In memory of T. A. Stephenson

Carbene Complexes. Part 21.[1] Synthesis and Characterisation of Bis(carbene)molybdenum(II) Complexes and Dimetal(0) Complexes of the Group 6 Elements containing Novel Bridging Bis(carbene) Ligands; *X*-Ray Structures of $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ $[L^{Et} = {=}CN(Et)(CH_2)_2NEt]$ and $[W(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}W(CO)_5]$ †,‡

David M. Anderson, Garry S. Bristow, Peter B. Hitchcock, Hatam A. Jasim, Michael F. Lappert, and Brian W. Skelton
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Treatment of the bis(carbene)tetracarbonylmolybdenum(0) complex *cis*-$[Mo(CO)_4(L^{Et})_2]$ $[L^{Et} = {=}CN(Et)(CH_2)_2NEt]$ with two equivalents of silver trifluoromethanesulphonate in tetrahydrofuran (thf) readily yields the molybdenum(II) complex $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**). Reaction of the complexes $[M(CO)_6]$ (M = Cr or W) with $Mg[(CH_2)_2C_6H_4\text{-}o](thf)$ (M = Cr) or $o\text{-}C_6H_4(CH_2MgCl)_2$ (M = W) in thf affords the crystalline yellow μ-bis(carbene)-dimetal(0) complex $[\{M(CO)_5[C(O)CH_2C_6H_4CH_2C(O)\text{-}o]M(CO)_5\}Mg(thf)_n]$ [M = Cr, *n* = 3 (**2a**); M = W, *n* = 4 (**2b**)], which when extracted into water and treated with $[Et_3O][BF_4]$ furnishes the appropriate orange μ-bis(carbene) bimetallic complex $[M(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}M(CO)_5]$ [M = Cr (**3a**) or W (**3b**)]. Complex (**3a**) with an excess of PEt_3 gives the red-orange complex $[\{Cr(CO)_4(PEt_3)\}\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}\{Cr(CO)_4(PEt_3)\}]$. Reaction of $[M(CO)_6]$ with $o\text{-}C_6H_4[CH(SiMe_3)Li(tmen)]_2$ $[tmen = Me_2N(CH_2)_2NMe_2]$ yields $[M(CO)_5\{C(OLi(OEt_2)(tmen)]\text{-}CH(SiMe_3)C_6H_4CH(SiMe_3)C[OLi(OEt_2)(tmen)]\text{-}meso\text{-}o\}M(CO)_5]$. In the crystalline bis(carbene)-molybdenum(II) complex (**1**), the Mo atom resides at the centre of a severely distorted octahedron $[C_{carb}\text{–}Mo\text{–}C_{carb'}$ 134.9(2)°], with the two five-membered L^{Et} rings arranged so as to be approximately parallel, and mean lengths $Mo\text{–}C_{carb}$ 2.154(5), Mo–CO 1.961(6), and Mo–O 2.177(4) Å. In the crystalline ditungsten(0) complex (**3b**), each W is in an octahedral environment and selected mean parameters include $W\text{–}C_{carb}$ 2.155(12), W–CO 2.03(4), and $C_{carb}\text{–}O$ 1.317(14) Å.

The original (Fischer) method of obtaining a carbenemetal complex involved reaction of an organolithium reagent LiR (*e.g.*, R = Me or Ph) with $[M(CO)_6]$ (M = Cr or W) and subsequent treatment of the derived lithium carbenemetalate(0) complex with various alternative reagents including $[Et_3O][BF_4]$.[2] An aim of the present investigation was to extend this procedure, using a lithium or magnesium reagent of a dicarbanion, to give access to bridged bis(carbene)-dimetal complexes; convenient candidate reagents for this purpose had recently been used by us in other contexts: $o\text{-}C_6H_4(CH_2MgCl)_2$ (or its chloride-free equivalent)[3] and $o\text{-}C_6H_4[CH(SiMe_3)Li(tmen)]_2$ $[tmen = Me_2N(CH_2)_2NMe_2]$.[4] The only previous use of such a strategy, employing (*a*) $Li_2(C_6H_4\text{-}o)$ had led to chelated *cis*-di(carbene)metal complexes $[M(CO)_4\{[C(OEt)]_2C_6H_4\text{-}o\}]$,[5a] or (*b*) PhCH(Li)CH(Li)Ph had given a low yield of the analogous chelate but also a trace of the binuclear complex.[5b]

A quite general synthesis of a related class of carbenemetal complexes, the bis(1,3-dialkylimidazolin-2-ylidene)metal (abbreviated as 'L^R–metal') derivatives, has an electron-rich olefin $[{=}CN(R)(CH_2)_2NR]_2$ (abbreviated as $L^R{}_2$) as the carbenoid starting material (see ref. 1, and earlier Parts in the series). Included among the many complexes of this type is *cis*-$[Mo(CO)_4(L^{Et})_2]$;[6] it is noteworthy that complexes containing the ligand L^R are more stable than the Fischer $[{=}C(OR')R]$ analogues. Silver(I) salts, such as $Ag[BF_4]$ have been shown to be convenient one-electron oxidants, and stable Cr^I complexes such as $[Cr(CO)_4(L^{Et})_2][BF_4]$ have been obtained.[7] Using a dihalogen as an oxidising agent, $L^R\text{–}M^{II}$ complexes, such as $[Mo(CO)_2Cl_2(L^{Et})_2]$, have been identified.[8] A further objective of this work was to obtain a crystalline $L^{Et}\text{–}Mo^{II}$ complex, and to use $Ag[OSO_2CF_3]$ as the oxidant; the expectation was that $[Mo(CO)_4(L^{Et})_2][OSO_2CF_3]_2$ might be obtained, and a crystallographic comparison with the *X*-ray characterised[9] *cis*- and *trans*-$[Mo(CO)_4(L^{Me})_2]$ would have been of interest.

In Scheme 1 are summarised relevant background synthetic results, for comparison with the new data, shown in Scheme 2.

Results and Discussion

Synthetic and Spectroscopic Aspects.—The transformations of Group 6 metal(0) hexacarbonyls leading to the new carbene(carbonyl)metal complexes (**1**)—(**5**) are outlined in Scheme 2. Data on yields, appearance, and microanalyses are

