphorus-donor-ligand complexes of metals in low formal oxidation states,[1] this is not true of neutral sulphur donors,[2] despite demonstrations that the π-bonding ability of alkyl sulphides is similar to that of related phosphines.[3] There have been few reports of Group 6 metal carbonyl complexes of chelating sulphur-donor ligands,[3,4] although such ligands are readily available and offer certain easily recognisable advantages, such as decreased sensitivity to aerial oxidation, over their phosphorus analogues.

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† Part II, ref 15.

[1] 'Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973.

[2] M. Akbar Ali and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1974, **13**, 101.

[3] F. A. Cotton and F. Zingales, *Inorg. Chem.*, 1962, **1**, 145; H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 1962, 4454.

[4] G. R. Dobson, *Inorg. Chem.*, 1969, **8**, 90; G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, 1967, **1**, 287; G. R. Dobson and G. C. Faber, *ibid.*, 1970, **4**, 87; R. Ros, M. Vidali, and R. Graziani, *Gazzetta*, 1970, **100**, 407; M. Cannas, G. Carta, D. de Filippo, G. Marongiu, and E. F. Trogu, *Inorg. Chim. Acta*, 1974, **10**, 145.

We have prepared three series of chelating disecondary sulphide complexes of chromium and molybdenum in order to examine the influence of the donor atom and of electronic substituent effects on the chelation process in comparison with ditertiary phosphines.[5] The results indicate some hitherto unrecognised characteristics of sulphur-donor ligands of this type which may find application elsewhere.

RESULTS

The ligands were prepared in moderate to good yield from the corresponding thiols by reacting these with 1,2-dibromoethane in alcoholic alkali.[6,7] The dithioethers obtained in this manner are odourless, crystalline, air-stable solids, readily converted to the corresponding disulphoxides on treatment with H_2O_2 in glacial acetic acid at room temperature and, on longer treatment with the same reagents at 350—360 K, to the disulphones.[7,8]

Pentacarbonyl Complexes.—Metal : ligand = 1 : 1. The complexes were all prepared in good yield from the reaction between equimolar proportions of the salt $[Me_4N][M(CO)_5Br]$ (M = Cr or Mo), the ligand $RSCH_2CH_2SR$, and $[Et_3O][BF_4]$ in CH_2Cl_2 solution at room temperature.[9] Attempts to isolate the complexes of nte were unsuccessful, although the existence of $[Cr(CO)_5(nte)]$ could be inferred from i.r. spectroscopy.* Whereas the molybdenum complexes were readily isolated in analytically pure form, we were unable to obtain rigorously pure samples of the chromium series by crystallisation from solution, precipitation or sublimation, with the sole and probably fortuitous exception of $[Cr(CO)_5(cte)]$. Chromatography of the chromium complexes resulted in complete decomposition. These complexes were therefore characterised by spectroscopy alone.

Metal : ligand = 2 : 1. Although we were usually unable to isolate the 1 : 1 chromium complexes $[Cr(CO)_5L]$ in analytically pure form, the reaction product could be characterised by mixing equimolar proportions of the 1 : 1 complex, $[Me_4N][Cr(CO)_5Br]$, and $[Et_3O][BF_4]$ in CH_2Cl_2 solution to form the 2 : 1 complex $[\{(OC)_5Cr\}_2L]$. These same 2 : 1 complexes could be prepared directly from the Lewis-acid-assisted reaction between the dithioether ligand (1 mol) and $[Et_4N][Cr(CO)_5Br]$ (2 mol). Interestingly, when either procedure was applied to the analogous molybdenum system, we were unable to isolate any 2 : 1 complex from the reaction; instead the 1 : 1 complex $[Mo(CO)_5L]$ was isolated in high yield. All attempts to prepare complexes of the type $[\{(OC)_5Mo\}_2L]$ with any of the ligands used in this work were unsuccessful.

Pure samples of 2 : 1 chromium complexes of the complete range of ligands, including nte, were isolated. The 2 : 1 complexes are less soluble than their 1 : 1 analogues in common organic solvents and a good separation of the two is possible in hexane. The 2 : 1 complexes are quite stable in the solid state both in an inert atmosphere and, for short periods, in moist air but they decompose quite rapidly in solution.

Tetracarbonyl Complexes.—The complex $[Cr(CO)_4(bte)]$ was prepared by heating $Cr(CO)_6$ and bte in xylene.[4] This method failed when applied to mte and dte, the common product of the reaction being $[Cr(CO)_3(\eta\text{-xylene})]$. The complexes $[Cr(CO)_4(mte)]$ and $[Cr(CO)_4(dte)]$ were obtained from the reaction between $Cr(CO)_6$ and the ligand heated under reflux in ethanol in the presence of a small quantity of tetrahydroborate.[10] Attempts to prepare $[Cr(CO)_4L]$ complexes (L = nte, pte, tte, or cte) by this method were unsuccessful, although there was evidence from the i.r. spectra of the reaction mixture that $[Cr(CO)_4(tte)]$ and $[Cr(CO)_4(cte)]$ were formed, but decomposed in solution. In contrast to this, it was possible to prepare all the *cis*-$[Mo(CO)_4L]$ complexes, with the exception of L = nte, in good yields by Chatt's method.[10] The solid complexes are stable in dry air at room temperature for several days and in solution in an inert atmosphere.

