

Sulphur Ligand Metal Complexes. Part V [1]. Disecundary Sulphide and Related Ligand Complexes of the Group VI Metal Carbonyls

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Complexes of the type $[M(CO)_5]_2L$ ($M = Cr$ or W , $L = RS(CH_2)_nSR$, $R = Me$ and $n = 6$, $R = Et$ and $n = 2$ or 4 ; $M = W$, $R = Me$ or $t-Bu$ and $n = 2$), $[M(CO)_5L]$ ($M = Cr$ or W , $L = MeSCH_2Ph$; $M = Cr$, $L = EtS(CH_2)_2SEt$) and $[M(CO)_4L]$ ($M = Cr$, Mo or W , $L = EtS(CH_2)_2SEt$) have been isolated and characterised by i.r., u.v.-visible and 1H n.m.r. spectroscopy. The bonding of alkyl sulphide ligand to group 6 metal carbonyls is discussed. The bridged ligand complexes with $n = 2$ decompose affording the related chelate complex and the present hexacarbonyl. Related bridged amine ligand complexes $[M(CO)_5]_2L$ ($M = Cr$ or W , $L = H_2N(CH_2)_nNH_2$, $n = 2$ or 12) are also reported and discussed.

Introduction

It is generally assumed that the π -bonding ability of dialkyl sulphide ligands is similar to that of related phosphines [2]. However, complexes containing sulphide ligands are not as common as the analogous phosphine derivatives although group 6 metal carbonyl complexes $[M(CO)_4L]$ where L is a chelating sulphide ligand, exhibit moderate stability towards aerial oxidation and thermal decomposition [3, 4]. In contrast, the complexes $[M(CO)_{6-x}L_x]$ where L is a monodentate R_2S ligand are often highly unstable e.g. $[Cr(CO)_5(Me_2S)]$ and $[W(CO)_5(Et_2S)]$, in some cases having only been characterised by i.r. spectroscopy [5]. In view of the suggested π accepting ability of the alkyl sulphide ligand, this is somewhat surprising, however detailed studies on such complexes are often hampered by their low stability. It is therefore of interest that in this paper we report the isolation and characterisation of a series of stable complexes containing the $M(CO)_5$ moiety bound to an alkyl sulphide ligand. The enhanced stability has been achieved by using the ligands $RS(CH_2)_nSR$ ($R = Me$, $n = 2$ or 6 ; $R = Et$, $n = 2$ or 4 ; $R = t-Bu$, $n = 2$) acting in a bridging fashion in the complexes $[M(CO)_5]_2L$ ($M = Cr$ or W). The potential of sulphide complexes as neutral precursors for the synthesis of other $[M(CO)_5(\text{ligand})]$ complexes, by displacement reactions has previously

been indicated [4]. Related complexes with benzylmethylsulphide and bridging amine ligands are also included for comparison.

Results

The complexes $[M(CO)_5]_2L$ ($M = Cr$ or W , $L = dto$ (3,6-dithiooctane), 2,9-dtd (2,9-dithiadecane) or 3,8-dtd (3,8-dithiadecane); $M = W$, $L = dth$ (2,5-dithiahexane), tmdto (2,2,7,7-tetramethyl-3,6-dithiooctane)).

(See Figure for the structural formulae of the ligands). These were obtained as moderately air-stable crystalline, yellow solids on addition of L (1 mol) to u.v.-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl complex (2 mol) except in the case of $M = Cr$ and $L = dto$ where the reaction yielded mainly the chelated complex $[Cr(CO)_4(dto)]$.

$RS(CH_2)_2SR$ ($R = Me$, dth ; $R = Et$, dto ; $R = t-Bu$, $tmdto$)

$MeS(CH_2)_6SMe$ (2,9-dtd)

$EtS(CH_2)_4SEt$ (3,8-dtd)

Figure 1.