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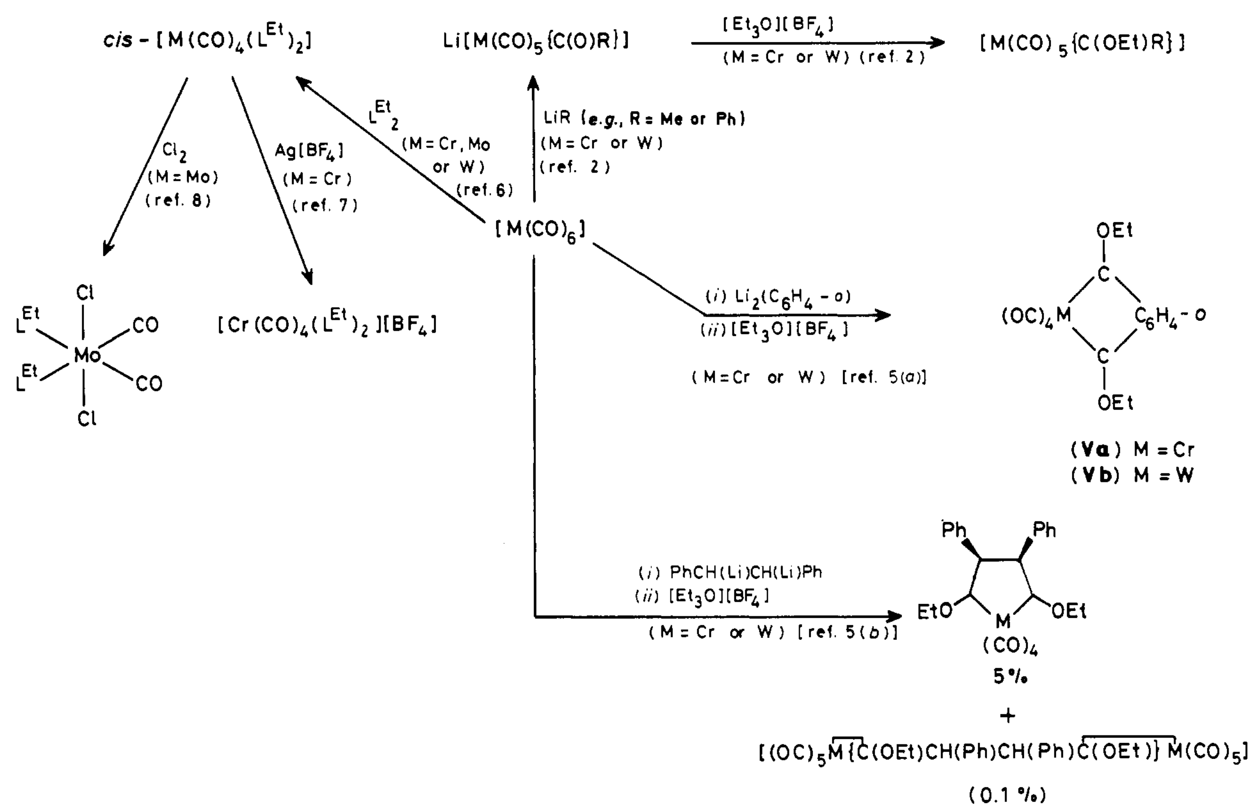
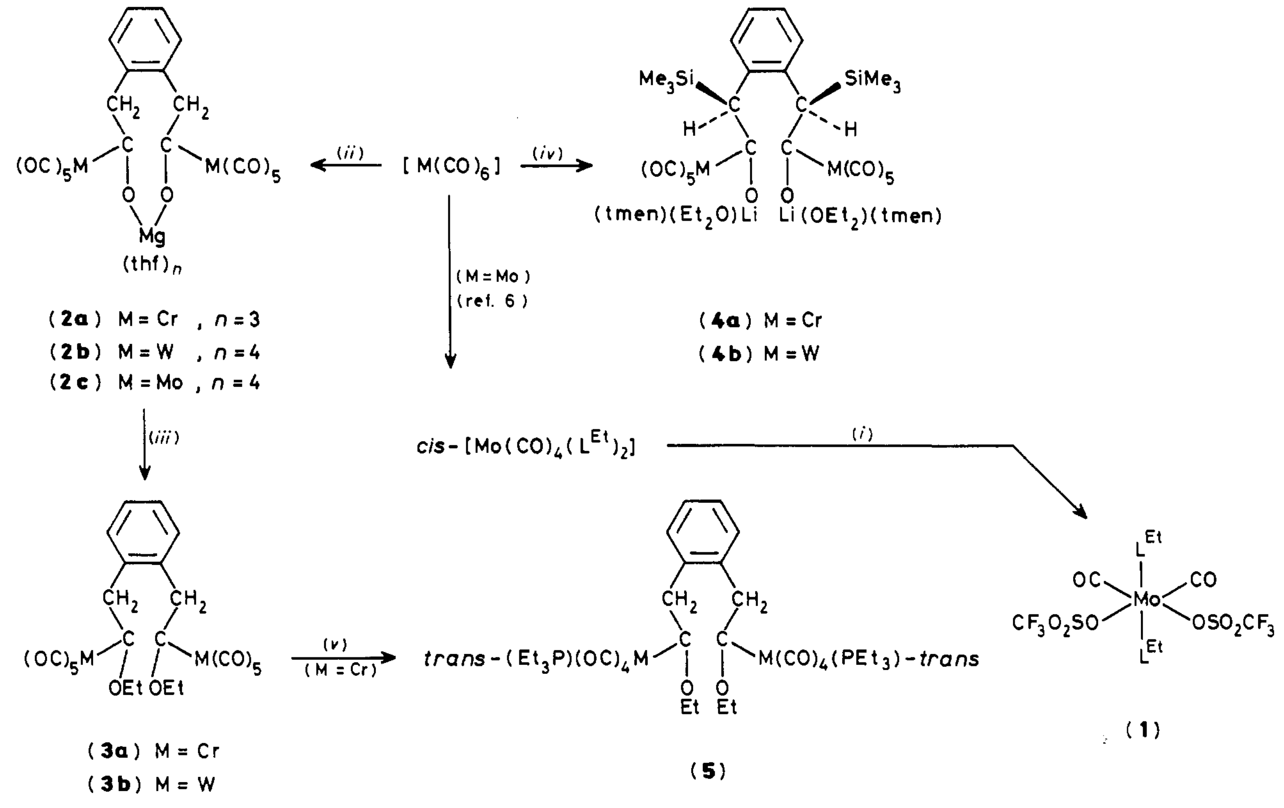
† *cis*-Dicarbonyl-*trans*-bis(1,3-diethylimidazolidin-2-ylidene)-*cis*-bis(trifluoromethanesulphonato)molybdenum(II) and μ-2,2′-*o*-phenylenedi(1-ethoxyethylidene)-bis[(pentacarbonyl)tungsten(0)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ No reprints available.



Scheme 1. The formation of some carbene–$\mathrm{Cr^0}$, $\mathrm{-Mo^0}$, $\mathrm{-W^0}$, $\mathrm{-Cr^I}$, and $\mathrm{-Mo^{II}}$ complexes; background literature data



Scheme 2. Reactions from Group 6 metal(0) carbonyls leading to (*a*) the di(carbene)molybdenum(II) complex (**1**), and (*b*) the bimetal(0) complexes (**2**)—(**5**) containing novel bridging bis(carbene) ligands. $\mathrm{L^{Et}} = \overline{=\mathrm{CN(Et)(CH_2)_2NEt}}$, thf = tetrahydrofuran, tmen = $\mathrm{Me_2N(CH_2)_2NMe_2}$. Reagents and conditions: (*i*) 2 $\mathrm{Ag[OSO_2CF_3]}$, thf, −78 °C (then reflux, 1 h); (*ii*) 1 $\mathrm{Mg[(CH_2)_2C_6H_4\text{-}\mathit{o}](thf)}$ or 1 o-$\mathrm{C_6H_4(CH_2MgCl)_2}$, thf, $\leqslant 25$ °C; (*iii*) *via* (**2a**) or (**2b**) prepared *in situ* [see (*ii*)], then 2 $\mathrm{[Et_3O][BF_4]}$; (*iv*) o-$\mathrm{C_6H_4[CH(SiMe_3)Li(tmen)]_2}$, $\mathrm{OEt_2}$, 15 °C; (*v*) excess $\mathrm{PEt_3}$, n-$\mathrm{C_6H_{14}}$, reflux, 6 h

Table 1. Yields, m.p.s, colours, and analytical data for the new carbene(carbonyl)metal complexes

				Found (Calc.) (%)	
Compound[a]	Yield[b]	M.p. (θ_c/°C)	Colour	C	H
(**1**)[c]	40	> 138 (decomp.)	Purple	30.6 (30.8)	4.05 (4.00)
(**2a**)	61	> 95 (decomp.)[d]	Yellow	46.8[e] (49.0)	4.15 (4.10)
(**2b**)	51	> 140 (decomp.)[d]	Yellow	37.3[e] (38.6)	3.50 (3.60)
(**2c**)	[f]	> 80 (decomp.)[d]	Yellow	[f]	[f]
(**3a**)	20	96—99	Orange	47.7 (47.8)	3.20 (3.00)
(**3b**)	44	*ca.* 83 (decomp.)	Orange	33.6 (33.3)	2.35 (2.10)
(**4a**)	84	[f]	Yellow	47.2[e] (50.9)	4.90 (5.15)
(**4b**)	89	[f]	Yellow	39.4[e] (41.0)	4.25 (4.15)
(**5**)	64	[f]	Orange-red	51.3 (52.3)	6.10 (6.20)

[a] See Scheme 2. [b] These refer to purified compounds. [c] N, 7.9 (8.0%). [d] Decomposition led to a white sublimate. [e] Low carbon figures consistently obtained. [f] Not determined.

Table 2. I.r. data (carbonyl region, $\nu_{max.}$/cm^{-1}) for some carbene(carbonyl)metal complexes $[M(CO)_5(carbene)]$

Compound[a]	Solvent	A_1(2) band	*E* band	A_1(1) band
(**2a**)	CH_2Cl_2	2 038	1 910	1 979
(**2b**)	CH_2Cl_2	2 055	1 916, 1 907	1 975
(**2b**)	thf	2 045	1 911, 1 904	1 892
(**3a**)	CH_2Cl_2	2 060	1 943	1 975
(**3b**)	CH_2Cl_2	2 068	1 940	1 975
$[MgCl(thf)_n][Cr(CO)_5\{C(O)CH_2Ph\}]$[b]	thf	2 047	1 912	1 892
$[Cr(CO)_5\{C(OEt)CH_2Ph\}]$[b]	n-C_6H_{14}	2 065.7	1 947.4	1 961.3
$[W(CO)_5\{C(OEt)CH_2Ph\}]$[b]	n-C_6H_{14}	2 074.6	1 944.8	1 957.0

[a] See Scheme 2. [b] From ref. 10.

