Reactions of Metallabromoalkanes $[M\{(CH_2)_nBr\}(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W, *n* = 3 or 4) with Transition Metal Anions. Dimetalla-alkane and Cyclic Carbene Complex Formation. Crystal and Molecular Structures of $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ and $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2\{\overline{C\text{-}O\text{-}(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)]$ †

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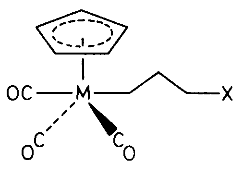
Reaction of $Br[CH_2]_3Br$ with excess $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ leads to the spectroscopically characterised $[(\eta\text{-}C_5H_5)(OC)_3MoMo(CO)_2\{\overline{C\text{-}O\text{-}(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)]$ containing a cyclic carbene ligand. This species is formed *via* the intermediate $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$. The related complex $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2\{\overline{C\text{-}O\text{-}(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)]$ is formed during reaction of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ with $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ and has been characterised by *X*-ray crystallography. This molecule crystallises as maroon needles, monoclinic, $a = 8.017(6)$, $b = 15.026(16)$, $c = 7.981(3)$ Å, $\beta = 92.88(5)°$; *R* converged to 0.0645 for 1 256 independent reflections for which $I/\sigma(I) > 3.0$. The molecule contains a Mo–W single bond of 3.239(4) Å, the cyclic carbene ligand is bonded to tungsten rather than molybdenum and is situated *trans* to the Mo–W bond regarding the co-ordination polyhedra of both metals as square-based pyramidal. Reaction of $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ with $I[CH_2]_nI$ leads to $[(\eta\text{-}C_5H_5)(OC)_3M\{(CH_2)_n\}M(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo, *n* = 4; M = W, *n* = 3 or 4). The structure of one member of this class $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ has been determined by *X*-ray crystallography. The molecule crystallises as yellow elongated plates, triclinic, $a = 6.978\,2(16)$, $b = 7.005\,1(10)$, $c = 11.315\,0(25)$ Å, $\alpha = 102.378(15)$, $\beta = 95.806(18)$, $\gamma = 105.909(15)°$; *R* converged to 0.0263 for 1 646 independent reflections. The molecule contains a crystallographically imposed centre of symmetry at the centre of the tetramethylene chain and the molecular structure may be compared to that of the known $[(\eta\text{-}C_5H_5)(OC)_2Fe\{(CH_2)_4\}Fe(CO)_2(\eta\text{-}C_5H_5)]$.

Several reactions of α,ω-dihalogenoalkanes with transition metal complex anions have been reported over the years.[1-5] The simplest are those in which a single halide is replaced so forming metallahalogenoalkanes such as (1)—(4).[2] In many other cases excess or residual metal anion reacts further; the second anion may either replace the remaining halide group resulting in dimetalla-alkanes such as (5) or (6) [1] or attack at the first metal resulting in metal–metal bond formation and eventual formation of carbene complexes such as (7).[4]

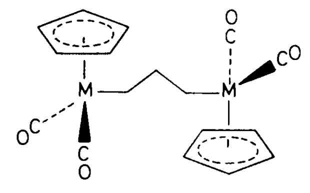
We have recently reported a reaction of 1,3-di-iodopropane with $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ in which displaced iodide attacks the initially formed complex (2) producing the cyclic carbene (8).[6,7] This paper describes further reactions of metallahalogenoalkanes of type (1)—(4) and illustrates the fine balance that determines which product is actually formed. Certain aspects of this work have been the subject of a preliminary communication.[6]

Results and Discussion

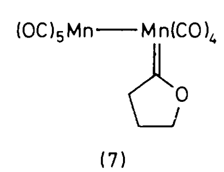
The metallahalogenoalkane complexes (1)—(4) react with iodide ion in tetrahydrofuran (thf) or 1,2-dimethoxyethane at reflux to form the cyclic carbene complexes (8) or (9) and a mechanism has been suggested involving initial attack of the halide ion