Attempts to prepare the complexes $[M(CO)_5L]$, where L is the bidentate ligand acting in a monodentate fashion, by reacting the ligand and $[M(CO)_5(\text{thf})]$ ($\text{thf} = \text{tetrahydrofuran}$) in equimolar proportions were with one exception unsuccessful, the bridged complexes $[M(CO)_5]_2L$ being obtained. However for $M = Cr$ and $L = dto$ the reaction afforded the complex $[Cr(CO)_5(dto)]$ as an unstable yellow oil, which was characterised by i.r. and n.m.r. spectroscopy (Table I). Moreover, reactions of this product with $[Cr(CO)_5(\text{thf})]$ in equimolar ratio, yielded the complex $[Cr(CO)_5]_2(dto)$ which had been unobtainable by the direct synthetic method. During the course of this work a related series of sulphide ligand complexes were reported by Connor [4]. Complexes $[M(CO)_5]_2L$ and $[M(CO)_5L]$ ($L = RS(CH_2)_2SR$, $R = p\text{-XC}_6\text{H}_4$ and $t\text{-Bu}$) were

TABLE I. Spectral Data for the Complexes.

Complex	$\nu(\text{CO})^a/\text{cm}^{-1}$	$^1\text{H n.m.r.}^h/\tau$
$[\{\text{W}(\text{CO})_5\}_2(\text{dth})]$	2077 w, 1984w, 1946vs, 1935sh ^b	i
$[\{\text{Cr}(\text{CO})_5\}_2(\text{dto})]$	2071w, 1985w, 1948vs, 1935sh	7.22s(-S(CH ₂) ₂ S-), 7.36q(-SCH ₂ CH ₃), 8.70t(-CH ₃)
$[\{\text{W}(\text{CO})_5\}_2(\text{dto})]$	2074w, 1984w, 1944vs, 1934s	6.92s(-S(CH ₂) ₂ S-), 7.06q(-SCH ₂ CH ₃), 8.60t(-CH ₃)
$[\text{Cr}(\text{CO})_5(\text{dto})]$	2068w, 1983w, 1944vs, 1936s	7.35m(-S(CH ₂) ₂ S-, -SCH ₂ CH ₃), 8.67q(-CH ₃)
$[\{\text{W}(\text{CO})_5\}_2(\text{tmdto})]$	2070w, 1977w, 1942vs, 1930s	6.84s(-S(CH ₂) ₂ S-), 8.52s(-C(CH ₃) ₃)
$[\{\text{Cr}(\text{CO})_5\}_2(3,8\text{-dtd})]$	2070w, 1984w, 1947vs, 1936sh	7.35m(-CH ₂ SCH ₂ -), 8.30m(-SCH ₂ CH ₂ -), 8.74t(-CH ₃)
$[\{\text{W}(\text{CO})_5\}_2(3,8\text{-dtd})]$	2070w, 1987w, 1947vs, 1938sh	j
$[\{\text{Cr}(\text{CO})_5\}_2(2,9\text{-dtd})]$	2070w, 1984w, 1945vs, 1935s	7.40m(-SCH ₂ -), 7.73s(-CH ₃), 8.50m(-SCH ₂ (CH ₂) ₂ -)
$[\{\text{W}(\text{CO})_5\}_2(2,9\text{-dtd})]$	2072w, 1986w, 1946vs, 1940sh	7.20m(-SCH ₂ -), 7.43s(-CH ₃), 8.50m(-SCH ₂ (CH ₂) ₂ -)
$[\text{Cr}(\text{CO})_5(\text{bms})]$	2070w, 1985w, 1944s, 1937s	2.60s(-C ₆ H ₅), 6.24s ^k (-SCH ₂ -), 7.81s ^l (-CH ₃)
$[\text{W}(\text{CO})_5(\text{bms})]$	2075w, 1983w, 1941vs, 1934s	2.74s(-C ₆ H ₅), 6.06s ^m (-SCH ₂ -), 7.57s ⁿ (-CH ₃)
$[\text{Cr}(\text{CO})_4(\text{dto})]$	2019w, 1917m, 1900s, 1885s	7.38q(-SCH ₂ CH ₃), 7.40s(-S(CH ₂) ₂ S-), 8.62t(-CH ₃)
$[\text{Mo}(\text{CO})_4(\text{dto})]$	2027m, 1921m, 1910s, 1890s	7.27s(-S(CH ₂) ₂ S-), 7.29q(-SCH ₂ CH ₃), 8.61t(-CH ₃)
$[\text{W}(\text{CO})_4(\text{dto})]$	2020m, 1916m, 1893s, 1885s	7.20q(-SCH ₂ CH ₃), 7.26s(-CH ₂) ₂ S-, 8.62t(-CH ₃)
$[\{\text{Cr}(\text{CO})_5\}_2(\text{en})]$	2072w, 1970sh, 1940vs, 1885m ^{c,d}	7.27s(-NCH ₂ -) ^o
$[\{\text{W}(\text{CO})_5\}_2(\text{en})]$	2073w, 1975sh, 1930vs, 1879m ^{c,e}	7.29s(-NCH ₂ -) ^o
$[\{\text{Cr}(\text{CO})_5\}_2(\text{dad})]$	2065w, 1975w, 1932vs, 1900sh ^{b,f}	7.50m(-CNH ₂ -), 8.72m(-NCH ₂ (CH ₂) ₅ -)
$[\{\text{W}(\text{CO})_5\}_2(\text{dad})]$	2073w, 1972w, 1928vs, 1900sh ^{b,g}	7.40m(-NCH ₂ -), 8.70m(-NCH ₂ (CH ₂) ₅ -)