Chelation of Pentacarbonyl Complexes.—This study was perforce restricted to the molybdenum complexes, $[Mo(CO)_5L]$, for the reasons indicated above. When these complexes were heated in hydrocarbon solution they were converted to the analogous chelated complexes, *cis*-$[Mo(CO)_4L]$, together with $Mo(CO)_6$ and the free ligand. A closer examination of this process, in which the chelation was monitored by i.r. spectrophotometry, both in the presence and absence of excess of ligand and carbon monoxide, showed that consumption of $[Mo(CO)_5L]$ was the result of competing reactions (1) and (2). In order to eliminate as far as possible the consumption of $[Mo(CO)_5L]$ by reaction (2), the kinetic studies were repeated in the presence of a large excess (*ca.* 20-fold) of the free ligand. The success of this procedure was indicated by the observation that the amount of $Mo(CO)_6$ produced was very small and remained effectively constant during the reaction under these conditions. First-order rate constants for reaction (1), measured for the chelation of a series of molybdenum complexes, are shown in Table 1. A Hammett plot [log (k/k_0) against σ_P] of these results gave a line of negative gradient ($\rho = -0{\cdot}25$), indicating that chelation is assisted by electron donation to the reaction site. The rate of chelation of bte was an order of magnitude less than that of pte.

$$[Mo(CO)_5L] \longrightarrow [Mo(CO)_4L] + CO \qquad (1)$$

$$[Mo(CO)_5L] \rightleftharpoons L + [Mo(CO)_5] \xrightarrow{CO} Mo(CO)_6 + L \qquad (2)$$

TABLE 1

Rate constants for the reaction $[Mo(CO)_5L] \longrightarrow$ *cis*-$[Mo(CO)_4L]$ + CO in n-nonane solutions at 357 K

L	$10^4k/s^{-1}$
pte	4·5 ± 0·1
tte	5·0
mte	5·4
dte	7·1
bte	0·4

Physical Properties.—I.r. spectra. Results for the series of mte complexes are given in Table 2 as a typical example of those obtained with other ligands of this type. Assign-

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* nte = 1,2-Di(*p*-nitrophenylthio)-, cte = 1,2-di(*p*-chlorophenylthio)-, pte = 1,2-diphenylthio-, tte = 1,2-di(*p*-tolylthio)-, mte = 1,2-di(*p*-methoxyphenylthio)-, dte = 1,2-di(*p*-dimethylaminophenylthio)-, and bte = 1,2-di(t-butylthio)-ethane.

[5] J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J.C.S. Dalton*, 1973, 347.

[6] E. Fromm, H. Benzinger, and F. Schäfer, *Annalen*, 1912, **394**, 325.

[7] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1928, 3189.

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[9] J. A. Connor, E. M. Jones, and G. K. McEwen, *J. Organometallic Chem.*, 1972, **43**, 357.

[10] J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometallic Chem.*, 1971, **29**, 105.

ments were straightforward on the basis of previous work.[11] For pentacarbonyl complexes, the *E* mode was usually observed as a doublet in hexane, but this was not resolved in CH_2Cl_2. The polarity of the solvent influences the A_1' mode in pentacarbonyl complexes and the B_1 mode in tetracarbonyl complexes, but has no significant effect on the other modes in either type. There was no significant substituent effect, produced by the *p*-substituent, on the carbonyl-stretching frequencies.

TABLE 2

I.r. spectra of $[\{(OC)_nM\}_x(mte)]$ (n = 4 or 5; x = 1 or 2) complexes in the 2 100—1 600 cm^{-1} region

M	*n*	*x*	Solvent	A_1''	B_1	*E*	A_1'
Cr	5	1	*a*	2 072m	1 987vw	1 948, 1 944vs	1 933s
			b	2 071m	1 987vw	1 943vs	1 920s
Mo	5	1	*a*	2 080m	1 986vw	1 956, 1 952vs	1 936s
			b	2 078m	1 987vw	1 946vs	1 917m
Cr	5	2	*a*	2 072m	1 989vw	1 951, 1 943vs	1 934s
			b	2 074m	1 983vw	1 947vs	1 924s
				A_1''	A_1'	B_2	B_1
Cr	4	1	*a*	2 021m	2 921vs	1 903vs	1 891s
			b	2 021m	1 912vs	1 899vs	1 867m
Mo	4	1	*a*	2 031m	1 926vs	1 912vs	1 897s
			b	2 028m	1 915vs	1 908vs	1 868s

[a] Hexane. [b] CH_2Cl_2.