Table 3. Hydrogen-1 n.m.r. data (chemical shifts, δ/p.p.m.) for the new carbene(carbonyl)metal complexes at ambient temperature and 90 MHz

Compound[a]	Solvent	Ring CH_2	$CH_3C\mathit{H}_2$	$C\mathit{H}_3CH_2$	Aryl CH_n	Aromatic H	$Si(CH_3)_3$	NCH_3
(**1**)	CD_2Cl_2	3.20 (s)	3.60 (q)[b]	1.13 (t)[b]	—	—	—	—
(**2a**)[c]	CD_2Cl_2	1.86 (br), 3.74 (br)	—	—	4.42 (br s)	7.10 (m)	—	—
(**2b**)[c]	CD_2Cl_2	1.89 (m), 3.77 (m)	—	—	4.23 (s)	7.10 (m)	—	—
(**2c**)[c]	$CDCl_3$	1.94 (m), 3.91 (t)	—	—	4.24 (s)	7.05 (m)	—	—
(**3a**)	$CDCl_3$	—	5.05 (q)	1.44 (t)	5.54 (s)	7.07 (m)	—	—
(**3b**)	$CDCl_3$	—	4.88 (q)	1.25 (t)	4.39 (s)	7.15 (m)	—	—
(**4a**)	$CDCl_3$	2.42 (s)[d]	3.44 (q)	1.14 (t)	5.27 (s)	7.08 (m)	0.5 (s)	2.22 (s)
(**4b**)	$CDCl_3$	2.67 (s)[d]	3.65 (q)	1.38 (t)	5.00 (s)	7.30 (m)	0.35 (s)	2.51 (s)
(**5**)[e]	$CDCl_3$	—	1.70 (q)[f] 4.92 (q)[g]	1.14 (t)[f] 1.48 (t)[g]	4.58 (s)	7.02 (m)	—	—

[a] See Scheme 2. [b] $^3J(^1H^1H)$ 7.5 Hz. [c] Integration revealed the presence of 3 (**2a**), 4 (**2b**), and 7 (**2c**) moles thf mol^{-1}, respectively (but see analytical data). [d] Tmen. [e] These data are for ^1H-$\{^{31}P\}$. [f] CH_3CH_2P. [g] CH_3CH_2O.

Table 4. ^{13}C-$\{^1H\}$ N.m.r. chemical shifts (δ in p.p.m.) for some of the new carbene(carbonyl)metal complexes at ambient temperature and 90.55 MHz

			Aromatic C					
Compound[a]	Solvent	Aryl CH_n				C_{carb}	CO_{cis}	CO_{trans}
(**1**)[b]	CD_2Cl_2	—		—		238.3	201.7	
(**2a**)	CD_2Cl_2	70.4	137.0	131.6	127.4	330.5	220.3	225.8
(**2b**)	CD_2Cl_2	74.6	137.9	131.8	127.4	311.4	201.4	206.4
(**2a**)	$CDCl_3$	66.6	135.1	130.3	128.3	354.9	216.9	222.9
(**3a**)	C_6D_6	66.9	135.4	130.4	127.4	355.0	216.7	222.9
(**3b**)	$CDCl_3$	68.9	135.5	130.5	127.3	328.6	197.2	[c]
(**3b**)	C_6D_6	69.1	135.8	130.7	129.2	328.5	197.4	203.0

[a] See Scheme 2. [b] Others: δ 119.8 [q,$^1J(^{13}C-^{19}F)$ 308.5 Hz, CF_3], 49.0 ($\mathit{C}H_2CH_3$), 44.9 (CH_2 ring), and 13.3 ($CH_2\mathit{C}H_3$). [c] Not observed.

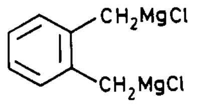
listed in Table 1. Selected carbonyl stretching frequencies, with assignments, are shown in Table 2. Hydrogen-1 and ^{13}C-$\{^1H\}$ n.m.r. spectroscopic data are listed in Tables 3 and 4, respectively.

Compound $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**) was obtained by oxidising *cis*-$[Mo(CO)_4(L^{Et})_2]$ with two equivalents of silver(I) trifluoromethanesulphonate in tetrahydrofuran (thf) at low temperature; an essentially quantitative precipitate of metallic silver was rapidly formed.

It is somewhat unexpected that the trifluoromethanesulphonato ligand should function as a covalently bound moiety in complex (**1**); the expected reaction (*cf.*, ref. 7 in Scheme 1) was that shown in equation (1) (*a*) leading to the ionic complex (**I**). It is possible that (**I**) was a transient intermediate along the pathway to complex (**1**), decomposing by the $^{-}OSO_2CF_3$/CO displacement process of equation (1) (*b*).

$$\begin{array}{l} cis\text{-}[\mathrm{Mo(CO)_4(L^{Et})_2}] + 2\mathrm{Ag[OSO_2CF_3]} \xrightarrow{(a)} \\ \qquad \underset{\mathbf{(I)}}{cis\text{-}[\mathrm{Mo(CO)_4(L^{Et})_2}][\mathrm{OSO_2CF_3}]_2} + 2\mathrm{Ag} \\ \qquad \Big\downarrow (b) \\ \qquad \underset{\mathbf{(1)}}{[\mathrm{Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2}]} + 2\mathrm{CO} \end{array} \tag{1}$$

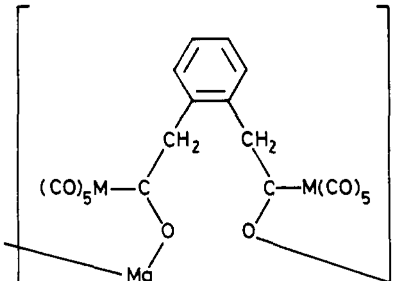
The Group 6 carbonyl $[M(CO)_6]$ (M = Cr or W) was allowed slowly to react with one equivalent of the bifunctional magnesium reagent $Mg[(CH_2)_2C_6H_4\text{-}o](thf)$ (M = Cr) [derived from



(**II**)

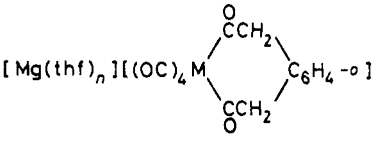
the di-Grignard reagent (**II**)[3]] or (**II**) (M = W) in thf at low temperature; removal of volatiles *in vacuo*, and subsequent extraction of the residue into dichloromethane gave yellow crystals of $[\{M(CO)_5[C(O)CH_2C_6H_4CH_2C(O)\text{-}o]M(CO)_5\}Mg(thf)_n]$ [M = Cr, *n* = 3 (**2a**); M = W, *n* = 4 (**2b**)]. A molybdenum analogue (**2c**) was obtained similarly (as for M = Cr), but was not as thoroughly characterised.

The evidence that complexes (**2**) have the structures proposed in Scheme 2 rests on the analytical and spectroscopic data of Tables 2—4. This does not, however, exclude the possibility that the complexes are polymers, containing a bridged, rather than a chelated, magnesium moiety, (**III**), although this is less likely because of their solubility in non-polar solvents. The assignment of five- or six-co-ordination for Mg^{2+} for the chromium (**2a**) (*n* = 3) and tungsten (**2b**) (*n* = 4) complexes, respectively is based primarily on the ^1H n.m.r. data (Table 3). It is consistent with (*a*) the greater moisture-sensitivity of the Cr complex, attributed to the co-ordinatively unsaturated Mg environment in (**2a**), and (*b*) the shorter $M\text{–}C_{carb}$ distance for the Cr than the W complex, and hence inadequate space between the two sets of *cis* carbonyls of (**2a**) for a $Mg(thf)_4$ moiety.