^a In cyclohexane unless otherwise stated. ^b In CHCl₃. ^c In CH₃NO₂. ^d $\nu(\text{NH})$ 3358, 3312 cm⁻¹. ^e $\nu(\text{NH})$ 3343, 3301 cm⁻¹. ^f $\nu(\text{NH})$ 3365, 3315 cm⁻¹. ^g $\nu(\text{NH})$ 3350, 3305 cm⁻¹. ^h In CDCl₃ unless otherwise stated. ⁱ Insoluble. ^j Not recorded. ^k $\Delta\tau = \tau(\text{C}_6\text{H}_6) - \tau(\text{CDCl}_3) = 0.67$. ^l $\Delta\tau = 0.83$. ^m $\Delta\tau = 0.66$. ⁿ $\Delta\tau = 0.77$. ^o In (CH₃)₂CO. q = quartet, s = singlet, t = triplet.

isolated in the case of M = Cr but for M = Mo the bridged complexes could not be obtained. In contrast we have only isolated bridged complexes for M = W which is a further indication of the differences in the chemistry of Cr, Mo and W carbonyl complexes.

I.r. and ¹H n.m.r. spectral data for the $[\{\text{M}(\text{CO})_5\}_2\text{L}]$ complexes are given in Table I. I.r. spectra in the CO stretching region showed a pattern typical of $[\text{M}(\text{CO})_5\text{L}]$ systems where L is an alkyl sulphide ligand [4, 5]. ¹H n.m.r. chemical shift values established the bridging nature of the RS(CH₂)_nSR ligands in that the R groups are observed to be equivalent and in the cases where n = 2 the methylene protons, -S(CH₂)₂S-, are observed as only one resonance. Moreover the i.r. spectra (nujol mulls) of the complexes $[\{\text{M}(\text{CO})_5\}_2\text{L}]$ (L = dth or dto) indicate the ligand has adopted a *trans* conformation. For L = dth the spectrum is similar to that observed for other complexes containing bridged dth ligands [6] where it has been reported that the most clear cut diagnosis of conformation comes from the CH₂ rocking region. In particular the absence of a strong band at about 840 cm⁻¹ confirms the *gauche* conformation is not present. The spectra of the dto complexes are more complicated but similar arguments appear to apply. Chelated dto ligands [7] show strong CH₂ rock absorptions at about 840 cm⁻¹ whereas the $[\{\text{M}(\text{CO})_5\}_2(\text{dto})]$ complexes showed no significant i.r. absorptions in the 800–900 cm⁻¹ range. Only one other example of a bridged dto

complex $[(\text{CuCl})_2(\text{dto})]_n$ has been reported previously [8]. The non-equivalence of each of the -SCH₂CH₃ protons and the -S(CH₂)₂S- protons in the complex $[\text{Cr}(\text{CO})_5(\text{dto})]$ is established from the n.m.r. spectrum consistent with the unidentate nature of the ligand. The i.r. spectrum (1400–600 cm⁻¹), which is similar to that observed for the bridging dto ligand, is indicative of a *trans* ligand conformation. The electronic spectral data (Table II) for the complexes are similar to those previously observed for alkyl sulphide ligand complexes containing the M(CO)₅ moiety [4].