Electronic spectra. Three main regions of absorption were usually observed at *ca.* 230, 255, and 420 nm. The band at *ca.* 255 nm (log ε *ca.* 4·5) is in the same region as the benzenoid (π–π*) transition of the ligand but clearly contains a component from the metal. This is indicated by the presence of a band in this region in the spectra of bte complexes. From the energy and intensity of the absorption, it is most probably a (L→M) charge-transfer transition. The band at *ca.* 420 nm (Table 3) is almost certainly to be assigned,[12] in the case of $[M(CO)_5L]$ complexes, to the (e→a_1) *d–d* transition. It has been argued [13] that the energy of this band, which has no counterpart in the spectrum of the free ligand, reflects the strength of the interaction between the ligand and the $M(CO)_5$ group. From our results it is clear that the substituents at sulphur cause extensive variation (Δλ *ca.* 50 nm) in the metal–ligand interaction.

TABLE 3

U.v.–visible spectra of $[\{(OC)_nM\}_xL]$ complexes in the region $\lambda_{max.}$ >350 nm, in absolute ethanol solution

M	Cr		Mo		Cr		Cr		Mo	
n	5		5		5		4		4	
x	1		1		2		1		1	
L	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε
bte	397	3·15	363	3·12	396	3·15	336	3·81	362	3·30
dte	396	3·03	402	3·01	412	3·00	400	2·86	375	2·80
mte	410	3·06	404	3·19	416	3·08	404	2·97	396	2·85
tte	415	2·84	403	3·27	415	3·16			384	2·99
pte	442	2·95	404	3·16	430	3·32			402	3·13
cte	434	3·16	405	3·26	437	3·00			397	3·02
nte					450	2·95				

^1H *N.m.r. spectra.* The values of the ^1H n.m.r. chemical shifts of the methylene protons in the free ligands, $\mathrm{RSC}H_2\mathrm{C}H_2\mathrm{SR}$, and in the complexes $[\{(OC)_nM\}_x(\mathrm{RSC}H_2\mathrm{C}H_2\mathrm{SR})]$ are given in Table 4. These results establish the unidentate character of the ligand in $[M(CO)_5L]$ complexes in that two methylene proton signals were observed. The more shifted of the two signals is assigned to that methylene group which is bound to the co-ordinated sulphur atom. This observation is in contrast to the analogous phosphorus complexes, $[M(CO)_5(R_2PCH_2CH_2PR_2)]$, where the methylene signals were not resolved, possibly as a consequence of *P–C–H* coupling. The bridging function of the ligand in $[\{(OC)_5Cr\}_2L]$ complexes is confirmed by the observation of only one methylene proton signal.

TABLE 4

^1H N.m.r. chemical shifts (δ/p.p.m.) for the methylene protons in $[\{(OC)_nM\}_xL]$ complexes in $CDCl_3$ solution

	M	Cr		Mo		Cr	Cr	Mo
	n	5		5		5	4	4
	x	1		1		2	1	1
L								
pte	3·02	3·14	3·03	3·08	3·04	3·11		3·18
tte	3·02	3·17	3·03	3·05	3·03	3·15		3·12
cte	3·03	3·10 [a]		3·09	3·03	3·10		3·16
mte	2·94	3·05	2·94	3·00	2·94	3·03	2·96	3·03
dte	2·90	3·11	3·01	3·00	2·96	3·02 [b]	2·96 [b]	2·98 [b]
bte	2·68	2·92	2·82	2·86	2·70	2·91	2·80	2·79

[a] Broad unresolved signal. [b] The CH_2 and $N\text{–}CH_3$ signals were not resolved.

Mass spectra. Considerable difficulty was experienced in obtaining mass spectra of the complexes reported here. Even at low source temperatures and low beam energies, electron impact caused fairly rapid decomposition to the free ligand and $M(CO)_6$. Notwithstanding these problems, we obtained satisfactory confirmatory evidence for the constitution and fragmentation of complexes containing bte, dte, and mte. The relative abundances of the ions in these spectra showed poor reproducibility but the fragmentation pattern for the different types of complex $[\{(OC)_nM\}_xL]$ is in agreement with expectation.[5] The spectra of the $[Mo(CO)_5L]$ complexes show that under electron impact process (3) occurs. This type of fragmentation was not observed in the analogous chromium system.

$$[Mo(CO)_5(RSCH_2CH_2SR)]^+ \longrightarrow [Mo(CO)_5(RSH)]^+ + RSCH{:}CH_2 \quad (3)$$

DISCUSSION

Extension of the Lewis-acid-assisted nucleophilic substitution reaction [9] to sulphur-donor ligands has

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[12] F. A. Cotton, W. T. Edwards, F. C. Rauch, M. A. Graham, R. N. Perutz, and J. J. Turner, *J. Co-ordination Chem.*, 1973, **2**, 247.