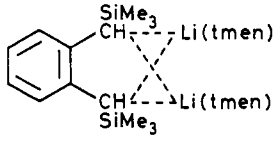


(**III**)

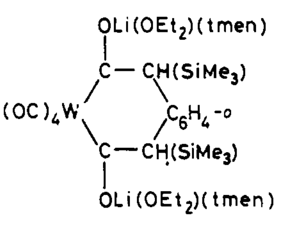
Complexes (**2**) appear to be the first examples of crystalline carbenemetal complexes having an O–Mg bond. It is noteworthy that they are thermally stable, and did not undergo further transformation to yield a chelating bis(carbene)metal complex (**IV**), as might have been expected by analogy with the reactions from $Li_2(C_6H_4\text{-}o)$ (see Scheme 1),[5] yielding the complex (**Va**) (M = Cr) or (**Vb**) (M = W). On the other hand, using the dilithio reagent (**VI**), related to (**II**), the bridging bis(carbene)dimetal complex $[W(CO)_5\{C[OLi(OEt_2)(tmen)]\text{-}CH(SiMe_3)C_6H_4CH(SiMe_3)]C[OLi(OEt_2)(tmen)]\text{-}meso\text{-}o\}W(CO)_5]$ (**4b**) was obtained. It is likely that steric effects prevented further intramolecular attack to yield (**VII**). The assignment of a *meso* configuration for the bridging ligand in complexes (**4**) is based on the ^1H n.m.r. equivalence of the two sets of benzylic substituents, H and $SiMe_3$ groups, respectively, Table 3.



(**IV**)



(**VI**)



(**VII**)

Comparison of the i.r. and ^{13}C n.m.r. spectra (Tables 2 and 4) of (*a*) complexes (**2a**) with (**Va**), and (*b*) (**2b**) with (**Vb**) shows that there are close similarities for each pair, for measurements in chlorinated hydrocarbons; however, complex (**2b**) in thf had the A_1 ν(CO) band considerably shifted (Table 2). This suggests that complexes (**2a**) and (**2b**) are correctly formulated as having covalent O–Mg bonds, whereas (**2b**) in thf is an ionic compound. This analysis is corroborated by noting that the i.r. spectra of (**2b**) in CH_2Cl_2 and thf were closely similar to those of the neutral carbenechromium(0) complex $[Cr(CO)_5\{C(OEt)CH_2Ph\}]$ and the carbene(pentacarbonyl)-chromate(0) in $[MgCl(thf)_n][Cr(CO)_5\{C(O)CH_2Ph\}]$, respectively.[10]

Each of the magnesium complexes (**2a**) and (**2b**), upon acid hydrolysis and treatment of the dichloromethane extract with $[Et_3O][BF_4]$, yielded yellow crystals of the appropriate bimetal(0) complex $[M(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}M(CO)_5]$ [M = Cr (**3a**) or W (**3b**)] containing a bridging bis(carbene) ligand. Similar reaction of the dimolybdenum–

magnesium complex (**2c**) gave decomposition products, consistent with the much lower thermal stability of carbene complexes $[M(CO)_5\{C(OEt)R\}]$ for M = Mo than for M = Cr or W.[2] Treatment of the chromium complex (**3a**) with an excess of triethylphosphine afforded $[\{Cr(CO)_4(PEt_3)\}\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}\{Cr(CO)_4(PEt_3)\}]$ (**5**).

The di(Group 6 metal)-magnesium or -lithium complexes (**2**) and (**4**) are evidently quite sterically hindered. This was demonstrated by the failure, under mild conditions, of the following reactions to proceed: (*a*) the ditungsten complex (**2b**) with $SiCl_2Me_2$, (*b*) the dichromium complex (**4a**) with $[Et_3O][BF_4]$, or (*c*) the dichromium complex (**2a**) or its ditungsten analogue (**2b**) with BBr_3 [this might have been expected to yield a bis(carbyne)bis(bromometal) complex[2]].

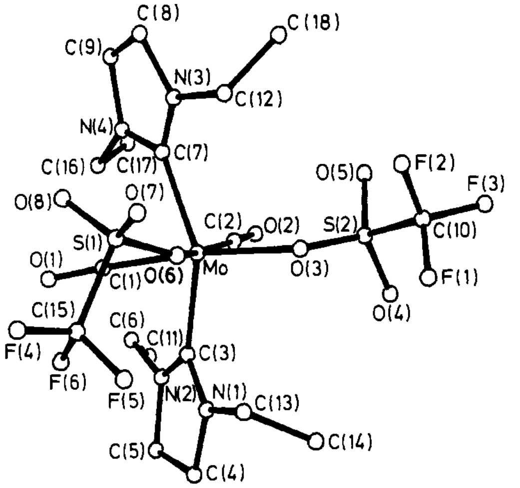


Figure 1. Molecular structure and atom-numbering scheme for $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**)

Structural Commentary.—(*a*) $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**). The molecular structure and atom-numbering scheme for complex (**1**) are shown in Figure 1. Intramolecular distances and angles are listed in Table 5 and fractional atomic co-ordinates in Table 6.

Each of the 1,3-diethylimidazolidin-2-ylidene rings (L^{Et}) is almost planar, and the two L^{Et} ligands are arranged so as to be nearly parallel. The molybdenum atom lies at the centre of a severely distorted octahedron, with C_{carb}–Mo–$C_{carb'}$ 134.9(2)°, presumably in order to minimise steric effects, the L^{Et} ligands being bent away from the bulky *cis* $OSO_2CF_3^-$ ligands and towards the *cis* carbonyls. The Mo atom and the four non-C_{carb} ligating atoms [C(1), C(2), O(3), and O(6)] are essentially co-planar, while the two C_{carb} atoms C(3) and C(7) are *ca.* 1.97 Å above and *ca.* 2.00 Å below this plane.

The mean of the Mo–C_{carb} bond lengths in the Mo^{II} complex (**1**), 2.154(5) Å, is significantly longer than the mean of Mo–CO, 1.961(6) Å, but by a closely similar increment to that found in the Mo^0 complex *trans*-$[Mo(CO)_4(L^{Me})_2]$ (**VIII**),[9] 2.232(2) and 2.001(2) Å. Other features of complexes (**1**) and (**VIII**) also show close correspondence; the short C_{carb}–N distances, the trigonal-planar nitrogen and C_{carb} environments, as well as the planar L^{Et} or L^{Me} rings and their mutually parallel arrangements. As for the last point, calculations on model octahedral *trans*-dicarbenemental complexes showed that an allene-like orthogonal placement of the two C_{carb} ligands is preferred.[11] The contrary findings for complexes (**1**) or (**VIII**) are consistent with the other data cited to indicate that there is little Mo $\overset{\dots}{-}$ C_{carb} multiple-bond character.

Table 5. Intramolecular bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**)