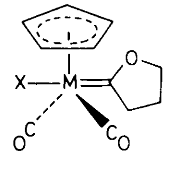
(1) M = Mo, X = Br
(2) M = Mo, X = I
(3) M = W, X = Br
(4) M = W, X = I



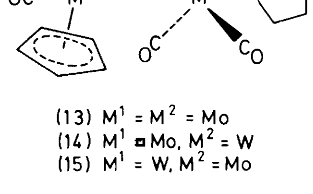
(5) M = Fe
(6) M = Ru



(7)



(8) M = Mo, X = I
(9) M = W, X = I
(10) M = Mo, X = CN
(11) M = Mo, X = SPh
(12) M = W, X = CN



(13) M¹ = M² = Mo
(14) M¹ = Mo, M² = W
(15) M¹ = W, M² = Mo

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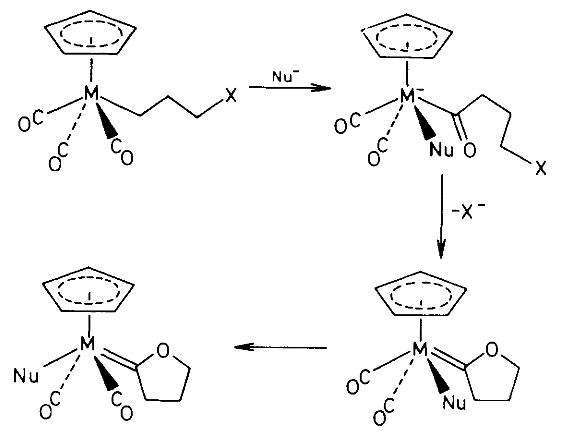
† μ-Tetramethylene-bis[tricarbonyl(η-cyclopentadienyl)molybdenum] and 1,1,1,2,2-pentacarbonyl-1,2-bis(η-cyclopentadienyl)-2-(1′-oxacyclopent-2′-ylidene)molybdenumtungsten(*Mo*–*W*).

Supplementary data available (No. SUP 23786, 32 pp.): isotropic and anisotropic thermal parameters, predicted H-atom positions, observed structure amplitudes and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme. Nu^- = nucleophile such as I^-, CN^-, or SPh

at the metal atom and alkyl ($^-[CH_2]_3X$) migration to an adjacent carbonyl group followed by a ring-closing step in which the nucleophilic acyl oxygen displaces X^- from the alkyl group so forming the carbene complex [6,7] (Scheme). In a similar fashion complexes (10)—(12) are available through treatment of the appropriate nucleophilic reagent KCN or NaSPh with (1) or (3).[7] We now report that transition metal anions may induce similar cyclisation reactions.

Solutions of the anion $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ produced from the dimer $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ by sodium amalgam cleavage are virtually colourless but are yellow-orange from reaction of $Na(C_5H_5)$ with $[Mo(CO)_6]$. We have not investigated the causes of this difference. Reactions of the anion with alkyl halides (*e.g.* MeI, $PhCH_2Br$) in thf result in yellow solutions containing the alkyl $[MoR(CO)_3(\eta\text{-}C_5H_5)]$. However, reaction with $Br[CH_2]_3Br$ proceeds to a bright red solution which after rapid chromatography provides two compounds, yellow $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (1) and the red dimolybdenum species (13). This complex is a crystalline compound which readily undergoes a complex reaction in solution producing $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ as the only recognisable product.

The ^1H n.m.r. spectrum of (13) displays two cyclopentadienyl signals and a triplet–triplet–quintet structure qualitatively very similar to those of related complexes (8)—(12). This, together with the two cyclopentadienyl signals, strongly suggest a structure containing a 2-oxacyclopentylidene ligand terminally bound to a molybdenum atom. A single cyclopentadienyl signal would suggest a symmetrically bridging carbene but would require (in order to satisfy the 18-electron rule) a bridging carbonyl. This is quite clearly not evident in the i.r. spectrum although a signal at 1 853 cm^{-1} is assignable to a semi-bridging carbonyl. The presence of two cyclopentadienyl signals suggests a static structure at room temperature and this is reinforced by the ^{13}C n.m.r. spectrum. The high-frequency signal at δ 316.2 p.p.m. is assignable to a terminally bonded carbene and three sharp signals (δ 236.2, 230.1, and 228.1) with approximate relative intensities 1 : 2 : 2 are assigned to a carbonyl (*trans* to Mo–Mo) and to two inequivalent pairs of mutually *trans* carbonyls.[8]