[13] R. N. Perutz and J. J. Turner, unpublished work.

given access to complexes of the type $[M(CO)_5L]$ and $[\{(OC)_5M\}_2L]$ ($L = RSCH_2CH_2SR$) which have not been prepared before. The particular advantage of these sulphur complexes is that they provide a neutral precursor for the synthesis of other $[M(CO)_5(\text{ligand})]$ complexes by displacement, *e.g.* equation (4). This

$$[Mo(CO)_5(cte)] + Me_2PCH_2CH_2PMe_2 \longrightarrow [Mo(CO)_5(dmpe)] + cte \quad (4)$$

exchange method is to be preferred to the Lewis-acid-assisted substitution of carbonylhalogenometallates [9] in cases where the nucleophile may be sensitive to acid, such as may be the case with olefins and alkynes. The displacement reaction is rapid and quantitative at room temperature and separation of the products is straightforward. The preparation of these sulphur-donor complexes also demonstrates the ability of aryl thioesters to function as ligands to chromium and molybdenum and, implicitly, to other metals which form complexes with arylphosphines. This application of aryl dithioethers has been largely overlooked in the past.[2,14]

The studies on chelation of disecondary sulphide ligands have shown the importance of electronic substituent effects in the ring-closure step. This has not been demonstrated experimentally in the past, so far as we are aware. The observations of steric hindrance (bte chelates more slowly than pte) and acceleration by electron donation (dte chelates more rapidly than pte) suggest that the associative contribution (I_a) to the chelation process is of relatively greater importance for sulphur-donor chelating ligands than for their phosphorus analogues. In the latter case, steric acceleration is observed,[15] which is consistent with a dominant dissociative (I_d) process in chelation. The distinction between phosphorus- and sulphur-donor ligands in the chelation process is further emphasised by the observation that the latter chelate more rapidly than the former. Thus, in the case of $[Mo(CO)_5(XCH_2CH_2X)]$ reacting to form *cis*-$[Mo(CO)_4(XCH_2CH_2X)]$, $k = 4{\cdot}5 \times 10^{-4}\ s^{-1}$ for X = PhS at 357 K and $2{\cdot}7 \times 10^{-5}\ s^{-1}$ for $X = Ph_2P$ at 362 K.

The results of this work show some interesting differences between analogous chromium and molybdenum complexes when viewed against the background of previous work on phosphorus-donor ligands. In general, molybdenum(0) shows a much greater affinity for neutral sulphur-donor ligands than does chromium(0). However, the bridged 2 : 1 complexes, $[\{(OC)_5Cr\}_2L]$, can be prepared with ease, whereas their molybdenum analogues could not be prepared.

EXPERIMENTAL

All preparations and reactions were carried out in an atmosphere of oxygen-free nitrogen. Solvents and liquid reagents were purified and dried in the usual manner and then carefully purged with nitrogen before use. The instrumentation and general procedures employed are those described in earlier papers.[5]

Ligands.—These were prepared from the corresponding thiol and fully characterised (analysis, and i.r., mass, n.m.r., and u.v.–visible spectroscopy) as: pte m.p. 69 (lit.,[7] 69), tte m.p. 79 (lit.,[7] 81), cte m.p. 94 (lit.,[16] 94), nte m.p. 125—128 (lit.,[6] 134), mte m.p. 98 (lit.,[17] 102), and bte b.p. 114—116 °C at 12 mmHg (lit.,[18] 114—116 °C at 124 mmHg). The ligand dte was obtained as follows. 4-Dimethylaminobenzenethiol [19] (1·89 g, 6·25 mmol) was slowly added to a vigorously stirred mixture of KOH (0·69 g, 6·25 mmol) and 1,2-dibromoethane (1·17 g, 6·25 mmol) in dry ethanol at 0 °C. As the reaction progressed a precipitate of KBr was formed and the yellow colour of the thiol was discharged. When addition of the thiol was complete the mixture was filtered and then concentrated by distillation under reduced pressure. The solution was set aside to crystallise at 0 °C. The product was recrystallised (EtOH) to give colourless crystals of 1,2-*di*(p-*dimethylaminophenylthio*)*ethane*, m.p. 134—135 °C (0·57 g, 1·73 mmol) (Found: C, 64·6; H, 7·2; N, 8·2; S, 19·4. $C_{18}H_{24}N_2S_2$ requires C, 65·0; H, 7·2; N, 8·4; S, 19·3%), $\nu_{max.}$ at 1 597, 1 510, 1 185, 1 165, 1 110, 1 100, 1 060, 810, 802, and 732 cm^{-1}, δ ($CDCl_3$) 2·82 (CH_3), 2·90 (CH_2), and 7·10 (C_6H_4) p.p.m., *m/e* (*I*/%) 332 (55, M^+), 304 (2), 180 (1), 166 (4), 152 (100), and 120 (1). The u.v. spectra of the pure ligands in ethanol showed the following features, $\lambda_{max.}$ (log ε): pte, 255 (4·38); tte, 257 (4·31); cte, 223 (4·36) and 262 (4·50); nte, 223 (4·07) and 338 (4·29); mte, 231 (4·42), 259 (4·33), and 282 (3·49); and dte, 277 (4·47) nm. The ligands were also characterised by conversion to the corresponding disulphoxides which were also fully characterised. For example, a solution of dte (0·3 g) in glacial acetic acid (20 cm^3) was treated with a solution of H_2O_2 (30 vol. %, 1·24 cm^3) in glacial acetic acid (10 cm^3). The mixture was stirred for 1 h at room temperature and then concentrated by distillation under reduced pressure. Addition of water (100 cm^{-3}) to the concentrate caused precipitation of the product, which was isolated by filtration, washed with water (4 × 5 cm^3), and dried *in vacuo* prior to recrystallisation from toluene which gave colourless crystals of 1,2-*di*-(p-*dimethylaminophenylsulphinyl*)*ethane*, m.p. 178—182 °C (Found: C, 58·8; H, 6·4; N, 7·4; S, 16·8. $C_{18}H_{24}N_2O_2S_2$ requires C, 59·4; H, 6·6; N, 7·7; S, 17·5%), $\nu_{max.}$ at 1 594, 1 513, 1 367, 1 090, and 1 032 cm^{-1}, δ ($CDCl_3$) 3·04 (CH_3,CH_2) and 7·11 (C_6H_4) p.p.m., *m/e* (*I*/%) 364 (2, M^+), 332 (6), 304 (5), 196 (12), 184 (25), 180 (20), 168 (39), 166 (8), 152 (100), and 120 (13), $\lambda_{max.}$ (log ε) 285 (4·71) nm (EtOH).