Mo–O(3)	2.173(3)	Mo–O(6)	2.181(4)	O(1)–C(1)	1.143(6)	O(2)–C(2)	1.139(8)
Mo–C(1)	1.953(5)	Mo–C(2)	1.970(6)	N(1)–C(3)	1.349(7)	N(1)–C(4)	1.486(7)
Mo–C(3)	2.157(5)	Mo–C(7)	2.152(5)	N(1)–C(13)	1.434(7)	N(2)–C(3)	1.340(7)
S(1)–O(6)	1.465(4)	S(1)–O(7)	1.426(5)	N(2)–C(5)	1.463(7)	N(2)–C(6)	1.466(8)
S(1)–O(8)	1.415(5)	S(1)–C(15)	1.816(8)	N(3)–C(7)	1.350(7)	N(3)–C(8)	1.484(7)
S(2)–O(3)	1.461(4)	S(2)–O(4)	1.421(6)	N(3)–C(12)	1.457(8)	N(4)–C(7)	1.339(7)
S(2)–O(5)	1.407(7)	S(2)–C(10)	1.824(7)	N(4)–C(9)	1.462(7)	N(4)–C(16)	1.469(7)
F(1)–C(10)	1.280(10)	F(2)–C(10)	1.278(10)	C(4)–C(5)	1.496(9)	C(6)–C(11)	1.392(13)
F(3)–C(10)	1.318(8)	F(4)–C(15)	1.305(8)	C(8)–C(9)	1.496(6)	C(12)–C(18)	1.517(10)
F(5)–C(15)	1.326(9)	F(6)–C(15)	1.314(9)	C(13)–C(14)	1.528(10)	C(16)–C(17)	1.508(10)
O(3)–Mo–O(6)	78.4(1)	O(3)–Mo–C(1)	166.1(2)	C(5)–N(2)–C(6)	117.7(5)	C(7)–N(3)–C(8)	111.9(4)
O(3)–Mo–C(2)	88.7(2)	O(3)–Mo–C(3)	105.3(2)	C(7)–N(3)–C(12)	128.4(4)	C(8)–N(3)–C(12)	119.1(5)
O(3)–Mo–C(7)	111.6(2)	O(6)–Mo–C(1)	89.1(2)	C(7)–N(4)–C(9)	113.0(4)	C(7)–N(4)–C(16)	129.3(5)
O(6)–Mo–C(2)	166.0(2)	O(6)–Mo–C(3)	110.3(2)	C(9)–N(4)–C(16)	117.2(5)	Mo–C(1)–O(1)	177.3(4)
O(6)–Mo–C(7)	101.9(2)	C(1)–Mo–C(2)	104.3(2)	Mo–C(2)–O(2)	177.8(5)	Mo–C(3)–N(1)	116.1(4)
C(1)–Mo–C(3)	73.2(2)	C(1)–Mo–C(7)	76.6(2)	Mo–C(3)–N(2)	135.0(4)	N(1)–C(3)–N(2)	108.6(4)
C(2)–Mo–C(3)	78.1(2)	C(2)–Mo–C(7)	77.8(2)	N(1)–C(4)–C(5)	102.8(4)	N(2)–C(5)–C(4)	103.5(5)
C(3)–Mo–C(7)	134.9(2)	O(6)–S(1)–O(7)	112.0(2)	N(2)–C(6)–C(11)	116.0(7)	Mo–C(7)–N(3)	116.7(4)
O(6)–S(1)–O(8)	113.6(3)	O(6)–S(1)–C(15)	102.0(3)	Mo–C(7)–N(4)	135.3(4)	N(3)–C(7)–N(4)	107.7(4)
O(7)–S(1)–O(8)	118.2(3)	O(7)–S(1)–C(15)	103.8(3)	N(3)–C(8)–C(9)	102.3(5)	N(4)–C(9)–C(8)	103.2(5)
O(8)–S(1)–C(15)	104.9(3)	O(3)–S(2)–O(4)	114.1(3)	S(2)–C(10)–F(1)	110.0(5)	S(2)–C(10)–F(2)	111.4(5)
O(3)–S(2)–O(5)	112.3(3)	O(3)–S(2)–C(10)	100.8(3)	S(2)–C(10)–F(3)	109.2(5)	F(1)–C(10)–F(2)	110.3(7)
O(4)–S(2)–O(5)	115.9(4)	O(4)–S(2)–C(10)	106.4(4)	F(1)–C(10)–F(3)	107.5(6)	F(2)–C(10)–F(3)	108.3(7)
O(5)–S(2)–C(10)	105.5(4)	Mo–O(3)–S(2)	134.2(2)	N(3)–C(12)–C(18)	111.2(5)	N(1)–C(13)–C(14)	111.1(5)
Mo–O(6)–S(1)	136.6(2)	C(3)–N(1)–C(4)	111.4(4)	S(1)–C(15)–F(4)	111.3(5)	S(1)–C(15)–F(5)	111.0(4)
C(3)–N(1)–C(13)	128.9(4)	C(4)–N(1)–C(13)	119.3(4)	S(1)–C(15)–F(6)	111.5(5)	F(4)–C(15)–F(5)	106.7(7)
C(3)–N(2)–C(5)	112.2(5)	C(3)–N(2)–C(6)	129.1(5)	F(4)–C(15)–F(6)	109.3(5)	F(5)–C(15)–F(6)	106.9(6)
				N(4)–C(16)–C(17)	112.9(5)		

Table 6. Fractional atomic co-ordinates (× 10^4) of the non-hydrogen atoms, with estimated standard deviations in parentheses, for $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	−33.8(5)	2 623.0(3)	3 702.2(2)	N(4)	−2 088(5)	568(3)	3 515(2)
S(1)	1 962(2)	2 039(1)	2 665(1)	C(1)	−1 366(5)	2 562(4)	2 962(2)
S(2)	1 992(2)	2 878(2)	5 031(1)	C(2)	−1 273(6)	2 643(4)	4 300(2)
F(1)	4 546(5)	3 526(5)	5 032(3)	C(3)	−1 014(6)	4 156(4)	3 569(2)
F(2)	4 354(5)	1 879(5)	5 023(2)	C(4)	−924(7)	5 969(4)	3 394(3)
F(3)	4 296(5)	2 727(5)	5 796(2)	C(5)	−2 449(7)	5 616(5)	3 286(3)
F(4)	1 981(6)	2 937(4)	1 664(2)	C(6)	−3 702(7)	3 927(6)	3 434(4)
F(5)	2 749(5)	3 909(4)	2 387(2)	C(7)	−814(5)	1 030(4)	3 674(2)
F(6)	523(5)	3 627(4)	2 158(2)	C(8)	−436(7)	−792(5)	3 616(3)
O(1)	−2 124(4)	2 564(3)	2 522(2)	C(9)	−2 008(7)	−581(5)	3 528(3)
O(2)	−1 951(5)	2 650(4)	4 659(2)	C(10)	3 927(8)	2 737(7)	5 223(3)
O(3)	1 800(4)	2 837(3)	4 394(2)	C(11)	−4 715(9)	4 355(7)	3 733(4)
O(4)	1 650(7)	3 868(5)	5 256(2)	C(12)	1 719(6)	366(4)	3 959(3)
O(5)	1 418(6)	1 989(5)	5 268(2)	C(13)	1 406(6)	4 980(5)	3 615(3)
O(6)	1 735(4)	2 493(3)	3 221(1)	C(14)	1 997(8)	5 641(6)	4 152(4)
O(7)	3 407(5)	1 715(4)	2 683(2)	C(15)	1 782(7)	3 183(6)	2 189(3)
O(8)	860(5)	1 348(3)	2 411(2)	C(16)	−3 520(6)	1 043(5)	3 410(3)
N(1)	−127(5)	4 965(3)	3 514(2)	C(17)	−4 360(7)	805(7)	3 889(3)
N(2)	−2 361(5)	4 515(4)	3 473(2)	C(18)	2 269(8)	−307(6)	4 489(3)
N(3)	177(5)	261(3)	3 785(2)				

Table 7. Intramolecular bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for $[W(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}W(CO)_5]$ (**3b**)