The enhanced stability of these bridged complexes $[\{\text{M}(\text{CO})_5\}_2\text{L}]$, especially the longer chain complexes prepared in this study may in part be related to the steric protection afforded to the M–S linkage by the ligand being bonded to another M(CO)₅ unit. The chromium complex containing the -S(CH₂)₂S- unit (L = dto) over a period of time (several months) decomposes to the related chelate complex. The analogous tungsten complexes are thermally more stable but do decompose on heating. For the case of M = W and L = dto this reaction has been investigated in more detail. Under conditions of reflux (cyclohexane, 4h) i.r. and n.m.r. spectra show the decomposition to be via equation (1):



and when the reaction is carried out in the presence

TABLE II. Lowest Energy Absorption Maxima for the Complexes $[M(CO)_5L]$ and $[M(CO)_5]_2L$.

Complex	λ_{\max} (log ϵ)	Solvent	Reference
<i>L = P donor</i>			
$[Cr(CO)_5P(OPh)_3]$	329 (3.27)	Hexane	14
$[Cr(CO)_5P(NMe_2)_3]$	340 (3.25)	Hexane	14
$[Cr(CO)_5P(C_6H_{11})_3]$	340 (3.27)	Hexane	14
$[Cr(CO)_5PPh_3]$	359 (3.14)	Hexane	14
<i>L = S donor</i>			
$[Cr(CO)_5]_2(3,8-dtd)$	395 (3.73)	CHCl ₃	a
$[Cr(CO)_5]_2(tmdto)$	396 (3.15)	EtOH	4
$[Cr(CO)_5]_2(dto)$	398 (3.45)	EtOH	a
$[Cr(CO)_5]_2(2,9-dtd)$	398 (3.57)	EtOH	a
$[Cr(CO)_5(SPM_3)]$	424 (3.20)	EtOH	23
$[W(CO)_5]_2(tmdto)$	368 (3.69), 412 (3.19)sh	CHCl ₃	a
$[W(CO)_5]_2(dto)$	371 (3.63), 418 (3.10)sh	CHCl ₃	a
$[W(CO)_5]_2(2,9-dtd)$	372 (3.53), 415 (3.08) sh	CHCl ₃	a
$[W(CO)_5(SPM_3)]$	378 (3.26), 420 (3.03)sh	EtOH	23
<i>L = N donor</i>			
$[Cr(CO)_5]_2(en)$	410 (3.77)	EtOH	a
$[Cr(CO)_5]_2(dad)$	419 (3.67)	CHCl ₃	a
$[Cr(CO)_5(HNC_5H_{10})]$	426 (3.54)	Cyclohexane	14
$[W(CO)_5]_2(en)$	397 (3.33), 450 (2.87)sh	EtOH	a
$[W(CO)_5(HNC_5H_{10})]$	403 (3.59), 440 (2.77)sh	Benzene	17
$[W(CO)_5]_2(dad)$	406 (3.82), 445 (3.05)sh	Benzene	a
$[W(CO)_5(NH_3)]$	408 (3.58), 440 (2.78)sh	Benzene	17

^a This work, spectra were recorded immediately after sample preparation.

of Ph_3P (1:1 mol ratio) the products are $[W(CO)_4(dto)]$ and $[W(CO)_5(PPh_3)]$. When $[W(CO)_4(dto)]$ and Ph_3P (in 1:6 mol ratio) are refluxed under the same conditions there is no clear evidence for the displacement of the dto by Ph_3P .