Complexes.—One example only will be given of the preparation of each type of complex, followed by relevant analytical and spectroscopic information for other complexes of that type made by the same method or insignificant variations thereof. Spectroscopic results refer to hexane (i.r.), ethanol (u.v.–visible), and $CDCl_3$ (n.m.r.) solutions. Other results are given in Tables 1—4.

Pentacarbonyl(1,2-*diphenylthioethane*)*molybdenum*,

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$[Mo(CO)_5(pte)]$. The ligand pte (0·67 g, 2·74 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added to a solution of $[Et_4N][Mo(CO)_5Br]$ (1·22 g, 2·74 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. A solution of $[Et_3O][BF_4]$ (0·52 g, 2·74 mmol) in CH_2Cl_2 (5 cm^3) was immediately added to the stirred mixture. The initial orange colour gave way within a few seconds to a pale yellow colour which persisted. Volatile materials were removed by distillation under reduced pressure. The residue was extracted with diethyl ether–hexane (1 : 1 v/v). Crystallisation of the extract at −40 °C gave pale yellow crystals of the *complex* which were recrystallised from diethyl ether–hexane (it is essential that all operations in solution are carried out as rapidly as possible and at the lowest convenient temperature in order to avoid contamination of the product by the chelated complex), m.p. 114—116 °C (decomp.) (1·13 g, 2·33 mmol, 85%) (Found: C, 47·3; H, 3·2; Mo, 20·3; S, 13·3. $C_{19}H_{14}MoO_5S_2$ requires C, 47·4; H, 2·9; Mo, 19·9; S, 13·3%), $\nu_{max.}$ at 2 077m, 1 989w, 1 954, 1 950vs, and 1 930m cm^{-1}, $\lambda_{max.}$ (log ε) 254 (4·03) nm, δ 7·46 p.p.m. Also prepared were: $[Mo(CO)_5(tte)]$ (90%), m.p. 98—100 °C (decomp.) (Found: C, 48·4; H, 3·8; Mo, 18·6; S, 12·3. $C_{21}H_{18}MoO_5S_2$ requires C, 49·5; H, 3·5; Mo, 18·8; S, 12·6%), $\nu_{max.}$ at 2 081m, 1 989w, 1 955, 1 951vs, and 1 935m cm^{-1}, $\lambda_{max.}$ (log ε) 220 (4·45) and 254 (4·55) nm, δ 2·23 (CH_3 free), 2·39 (CH_3 bound), and 7·33 p.p.m., *m/e* (*I*/%) 454 (43), 426 (14), 398 (43), and 370 (100); $[Mo(CO)_5(cte)]$ (63%), m.p. 78—79 °C (decomp.) (Found: C, 40·5; H, 2·5; Cl, 11·4; S, 11·9. $C_{19}H_{12}Cl_2MoO_5S_2$ requires C, 41·4; H, 2·2; Cl, 12·9; S, 11·6%), $\nu_{max.}$ at 2 080m, 1 990w, 1 956, 1 952vs, and 1 939m cm^{-1}, $\lambda_{max.}$ (log ε) 225 (4·33) and 254 (4·60) nm, δ 7·35 p.p.m.; $[Mo(CO)_5(mte)]$ (60%), m.p. 113—115 °C (decomp.) (Found: C, 46·2; H, 3·5; Mo, 17·2; S, 11·5. $C_{21}H_{18}MoO_7S_2$ requires C, 46·5; H, 3·3; Mo, 19·5; S, 11·8%), $\lambda_{max.}$ (log ε) 231 (4·40) and 253 (4·48) nm, δ 3·81 (OCH_3) and 7·16 (C_6H_4) p.p.m.; $[Mo(CO)_5(dte)]$ (48%), m.p. 160—163 °C (decomp.) (Found: C, 48·6; H, 4·0; N, 4·9; S, 11·4. $C_{23}H_{24}MoN_2O_5S_2$ requires C, 48·6; H, 4·2; N, 4·9; S, 11·3%), $\nu_{max.}$ at 2 077m, 1 987vw, 1 954, 1 949vs, and 1 931s cm^{-1}, $\lambda_{max.