W(1)–C(1)	2.03(2)	W(1)–C(2)	2.02(2)	C(6)–O(12)	1.314(14)	C(7)–O(7)	1.12(2)
W(1)–C(3)	2.03(2)	W(1)–C(4)	2.06(2)	C(8)–O(8)	1.14(2)	C(9)–O(9)	1.15(2)
W(1)–C(5)	2.040(12)	W(1)–C(6)	2.160(12)	C(10)–O(10)	1.07(1)	C(11)–O(11)	1.10(2)
W(2)–C(7)	2.00(2)	W(2)–C(8)	1.988(12)	C(12)–C(13)	1.54(2)	C(12)–O(13)	1.319(14)
W(2)–C(9)	2.04(2)	W(2)–C(10)	2.10(2)	C(13)–C(14)	1.541(15)	C(14)–C(15)	1.37(2)
W(2)–C(11)	2.08(2)	W(2)–C(12)	2.150(12)	C(14)–C(19)	1.423(15)	C(15)–C(16)	1.38(2)
C(1)–O(1)	1.20(2)	C(2)–O(2)	1.15(2)	C(16)–C(17)	1.42(2)	C(17)–C(18)	1.34(2)
C(3)–O(3)	1.12(2)	C(4)–O(4)	1.12(2)	C(18)–C(19)	1.47(2)	C(19)–C(20)	1.43(2)
C(5)–O(5)	1.11(2)	C(6)–C(20)	1.52(2)	C(21)–C(22)	1.50(2)	C(21)–O(12)	1.439(14)
				C(23)–C(24)	1.47(2)	C(23)–O(13)	1.47(2)
C(1)–W(1)–C(2)	91.2(9)	C(1)–W(1)–C(3)	172.7(5)	W(1)–C(1)–O(1)	174(1)	W(1)–C(2)–O(2)	169(2)
C(1)–W(1)–C(4)	92.7(7)	C(1)–W(1)–C(5)	85.1(6)	W(1)–C(3)–O(3)	172(1)	W(1)–C(4)–O(4)	171(1)
C(1)–W(1)–C(6)	96.2(5)	C(2)–W(1)–C(3)	90.0(9)	W(1)–C(5)–O(5)	177(1)	W(1)–C(6)–C(20)	122.6(8)
C(2)–W(1)–C(4)	175.4(7)	C(2)–W(1)–C(5)	86.4(6)	W(1)–C(6)–O(12)	130.1(9)	C(20)–C(6)–O(12)	107(1)
C(2)–W(1)–C(6)	88.7(6)	C(3)–W(1)–C(4)	86.5(8)	W(2)–C(7)–O(7)	177(2)	W(2)–C(8)–O(8)	175(1)
C(3)–W(1)–C(5)	87.7(6)	C(3)–W(1)–C(6)	91.1(5)	W(2)–C(9)–O(9)	176(1)	W(2)–C(10)–O(10)	176(3)
C(4)–W(1)–C(5)	96.4(6)	C(4)–W(1)–C(6)	88.4(6)	W(2)–C(11)–O(11)	176(2)	W(2)–C(12)–C(13)	119.1(8)
C(5)–W(1)–C(6)	174.9(5)	C(7)–W(2)–C(8)	175.9(6)	W(2)–C(12)–O(13)	133.0(9)	C(13)–C(12)–O(13)	108(1)
C(7)–W(2)–C(9)	90.2(6)	C(7)–W(2)–C(10)	89.4(8)	C(12)–C(13)–C(14)	111.6(9)	C(13)–C(14)–C(15)	123(1)
C(7)–W(2)–C(11)	87.8(8)	C(7)–W(2)–C(12)	90.2(6)	C(13)–C(14)–C(19)	116(1)	C(15)–C(14)–C(19)	121(1)
C(8)–W(2)–C(9)	86.0(6)	C(8)–W(2)–C(10)	89.0(8)	C(14)–C(15)–C(16)	123(1)	C(15)–C(16)–C(17)	117(1)
C(8)–W(2)–C(11)	93.3(7)	C(8)–W(2)–C(12)	93.4(6)	C(16)–C(17)–C(18)	122(1)	C(17)–C(18)–C(19)	121(1)
C(9)–W(2)–C(10)	87(1)	C(9)–W(2)–C(11)	86.4(7)	C(14)–C(19)–C(18)	115(1)	C(14)–C(19)–C(20)	124(1)
C(9)–W(2)–C(12)	175.7(4)	C(10)–W(2)–C(11)	173(1)	C(18)–C(19)–C(20)	121(1)	C(6)–C(20)–C(19)	119(1)
C(10)–W(2)–C(12)	89(1)	C(11)–W(2)–C(12)	97.9(7)	C(22)–C(21)–O(12)	109(1)	C(24)–C(23)–O(13)	108(1)
				C(6)–O(12)–C(21)	122(1)	C(12)–O(13)–C(23)	120(1)

(*b*) $[W(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}W(CO)_5]$ (**3b**). The molecular structure and atom-numbering scheme for complex (**3b**) are shown in Figure 2. Intramolecular distances and angles are listed in Table 7 and fractional atomic co-ordinates in Table 8.

The geometry around each of the two tungsten atoms in complex (**3b**) is similar and close to octahedral. The bond lengths $W{-}C_{carb}$, $C_{carb}{-}O$, W–CO(*trans* to C_{carb}), and W–CO(*cis* to C_{carb}), the trigonal planar C_{carb} environment, and the *ca.* 120° $C_{carb}{-}O{-}Et$ angles are each unexceptional, and are close to those found in two other complexes which likewise have the general formula $[W(CO)_5\{C(OEt)R\}]$,[2] $[W(CO)_5\{C(OEt)(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)\}]$,[12] or $[W(CO)_5\{CCH_2CH(CHCPh_2)CH_2CH_2\}]$.[13]

The two tungsten-centred octahedra of complex (**3b**) are similarly orientated, and the angle between the respective mean planes through W(1), C(1), C(6), C(3), C(5), and W(2), C(12), C(7), C(8), C(9) is 14.3°. The dihedral angle between the mean planes through the two sets of C_{carb}, C, O, and W atoms is 64.5°.

The structural parameters within the $CH_2C_6H_4CH_2\text{-}o$ moiety are similar to those found in $[\{Mg(\mu\text{-}\sigma{:}\sigma'\text{-}CH_2C_6H_4CH_2\text{-}o)(thf)_2\}_3]$.[3]

Table 8. Fractional atomic co-ordinates (× 10⁴) of the non-hydrogen atoms, with estimated standard deviations in parentheses, for [$\overline{W(CO)_5\{C}(OEt)CH_2C_6H_4CH_2\overline{C(OEt)\text{-}o\}W}(CO)_5$] (**3b**)

Atom	*x*	*y*	*z*
W(1)	3 471.8(9)	7 314.4(8)	2 386.0(7)
W(2)	635.7(10)	12 902.6(8)	1 289.9(7)
C(1)	4 391(28)	7 969(19)	977(19)
C(2)	5 627(33)	6 742(28)	2 659(27)
C(3)	2 510(31)	6 485(22)	3 714(22)
C(4)	1 218(35)	7 918(28)	2 228(21)
C(5)	3 647(24)	5 817(18)	1 762(19)
C(6)	3 464(22)	8 833(18)	3 101(16)
C(7)	1 219(35)	11 374(24)	741(17)
C(8)	185(26)	14 458(19)	1 765(21)
C(9)	1 882(27)	13 663(24)	3(17)
C(10)	2 718(42)	12 624(29)	1 842(47)
C(11)	−1 240(40)	13 191(32)	563(25)
C(12)	−524(23)	12 094(19)	2 695(15)
C(13)	298(23)	10 977(19)	3 167(16)
C(14)	1 110(23)	11 211(18)	3 989(14)
C(15)	961(26)	12 269(21)	4 323(19)
C(16)	1 742(26)	12 483(21)	5 034(17)
C(17)	2 725(30)	11 550(27)	5 428(20)
C(18)	2 897(25)	10 495(22)	5 135(17)
C(19)	2 115(22)	10 263(19)	4 355(14)
C(20)	2 298(27)	9 129(20)	4 056(17)
C(21)	5 672(25)	9 593(21)	2 002(18)
C(22)	6 787(26)	10 382(21)	2 108(20)
C(23)	−2 958(29)	13 385(27)	3 033(24)
C(24)	−4 398(35)	13 411(35)	3 816(25)
O(1)	4 797(26)	8 351(20)	120(14)
O(2)	6 730(21)	6 392(22)	2 978(18)
O(3)	1 949(28)	5 939(20)	4 390(17)
O(4)	46(21)	8 203(22)	2 020(18)
O(5)	3 793(24)	4 981(19)	1 444(18)
O(7)	1 605(32)	10 531(23)	410(18)
O(8)	30(23)	15 329(20)	2 068(21)
O(9)	2 595(24)	14 138(21)	−689(15)
O(10)	3 790(18)	12 430(22)	2 102(17)
O(11)	−2 274(23)	13 313(27)	222(17)
O(12)	4 391(17)	9 635(14)	2 856(12)
O(13)	−1 898(16)	12 347(14)	3 287(12)

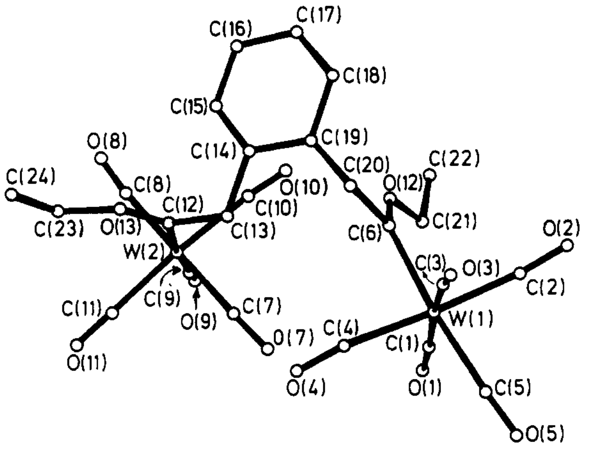


Figure 2. Molecular structure and atom-numbering scheme for [$\overline{W(CO)_5\{C}(OEt)CH_2C_6H_4CH_2\overline{C(OEt)\text{-}o\}W}(CO)_5$] (**3b**)