The Complexes $[M(CO)_4(dto)]$ ($M = Cr$ or W)

Previously reported chelated sulphide complexes have been prepared by thermal methods [3]. Yields are often low and long reflux times are required, especially in the case of tungsten. Although the photochemical method has been used for preparing mixed monodentate ligand complexes $[M(CO)_4LL^1]$ ($L =$ amine, $L^1 =$ phosphine) [9] it has been used less frequently for the preparation of chelate complexes $[M(CO)_4L]$. In this study the $[M(CO)_4(dto)]$ complexes have been readily isolated from u.v.-irradiated thf solutions of the ligand and the appropriate metal carbonyl. Spectral data for the complexes are listed in Table I. In the n.m.r. the resonances assignable to the $-S(CH_2)_2S-$ methylene protons occur at higher field (*ca.* 0.2 τ) than for the related bridged complexes.

It is of interest that it has not been possible to isolate chelate complexes utilising the longer chain ligands 3,8-dtd and 2,9-dtd. For example in the

case of Cr and 3,8-dtd after irradiation of the thf solution for 3 hr only $[Cr(CO)_5L]$ species were detectable in the i.r. From this solution the bridged ligand complex $[Cr(CO)_5]_2(3,8-dtd)$ was isolated.

The complexes $[M(CO)_5L]$ ($M = Cr$ or W , $L = bms$ (benzylmethylsulphide))

These complexes, which were isolated in a manner similar to that described for the $[M(CO)_5]_2L$ bridged ligand complexes, were found to be thermally unstable. In the case of $[W(CO)_5(bms)]$ the parent ion was not observed in the mass spectrum however the $[W(CO)_6]^+$ ion appeared in high abundance and the $[W(CO)(bms)]^+$ and $[W(bms)]^+$ ions in lower abundances. Included in Table I are values of the aromatic-solvent-induced shift, $\Delta\tau$. As in phosphine and other ligand systems [10, 11], the increase in the $\Delta\tau$ values for the methyl and methylene protons (to *ca.* 0.7 τ , *cf.* the free ligand value of 0.2 τ) on coordination may be related to an increase in positive charge on the sulphur atom.

The Complexes $[M(CO)_5]_2L$ ($M = Cr$ and W , $L = en$ (1,2-diaminoethane) and dad (1,12-diaminododecane))

Although chelating amine ligand metal carbonyl complexes are well known [12] no bridged ligand

complexes have been reported previously. Isolation of the bridged amine ligand complexes was achieved in a manner similar to that described for the bridged sulphide complexes and again an enhanced stability was observed when compared to related monodentate amine $[M(CO)_5L]$ complexes. It was not possible to prepare bridging complexes utilising the amines *N,N*-diethylethylenediamine and *N,N,N',N'*-tetramethylethylenediamine although they were detected by i.r. spectroscopy in solution. Spectral data for the complexes (Table I) confirm the bridging nature of the ligands. In the case of *en* the *trans* conformation is adopted by the ligand in the complexes as the i.r. spectrum is similar to that of $[HgCl_2(en)]$ for which this conformation has definitely been established by X-ray analysis [13]. The observation of only two $\nu(N-H)$ bands (Table I) due to the asymmetric and symmetric modes indicates the equivalence of the coordinated nitrogen atoms as expected for the bridged formulation.

Discussion

As yet the electronic spectra of metal carbonyl complexes are not completely understood, however it is apparent that for $[M(CO)_5L]$ systems the wavelength of the lowest energy absorption maximum can provide a sensitive indication of the nature and strength of the M-L interaction [14-16]. The absorption band (Table II) which generally appears in the 350-425 nm range may be assigned to an $e \rightarrow a_1$ ligand field transition and the low energy shoulder at *ca.* 400-450 nm for the tungsten complexes to the corresponding singlet \rightarrow triplet transition [16, 17]. Alternatively it has been suggested that the $e \rightarrow a_1$ transition is charge transfer from *d* orbitals to a combination of CO 2π orbitals [14, 15]. Although there is disagreement over the acceptor orbital it is apparent that the energy of the $e \rightarrow a_1$ transition reflects the nature of the M-L bonding and since good π acceptors will stabilize the *d* donor orbitals, the π acceptor ability of the ligand L. It has been argued that this is the biggest single effect [14, 15]. The alkyl sulphide complexes prepared in this study show bands at *ca.* 400 nm for *M* = Cr and at *ca.* 370 nm for *M* = W. In contrast phosphine ligand complexes absorb at shorter wavelengths (330-360 nm) dependent on the π acidity of the ligand, whereas the σ donor amine ligand complexes absorb at longer wavelengths (400-430 nm). Also included in Table II are data for complexes of the ligand Me_3PS , which has been shown to have a minimal π accepting ability [11, 18]. From the position of the $e \rightarrow a_1$ absorption it appears that the M-S interaction for the alkyl sulphide ligand complexes is comparatively weaker than the typical M-P interaction. In contrast CO frequencies and force constants for related alkyl