}$ (log ε) 230 (4·52) and 253 (4·48) nm, δ 2·88 (NCH_3) and 7·16 (C_6H_4) p.p.m., *m/e* (*I*/%) 456 (320) and 428 (100); $[Mo(CO)_5(bte)]$ (75%), m.p. 83—84 °C (decomp.) (Found: C, 41·4; H, 5·2; Mo, 21·4; S, 15·1. $C_{15}H_{22}MoO_5S_2$ requires C, 40·7; H, 5·0; Mo, 21·7; S, 14·5%), $\nu_{max.}$ at 2 078m, 1 991vw, 1 955, 1 949vs, and 1 937m cm^{-1}, $\lambda_{max.}$ (log ε) 248 (4·45) and 305 (3·82) nm, δ 1·32 (CMe_3, free) and 1·40 (CMe_3, bound) p.p.m., *m/e* (*I*/%) 386 (360), 358 (320), 330 (440), and 302 (100); $[Cr(CO)_5(pte)]$, $\nu_{max.}$ at 2 073m, 1 990vw, 1 953, 1 949vs, and 1 938m cm^{-1}, $\lambda_{max.}$ (log ε) 254 (4·02) nm, δ 7·26 p.p.m., *m/e* (*I*/%) 438 (7, M^+), 410 (3), 382 (2), 354 (8), 326 (31), and 298 (100); $[Cr(CO)_5(tte)]$, $\nu_{max.}$ at 2 071m, 1 986vw, 1 949vs, and 1 933m cm^{-1}, $\lambda_{max.}$ (log ε) 220 (4·43) and 256 (4·42) nm, δ 2·38 (CH_3, free), 2·42 (CH_3, bound), and 7·30 (C_6H_4) p.p.m., *m/e* (*I*/%) 382 (6), 354 (30), and 326 (100); $[Cr(CO)_5(cte)]$ (85%), m.p. 114—116 °C (decomp.) (Found: C, 44·6; H, 2·8; S, 12·1. $C_{19}H_{12}Cl_2CrO_5S_2$ requires C, 44·9; H, 2·4; S, 12·6%), $\nu_{max.}$ at 2 071m, 1 986vw, 1 949, 1 944vs, and 1 937m cm^{-1}, $\lambda_{max.}$ (log ε) 222 (4·61) and 260 (4·68) nm, δ 7·39 p.p.m.; $[Cr(CO)_5(nte)]$, $\nu_{max.}$ at 2 074m, 1 952vs, and 1 945m cm^{-1}; $[Cr(CO)_5(mte)]$, $\lambda_{max.}$ (log ε) 233 (4·62) and 254 (4·59) nm, δ 3·93 (OCH_3) and 7·21 (C_6H_4) p.p.m., *m/e* (*I*/%) 470 (1), 442 (3), 414 (14), 386 (70), and 358 (100); $[Cr(CO)_5(dte)]$, $\nu_{max.}$ at 2 071m, 1 987vw, 1 946, 1 943vs, and 1 930m cm^{-1}, $\lambda_{max.}$ (log ε) 274 (4·67) nm, δ 2·97 (NCH_3) and 6·98 (C_6H_4) p.p.m., *m/e* (*I*/%) 496 (1), 468 (1), 440 (3), 412 (10), and 384 (100); $[Cr(CO)_5(bte)]$, $\nu_{max.}$ at 2 071m, 1 985vw, 1 949s, 1 941, and 1 935vs cm^{-1}, $\lambda_{max.}$ (log ε) 225 (3·25) and 247 (4·24) nm, δ 1·32 (CMe_3, free) and 1·49 (CMe_3, bound) p.p.m., *m/e* (*I*/%) 398 (30, M^+), 370 (19), 314 (2), and 258 (100).

*μ-[1,2-Di(*p*-chlorophenylthio)ethane]-bis(pentacarbonyl chromium)*, $[\{(OC)_5Cr\}_2(cte)]$. *Method* (*A*). The complex $[Cr(CO)_5(cte)]$ (0·32 g, 0·64 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added to a solution of $[Et_4N][Cr(CO)_5Br]$ (0·26 g, 0·64 mmol) in CH_2Cl_2 (5 cm^3) at room temperature. A solution of $[Et_3O][BF_4]$ (0·12 g, 0·64 mmol) in CH_2Cl_2 (5 cm^3) was added to the stirred mixture which changed colour from orange to pale yellow. After removal of volatile material, the residue was extracted with diethyl ether–hexane (2 : 1 v/v) and the extracts crystallised at −40 °C. The *product* was isolated by filtration and washed with hexane to remove any unchanged $[Cr(CO)_5(cte)]$. The bright yellow complex was purified by recrystallisation from dichloromethane–hexane (1 : 1 v/v) at −40 °C.