Conclusions

The following generalisations emerge from the present study. (*i*) The reagent Ag[OSO_2CF_3] can behave as a one-electron oxidant, introducing the ligand $OSO_2CF_3^-$ into the inner co-ordination sphere of octahedral d^4 Mo^{2+}; this was illustrated by the conversion of *cis*-[$Mo(CO)_4(L^{Et})_2$] into [$Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2$] (**1**). (*ii*) Lithium or magnesium derivatives of dicarbanions can be used as precursors to bridged bis(carbene)-bimetallic complexes; as demonstrated here by the conversion of the di-Grignard reagent *o*-$C_6H_4(CH_2MgCl)_2$ (**II**) (or its chloride-free equivalent) or *o*-$C_6H_4[CH(SiMe_3)Li(tmen)]_2$ (**VI**) into [{$M(CO)_5[C(O)CH_2C_6H_4CH_2C(O)\text{-}o]M(CO)_5$}Mg(thf)$_n$], (**2a**)—(**2c**), or [$M(CO)_5\{C[OLi(OEt_2)(tmen)]CH(SiMe_3)C_6H_4CH(SiMe_3)C[OLi(OEt_2)(tmen)]$-*meso*-*o*}$M(CO)_5$], (**4a**) or (**4b**), respectively; each of complexes (**2a**) or (**2b**) was in turn converted into [$M(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}M(CO)_5$], (**3a**) or (**3b**).

Further noteworthy points are the following. (*iii*) Compound (**1**) is the first stable *X*-ray characterised carbenemolybdenum(II) complex not containing an η^5 ligand.[2] (*iv*) Compounds (**3a**) and (**3b**) are extremely rare examples of bimetallic compounds having a bridging bis(carbene) ligand [see also refs. 5(*b*) and 14]. (*v*) Compound (**1**) is also a rare *X*-ray characterised carbene Group 6 metal(II) complex;[2] (*vi*) such data are likewise scant for a covalent sulphonatometal complex.[15] (*vii*) Compounds (**2**) appear to be the first crystalline carbenemetal complexes containing a covalently bound magnesium, C_{carb}–O–Mg. (*viii*) Compounds (**2**) or (**4**) are stable both to intramolecular elimination, or to reaction with a large electrophile such as $SiCl_2Me_2$.

Experimental

General procedures were similar to those described in earlier Parts.[1] The [$M(CO)_6$] samples were freshly sublimed before use.

Preparation of cis-*Dicarbonyl*-trans-*bis*(1,3-*diethylimidazolidin*-2-*ylidene*)-cis-*bis*(*trifluoromethanesulphonato*)*molybdenum*(II), (**1**).—A solution of silver trifluoromethanesulphonate (3.86 g, 15.0 mmol) in thf (50 cm³) was added dropwise to a stirred solution of *cis*-[$Mo(CO)_4(L^{Et})_2$][6] (3.45 g, 7.5 mmol in 50 cm³ thf) at −78 °C. The mixture was slowly (3 h) warmed to ambient temperature and briefly (1 h) heated to reflux temperature, filtered through Celite to remove the black coagulated precipitate of silver metal (1.47 g, 90%), concentrated to *ca.* one tenth of its volume, and then cooled (−25 °C) for several days to afford dark purple crystals of the *product* (**1**), which were removed by filtration, washed with diethyl ether (2 × 5 cm³), and dried *in vacuo*.

X-Ray diffraction quality crystals were grown by cooling (−25 °C) a saturated dichloromethane solution of complex (**1**) for several days.

Preparation of the Dimetal(O) *Complexes* [{$M(CO)_5[C(O)CH_2C_6H_4CH_2C(O)\text{-}o]M(CO)_5$}Mg(thf)$_n$].—(*a*) M = Cr, *n* = 3 (**2a**). Solid Mg[$(CH_2)_2C_6H_4$-*o*](thf)³ [1.11 g, 5.54 mmol (based on empirical formula)] was added in small portions to a cooled (−40 °C) solution of hexacarbonylchromium(0) (1.22 g, 5.55 mmol) in thf (80 cm³). The solution was set aside for 5 d at −15 °C, during which time it became yellow. The solution was then allowed to warm to ambient temperature. Volatiles were removed *in vacuo* to give a pale yellow solid. This was extracted into dichloromethene (10 cm^3) and the extract filtered. On cooling the filtrate to −30 °C, yellow crystals formed; removal of the supernatant liquor by decantation left yellow crystals which were washed with n-pentane and dried *in vacuo* to give the *product* (**2a**) (1.32 g, 61%). (The yield was significantly reduced when the initial reaction was carried out without cooling.)

(*b*) M = W, *n* = 4 (**2b**). Hexacarbonyltungsten(0) (2.60 g, 5.68 mmol) was added in small portions to a thf solution of o-$C_6H_4(CH_2MgCl)_2$ (55 cm^3, 0.055 mol dm^{-3}, 3.03 mmol) at ambient temperature. The solution immediately became yellow and turned brown after *ca.* 1 h. Volatiles were removed *in vacuo*. The resulting brown paste was extracted into dichloromethane (20 cm^3) and the extract filtered. The volume of the filtrate was reduced to *ca.* 5 cm^3 *in vacuo*. The filtrate was cooled to give yellow-brown crystals, from which the supernatant liquor was decanted. Washing the crystals with n-pentane and drying them *in vacuo* yielded yellow crystals of the *product* (**2b**) (1.63 g, 51%), which were recrystallised (CH_2Cl_2–C_5H_{12}).

(*c*) M = Mo, *n* = 4 (**2c**). A thf solution of $Mg[(CH_2)_2C_6H_4$-o](thf) (55 cm^3, 0.060 mol dm^{-3}, 3.3 mmol) was added to a solution of hexacarbonylmolybdenum(0) (1.76 g, 6.67 mmol) in thf (50 cm^3) at −10 °C. The mixture was set aside for 12 h at −30 °C, whereafter volatiles were removed at 25 °C, 10^{-1} Torr. The residue was extracted into chloroform (100 cm^3). The extract was concentrated to *ca.* 10 cm^3 *in vacuo* to yield crystals of the *product* (**2c**).

Preparation of the Complexes [M(CO)$_5${C(OEt)CH$_2$C$_6$H$_4$-CH$_2$C(OEt)-*o*}M(CO)$_5$].—(*a*) M = Cr (**3a**). A thf solution of o-$C_6H_4(CH_2MgCl)_2$ (17 cm^3, 0.067 mmol dm^{-3}, 1.14 mmol) was added to a suspension of $[Cr(CO)_6]$ (0.50 g, 2.27 mmol) in thf (20 cm^3) at ambient temperature. The solution turned yellow immediately and after 2 h had become brown. Volatiles were removed *in vacuo*. Thereafter, no attempt was made to exclude air from the reaction mixture. The residue, a brown paste, was extracted with 50-cm^3 portions of deionised water until the water ceased to acquire a yellow colour. The mixture was filtered, acidified with $[Et_3O][BF_4]$, and rapidly extracted into n-pentane (3 × 100 cm^3). The combined yellow extracts were dried (Na_2CO_3) and filtered. The filtrate was reduced *in vacuo* to *ca.* 30 cm^3. This orange solution was cooled to −30 °C to give orange crystals of the *product* (**3a**).

(*b*) M = W (**3b**). In a similar fashion from $[W(CO)_6]$ (1.50 g, 4.26 mmol) and o-$C_6H_4(CH_2MgCl)_2$ in thf (40 cm^3, 0.067 mol dm^{-3}, 2.68 mmol) orange crystals of the *product* (**3b**) (0.82 g, 44%) were obtained.

(*c*) M = Mo (*an unsuccessful attempt*). Similarly, complex (**2c**) (1.61 g) and $[Et_3O][BF_4]$ (0.66 g) in thf (30 cm^3) were mixed at −15 °C. After removal of solvent, i.r. and n.m.r. examination of the residue revealed unidentified products; there was no evidence for the presence of a Mo analogue of complexes (**3a**) or (**3b**).

Preparation of [M(CO)$_5${C[OLi(OEt$_2$)(tmen)]CH(SiMe$_3$)-C$_6$H$_4$CH(SiMe$_3$)C[OLi(OEt$_2$)(tmen)]-*meso*-*o*}M(CO)$_5$].—(*a*) M = Cr (**4a**). o-$C_6H_4[CH(SiMe_3)Li(tmen)]_2$[4] (0.70 g, 1.42 mmol) was added to a suspension of $[Cr(CO)_6]$ (0.62 g, 2.81 mmol) in OEt_2 (75 cm^3) at −15 °C, and the mixture was set aside at −15 °C for 12 h. This yielded yellow crystals of *complex* (**4a**) (1.30 g, 84%).