sulphide and phosphine $[M(CO)_{6-x}L_x]$ complexes are somewhat similar and this has previously been interpreted to indicate that the bonding of the two ligand types is not significantly different [2, 19]. However although CO frequencies and force constants or derived parameters provide a reliable estimate of the total electron availability at the metal, attempts to compare relative σ and π components for ligands with different donor atoms must be treated with caution [20]. Therefore, a likely explanation for these results is that alkyl sulphide ligands are both weaker σ donors and π acceptors than phosphine ligands thus coincidentally giving rise to similar CO frequencies and force constants, but longer wavelength absorption maxima for the $e \rightarrow a_1$ transition. The results of a single crystal X-ray determination on one of the complexes $[Cr(CO)_4(dto)]$ prepared in this work have led to similar conclusions [21]. A comparison of the structure with that of $[Cr(CO)_4(diphos)]$ (*diphos* = $Ph_2PCH_2CH_2PPh_2$) [22] shows that the Cr-CO distances are identical thus implying the total electron contribution from the two ligands is similar. However, although the mean Cr-S distance at 2.418(1) Å is less than expected for a single bond (~ 2.52 Å) the shortening is less significant than that observed for the Cr-P bond, thus implying an overall weaker metal ligand interaction for alkyl sulphide ligands.

Experimental

I.r. spectra were recorded on a Beckman I.R.20 spectrophotometer, n.m.r. spectra on a JEOL JNM-C-60 HL spectrometer and electronic spectra on Perkin-Elmer 402 and Shimadzu MPS-5000 instruments. Microanalyses were carried out by Professor A. Campbell, University of Otago (Table III).

All reactions were carried out under an atmosphere of oxygen-free dinitrogen, tetrahydrofuran (thf) was sodium dried. The sulphide ligands were obtained from K. and K. Laboratories and the amine ligands from the Aldrich Chemical Company.

*The Complexes $\{[M(CO)_5]_2L\}$ (*M* = Cr or W; *L* = 2,9-dtd, 3,8-dtd, *en* or *dad*; *M* = W; *L* = *dth*, *dto* or *tmdto*)*

These were obtained by similar methods of which the following is typical.

The complex $[Cr(CO)_6]$ (0.66 g, 3 mmol) was dissolved in thf (60 cm³) and the solution irradiated in an u.v. cell for 1 hr. The ligand 2,9-dtd (0.25 cm³, ~ 1.5 mmol) dissolved in thf (20 cm³) was added to the orange solution and the mixture stirred for 5 min. The solvent was completely removed under vacuum and the excess of $[Cr(CO)_6]$ sublimed from the residue *in vacuo* at room temperature. The resultant solid was dissolved in benzene (50 cm³) and filtered

TABLE III. Analytical Data and M.p.s. for the Complexes.