Method (*B*). The ligand cte (0·62 g, 2 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of $[Et_4N][Cr(CO)_5Br]$ (1·6 g, 4 mmol) in CH_2Cl_2 (10 cm^3) at room temperature; $[Et_3O][BF_4]$ (0·76 g, 4 mmol) in CH_2Cl_2 (5 cm^3) was added as rapidly as possible to the vigorously stirred solution. Elaboration of the reaction then continued as in (*A*). The yield of $[\{(OC)_5Cr\}_2(cte)]$ by both methods was in the range 70—80%, m.p. 118—119 °C (decomp.) (Found: C, 41·1; H, 1·8; Cl, 10·3; S, 8·7. $C_{24}H_{12}Cl_2Cr_2O_{10}S_2$ requires C, 41·2; H, 1·7; Cl, 10·2; S, 9·1%), $\nu_{max.}$ at 2 072m, 1 990vw, 1 952s, and 1 940m cm^{-1}, $\lambda_{max.}$ (log ε) 224 (4·19) and 257 (4·26) nm, δ 7·50 p.p.m., *m/e* (*I*/%) 531 (2), 503 (5), 475 (3), 447 (6), 419 (9), and 367 (100). Also prepared were: $[\{(OC)_5Cr\}_2(pte)]$ (91%), m.p. 99—102 °C (decomp.) (Found: C, 45·1; H, 2·3; Cr, 16·8; S, 10·2. $C_{24}H_{14}Cr_2O_{10}S_2$ requires C, 45·6; H, 2·2; Cr, 16·5; S, 10·1%), $\nu_{max.}$ at 2 072m, 1 990vw, 1 953vs, and 1 937m cm^{-1}, $\lambda_{max.}$ (log ε) 251 (4·64), δ 7·45 p.p.m.; $[\{(OC)_5Cr\}_2(tte)]$ (84%), m.p. 127—128 °C (decomp.) (Found: C, 47·4; H, 2·7; Cr, 15·6; S, 10·0. $C_{26}H_{18}Cr_2O_{10}S_2$ requires C, 47·4; H, 2·7; Cr, 15·8; S, 9·8%), $\nu_{max.}$ at 2 074m, 1 990vw, 1 950, 1 946vs, and 1 942m cm^{-1}, $\lambda_{max.}$ (log ε) 225 (4·73) and 250 (4·73) nm, δ 2·49 (CH_3) and 7·39 (C_6H_4) p.p.m.; $[\{(OC)_5Cr\}_2(mte)]$ (60%), m.p. 108—109 °C (decomp.) (Found: C, 44·7; H, 2·8; Cr, 14·9; S, 9·6. $C_{26}H_{18}Cr_2O_{12}S_2$ requires C, 45·1; H, 2·6; Cr, 15·1; S, 9·3%), $\lambda_{max.}$ (log ε) 234 (4·36) and 253 (4·36), δ 3·92 (OCH_3) and 7·28 (C_6H_4) p.p.m., *m/e* (*I*/%) 494 (2), 470 (1), 442 (1), 438 (0), 414 (3), 410 (1), 386 (42), and 358 (100); $[\{(OC)_5Cr\}_2(dte)]$ (80%), m.p. 130—132 °C (decomp.) (Found: C, 47·0; H, 3·2; N, 4·2; S, 9·2. $C_{28}H_{24}Cr_2N_2O_{10}S_2$ requires C, 46·9; H, 3·3; N, 3·9; S, 9·0%), $\nu_{max.}$ at 2 071m, 1 950, 1 946vs, and 1 931m cm^{-1}, $\lambda_{max.}$ (log ε) 266 (4·36), δ 7·00 p.p.m.; and $[\{(OC)_5Cr\}_2(bte)]$ (40%), m.p. 115—116 °C (decomp.) (Found: C, 40·3; H, 4·0; Cr, 17·0. $C_{20}H_{22}Cr_2O_{10}S_2$ requires C, 40·6; H, 3·8; Cr, 17·6%), $\nu_{max.}$ at 2 070m, 1 986vw, 1 948s, 1 941, and 1 934vs cm^{-1}, $\lambda_{max.}$ (log ε) 233 (3·91) and 247 (3·87) nm, δ 1·56 p.p.m., *m/e* (*I*/%) 422 (12), 394 (52), 366 (57), 338 (31), 310 (48), 286 (9), and 258 (100).