(*b*) M = W (**4b**). In a similar fashion, the dilithium reagent (1.04 g, 2.11 mmol) and $[W(CO)_6]$ (1.48 g, 4.21 mmol) in OEt_2 (150 cm^3) afforded the yellow crystalline complex (**4b**) (3.16 g, 89%).

Preparation of [Cr(CO)$_4$(PEt$_3$)}{C(OEt)CH$_2$C$_6$H$_4$CH$_2$-C(OEt)-*o*}{Cr(CO)$_4$(PEt$_3$)}] (**5**).—Triethylphosphine (0.8 cm^3, a considerable excess) was added to a solution of complex (**3a**) (1.20 g) in n-hexane (100 cm^3) at ambient temperature, and the solution was heated under reflux for 6 h, with an accompanying colour change from orange to orange-red. The volume of solution was reduced to *ca.* 20 cm^3 *in vacuo*. Cooling to −30 °C produced a wax. Recrystallisation (n-C_6H_{14}, 5 cm^3, −78 °C) yielded the orange-red crystals of the *product* (**5**) (0.95 g, 64%).

Lack of Reaction.—(*a*) *Between complex* (**2b**) *and* $SiCl_2Me_2$ *at* 25 °C. Dichlorodimethylsilane (0.13 cm^3, 0.14 g, 1.08 mmol) was added to a solution of complex (**2b**) (0.73 g, 0.65 mmol) in dichloromethane (30 cm^3). The solution darkened slightly and a trace of white precipitate gradually (*ca.* 10 min) formed. After 15 h the mixture was filtered. Volatiles were removed from the filtrate *in vacuo* to give a yellow-brown solid, the ^1H n.m.r. spectrum (in $CDCl_3$) of which showed only peaks assignable to complex (**2b**). The solid was dissolved in CH_2Cl_2 and reprecipitated by careful addition of n-pentane to give complex (**2b**) (0.40 g, 55%).

(*b*) *Between complex* (**2a**) *or* (**2b**) *and* BBr_3 *at* −15 °C. Treatment of the chromium complex (**2a**) (0.96 g) with BBr_3 (0.8 cm^3) in n-pentane (10 cm^3) at −15 °C for 0.5 h, followed by removal of volatiles *in vacuo* and recrystallisation of the residue, gave orange crystals of (**2a**). Similarly, orange crystalline complex (**2b**) was recovered from a CH_2Cl_2 solution, when (**2b**) (2.85 g) and BBr_3 (0.64 cm^3, 1.65 g) in n-C_5H_{12} at −15 °C were treated as in (*a*).

(*c*) *Between complex* (**4a**) *and* $[Et_3O][BF_4]$. The tetrafluoroborate (0.12 g) in CH_2Cl_2 (5 cm^3) was added slowly to a solution of (**4a**) (0.45 g) in the same solvent (10 cm^3) at −15 °C, with concomitant colour change from yellow to orange. The solution was set aside at −15 °C for 12 h, whereafter volatiles

Table 9. The crystal data and refinement parameters for [Mo(CO)$_2$(L^{Et})$_2$(OSO$_2$CF$_3$)$_2$] (**1**) and [W(CO)$_5${C(OEt)CH$_2$C$_6$H$_4$CH$_2$-C(OEt)-*o*}W(CO)$_5$] (**3b**)

Compound	$C_{18}H_{28}F_6MoN_4O_8S_2$	$C_{24}H_{18}O_{12}W_2$
M	702.5	866
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	9.501(3)	8.841(2)
b/Å	12.701(3)	11.836(2)
c/Å	23.239(4)	13.727(3)
α/°	—	82.18(1)
β/°	99.97(3)	77.23(1)
γ/°	—	80.80(1)
U/Å^3	2 762	1 375
D_c/g cm^{-3}	1.69	2.09
F(000)	1 424	812
μ/cm^{-1}	6.9	89.2
λ(Mo-K_α)/Å	0.710 69	0.710 69
Size/mm	0.20 × 0.15 × 0.12	0.30 × 0.20 × 0.05
Reflections measured	4 865	4 844
No. of observed reflections [$I > \sigma(I)$]	3 278	3 666
No. of parameters refined	352	343
R	0.046	0.095
R'	0.049	0.124
Maximum shift/e.s.d.	0.06	0.3
$2\theta_{max.}$	50	50
Z	4	2
Weighting	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
Residual peaks (e Å^{-3}) near M	0.8	4.0

were removed *in vacuo*. Recrystallisation (OEt_2, −30 °C) afforded yellow crystals of complex (**4a**).

Crystal Data and Structural Solutions for $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$ (**1**) *and* $[\overline{W(CO)_5\{C}(OEt)CH_2C_6H_4CH_2\overline{C(OEt)\text{-}o\}W}(CO)_5]$ (**3b**).—The crystal data and refinement parameters for these two complexes are given in Table 9.

The appropriate crystal of complex (**1**) or (**3b**) was sealed in a Lindemann capillary under argon and mounted on an Enraf-Nonius CAD4 diffractometer. Unique data were measured by an ω–2θ scan with a maximum scan time of 2 min. Data were corrected for Lorentz polarisation (L_p) effects and for absorption. Reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$.

Each structure was solved by routine heavy-atom methods and non-H atoms refined anisotropically by full-matrix least-squares methods. For (**1**), hydrogen atoms were placed at calculated positions (C–H 1.08 Å) and held fixed with a common B_{iso} of 6.0 Å^2 and for (**3b**) hydrogen atoms were omitted.

All calculations were performed on a PDP11/34 computer, using the Enraf-Nonius SDP-Plus program package.

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References

1 Part 20, P. B. Hitchcock, M. F. Lappert, S. A. Thomas, A. J. Thorne, A. J. Carty, and N. J. Taylor, *J. Organomet. Chem.*, 1986, **315**, 27.
2 *cf.*, 'Transition Metal Carbene Complexes,' eds. K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, and K. Weiss, Verlag Chemie, Weinheim, 1983.
3 M. F. Lappert, T. R. Martin, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 1959.
4 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 14.
5 (*a*) E. O. Fischer, W. Röll, U. Schubert, and K. Ackermann, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 611; (*b*) E. O. Fischer, W. Röll, N. H. T. Huy, and K. Ackermann, *Chem. Ber.*, 1982, **115**, 2951.
6 Part 9, M. F. Lappert, P. L. Pye, and G. M. McLaughlin, *J. Chem. Soc., Dalton Trans.*, 1977, 1272.
7 M. F. Lappert, R. W. McCabe, J. J. MacQuitty, P. L. Pye, and P. I. Riley, *J. Chem. Soc., Dalton Trans.*, 1980, 90.
8 Part 10, M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 1283.
9 Part 17, M. F. Lappert, P. L. Pye, A. J. Rogers, and G. M. McLaughlin, *J. Chem. Soc., Dalton Trans.*, 1981, 701.
10 D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 1971, **15**, 247.
11 R. Hoffmann, C. N. Wilker, and O. Eisenstein, *J. Am. Chem. Soc.*, 1982, **104**, 632.
12 E. O. Fischer, F. J. Gammel, J. O. Besenhard, A. Frank, and D. Neugebauer, *J. Organomet. Chem.*, 1980, **191**, 261.
13 J. C. Daran and Y. Jeannin, *Acta Crystallogr., Sect. B*, 1982, **36**, 1392.
14 E. O. Fischer, D. Wittmann, D. Himmelreich, and D. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 444; W. A. Herrmann, J. Plank, J. L. Hubbard, B. B. Kriechbaum, W. Kalcher, B. Koumbouris, G. Ihl, A. Schäfer, M. L. Ziegler, H. Pfisterer, C. Pahl, J. L. Atwood, and R. D. Rogers, *Z. Naturforsch., Teil B*, 1983, **38**, 1392.
15 F. A. Cotton, A. H. Reid, and W. Schwotzer, *Inorg. Chem.*, 1985, **24**, 3965; S. Komiya, J. C. Huffman, and J. K. Kochi, *ibid.*, 1977, **16**, 2138; O. P. Anderson and A. B. Packard, *ibid.*, 1979, **18**, 1129.

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