Complex	Analyses ^a /%			M.p./°C
	C	H	S	
{W(CO) ₅ } ₂ (dth)	22.2 (21.8)	1.4 (1.3)	8.5 (8.3)	128–9
{Cr(CO) ₅ } ₂ (dto)	36.2 (36.0)	3.1 (2.6)	12.4 (12.0)	83–6
{W(CO) ₅ } ₂ (dto)	24.0 (24.1)	1.8 (1.75)	8.1 (8.0)	105–6
{W(CO) ₅ } ₂ (tmdto)	28.4 (28.1)	2.6 (2.6)	7.5 (7.5)	148–9
{Cr(CO) ₅ } ₂ (3,8-dtd)	39.0 (38.4)	3.45 (3.2)	11.7 (11.4)	109
{W(CO) ₅ } ₂ (3,9-dtd)	26.5 (26.2)	2.7 (2.2)	8.2 (7.8)	128–30
{Cr(CO) ₅ } ₂ (2,9-dtd)	38.8 (38.4)	3.4 (3.2)	11.4 (11.4)	77–8
{W(CO) ₅ } ₂ (2,9-dtd)	26.9 (26.2)	2.5 (2.2)	8.0 (7.8)	87
Cr(CO) ₅ (bms)	47.6 (47.3)	3.2 (3.0)	9.4 (9.7)	Oil
W(CO) ₅ (bms)	34.1 (33.75)	2.6 (2.2)	7.1 (6.9)	38–40
Cr(CO) ₄ (dto)	38.4 (38.3)	4.7 (4.5)	20.3 (20.4)	97–9
Mo(CO) ₄ (dto)	33.9 (33.55)	3.85 (3.9)	17.4 (17.9)	112–4
W(CO) ₄ (dto)	26.6 (26.9)	3.1 (3.1)	14.1 (14.4)	126–8
{Cr(CO) ₅ } ₂ (en)	32.4 (32.2)	1.8 (1.9)	6.3 (6.6) ^b	>270
{W(CO) ₅ } ₂ (en)	20.45 (20.4)	1.35 (1.1)	4.0 (4.0) ^b	>270
{Cr(CO) ₅ } ₂ (dad)	46.5 (45.2)	5.5 (4.8)	5.0 (4.8) ^b	>270
{W(CO) ₅ } ₂ (dad)	32.0 (31.1)	3.9 (3.3)	3.1 (3.3) ^b	111–112

^a Calculated values are given in parentheses. ^b N.

through Kieselguhr to give a yellow solution which was reduced in volume to 10 cm³. On addition of n-hexane, bright yellow crystals (0.58 g, 69%) were formed.

For L = dth, tmdto and en, the product was extracted with benzene to remove any contaminating [M(CO)₄L] complex and then recrystallized from acetone. For L = 3,8-dtd the product was extracted into acetone/thf before filtering through Kieselguhr.

The Complex [{Cr(CO)₅}₂(dto)]

The complex [Cr(CO)₆] (0.44 g, 2 mmol) was irradiated in a thf solution as in the previous method after which the ligand dto (0.30 cm³, ~ 2 mmol) dissolved in thf (20 cm³) was added and the solution stirred for 5 min. The solution was reduced in volume to about 20 cm³ and then added to a solution of [Cr(CO)₅(thf)] (2 mmol) prepared as above. After stirring for 10 min the solvent was completely removed and the residue was extracted into n-pentane and filtered through Kieselguhr. The pentane insoluble fraction was mainly the complex [Cr(CO)₄(dto)]. The n-pentane was removed under vacuum and the residue was extracted with the minimum volume of n-hexane to remove the contaminating chelate complex. The product remained as bright yellow crystals (0.15 g, 14%).

The Complexes [M(CO)₅L] (M = Cr or W, L = bms; M = Cr, L = dto)

These were obtained by similar methods of which the following is typical.

After irradiating complex [W(CO)₆] (0.70 g, 2 mmol) in thf as in the above method, the ligand bms (0.2 cm³, ~ 2 mmol) was added and the solution stirred for 5 min. The solvent was removed and the residue extracted with n-pentane. The solution was filtered through Kieselguhr and after solvent removal, the excess of [W(CO)₆] removed by sublimation *in vacuo*. The product was obtained from a pentane solution (cooled to solid CO₂/acetone temp.) as yellow crystals (0.25 g, 27%). For M = Cr the products were obtained as thermally unstable yellow oils at room temperature. In the case of L = dto the product was separated from the chelate complex by chromatography on silica (100–200 mesh) eluting with benzene/hexane.

The Complexes [M(CO)₄(dto)] (M = Cr or W)

These were prepared by similar methods of which the following is typical.

The complex [W(CO)₆] (0.70 g, 2 mmol) and the ligand dto (0.6 cm³, ~ 4 mmol) were irradiated in 1:1 thf/n-heptane solution for 3 hr. The resulting yellow solution was then treated as described for the bridged ligand complexes. Yield 0.41 g, 54%. For M = Mo the complex was prepared by a thermal method [3].

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