cis-*Tetracarbonyl[1,2-di(*p*-tolylthio)ethane]molybdenum*, $[Mo(CO)_4(tte)]$. Sodium tetrahydroborate (*ca.* 10 mg) was added to a solution containing $Mo(CO)_6$ (0·5 g, 2 mmol) and tte (0·55 g, 2 mmol) in absolute ethanol. The clear solution was heated under reflux for 6 h, during which the solution turned yellow and sublimed $Mo(CO)_6$ was periodically returned to the flask. The solution was concentrated by distillation and then allowed to crystallise at 0 °C. The product was isolated by filtration and washed with ethanol prior to recrystallisation from hot ethanol which gave the *complex* as yellow needles (80% yield), m.p. 130—132 °C (decomp.) (Found: C, 50·0; H, 3·9; Mo, 20·3; S, 13·0. $\mathrm{C_{20}H_{18}MoO_4S_2}$ requires C, 49·9; H, 3·7; Mo, 20·0; S, 13·2%), $\nu_{\mathrm{max.}}$ at 2 031m, 1 925vs, 1 915vs, and 1 893s cm^{-1}, $\lambda_{\mathrm{max.}}$ (log ε) 220 (4·33) and 255 (4·26) nm, δ 2·42 ($\mathrm{C}H_3$) and 7·42 ($\mathrm{C_6}H_4$) p.p.m. Also prepared were: [Mo(CO)$_4$(pte)] (60%), m.p. 116—120 °C (decomp.) (Found: C, 47·6; H, 3·2; Mo, 21·5; S, 14·2. $\mathrm{C_{18}H_{18}MoO_4S_2}$ requires C, 47·6; H, 3·1; Mo, 21·1; S, 14·1%), $\nu_{\mathrm{max.}}$ at 2 032m, 1 925vs, 1 917vs, and 1 895s cm^{-1}, $\lambda_{\mathrm{max.}}$ (log ε) 254 (4·51) nm, δ 7·56 p.p.m.; [Mo(CO)$_4$(cte)] (53%), m.p. 145—150 °C (decomp.) (Found: C, 41·7; H, 2·4; Cl, 13·3; Mo, 18·5; S, 12·8. $\mathrm{C_{18}H_{12}Cl_2MoO_4S_2}$ requires C, 41·4; H, 2·3; Cl, 13·6; Mo, 18·4; S, 12·2%), $\nu_{\mathrm{max.}}$ at 2 032m, 1 926vs, 1 916vs, and 1 898s cm^{-1}, $\lambda_{\mathrm{max.}}$ (log ε) 221 (4·50) and 258 (4·56) nm, δ 7·55 p.p.m.; [Mo(CO)$_4$(mte)] (65%), m.p. 103—105 °C (Found: C, 47·9; H, 3·8; Mo, 18·1; S, 12·6. $\mathrm{C_{20}H_{18}MoO_6S_2}$ requires C, 46·8; H, 3·5; Mo, 18·6; S, 12·5%), $\lambda_{\mathrm{max.}}$ (log ε) 231 (4·39) and 254 (4·39) nm, δ 3·87 ($\mathrm{OC}H_3$) and 7·29 ($\mathrm{C_6}H_4$) p.p.m.; [Mo(CO)$_4$(dte)] (50%), m.p. 165—167 °C (decomp.) (Found: C, 48·1; H, 4·2; N, 4·9; S, 11·7. $\mathrm{C_{22}H_{24}MoN_2O_4S_2}$ requires C, 48·8; H, 4·4; N, 5·2; S, 11·8%), $\nu_{\mathrm{max.}}$ at 2 031m, 1 925vs, 1 914vs, and 1 895s cm^{-1}, $\lambda_{\mathrm{max.}}$ (log ε) 276 (4·40) nm, δ 7·11 p.p.m., *m/e* (*I*/%) 512 (150), 456 (600), and 428 (100); [Mo(CO)$_4$(bte)] (88%), m.p. 100—102 °C (decomp.) (Found: C, 40·6; H, 5·5; Mo, 22·4; S, 15·3. $\mathrm{C_{14}H_{22}MoO_4S_2}$ requires C, 40·6; H, 5·3; Mo, 23·2; S, 15·4%), $\nu_{\mathrm{max.}}$ at 2 027m, 1 924s, 1 914vs, and 1 884s cm^{-1}, $\lambda_{\mathrm{max.}}$ (log ε) 243 (4·42) and 305 (3·97) nm, δ 1·47 p.p.m., *m/e* (*I*/%) 414 (220), 386 (243), 358 (28), 330 (391), and 302 (100); [Cr(CO)$_4$(dte)] (30%), m.p. 136—138 °C (decomp.) (Found: C, 53·1; H, 5·1; Cr, 10·3; S, 13·1. $\mathrm{C_{22}H_{24}CrN_2O_4S_2}$ requires C, 53·1; H, 4·9; Cr, 10·5; S, 12·9%), $\nu_{\mathrm{max.}}$ at 2 017m, 1 914vs, 1 897vs, and 1 884s cm^{-1}, $\lambda_{\mathrm{max.}}$ (log ε) 276 (4·21) nm, δ 6·96 p.p.m., *m/e* (*I*/%) 496 (6), 468 (3), 440 (9), 412 (12), and 384 (100); and [Cr(CO)$_4$(mte)] (40%), m.p. 109—111 °C (decomp.) (Found: C, 51·0; H, 3·9; S, 13·8. $\mathrm{C_{20}H_{18}CrO_6S_2}$ requires C, 51·1; H, 3·8; S, 13·6%), $\lambda_{\mathrm{max.}}$ (log ε) 235 (4·31) and 253 (4·31) nm, δ 3·82 ($\mathrm{OC}H_3$) and 7·27 ($\mathrm{C_6}H_4$) p.p.m., *m/e* (*I*/%) 442 (1), 414 (3), 386 (28), and 358 (100).

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