The yield of (13) is maximised by using an excess of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and minimised by an excess of $Br[CH_2]_3Br$. Formation of the dimetal species is suggested to proceed *via* attack of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ upon initially formed $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (1) to form an intermediate anionic acyl which undergoes elimination of Br^- to form the carbene ligand in a manner similar to the formations of (7) [9] and (8)—(12) [6,7] (Scheme).

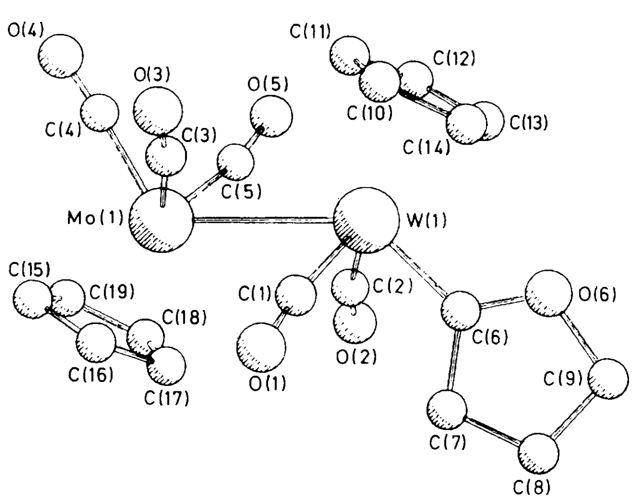


Figure 1. The molecular structure with atom labelling for $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$ (14)

A synthetically useful reaction of the dimer $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ is its ability to undergo thermal decarbonylation to the compound $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ containing a Mo≡Mo bond.[10,11] Analogous reaction of complex (13) generating a species containing both a Mo≡Mo bond and a carbene ligand would suggest interesting possibilities but in the event a facile reaction occurs in toluene upon warming so that formation of $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ from (13) is complete by the time reflux temperature has been reached. This is considerably more rapid than the corresponding decarbonylation of $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ but not a synthetically useful procedure. For these reasons we have not been able to study variable-temperature n.m.r. spectra of (13) with the aim of observing possible reversible migration of carbene along the Mo–Mo bond.

Our suggestions for the mechanism of formation of (13) are reinforced by the observation of an interesting heterodimetal species from the reaction of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ with (1). The only product isolated is complex (14), in which the carbene ligand is bonded to tungsten rather than molybdenum [as in the hypothetical complex (15)] and which is somewhat less prone to decomposition than (13). Inspection of the ^{13}C n.m.r. spectrum quite clearly shows the carbene ligand to be bonded to tungsten since the high-frequency signal (δ 290.4 p.p.m.) assigned to the carbene atom displays ^{183}W satellites [J(WC) 173 Hz]. There are also three signals assignable to carbonyl carbon atoms in approximate ratios 2 : 2 : 1. One of the more intense shows clear ^{183}W satellites [J(WC) 120 Hz] demonstrating the presence of mutually *trans* carbonyl groups in equivalent environments. The other two signals are assigned to the $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragment and show the expected intensity ratios and positions for *cis* and *trans* carbonyl ligands in a $[MoR(CO)_3(\eta\text{-}C_5H_5)]$ molecule.[8]

Physical and spectroscopic data for complexes (13) and (14) are presented in Tables 1 and 2.

Complex (14) has been the subject of an *X*-ray diffraction study.

The structure of the molecule is illustrated in Figure 1 with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables 3 and 4. The molecule comprises two fragments, each involving a metal, cyclopentadienyl, and three unidentate ligands joined together by a long metal–metal bond. The co-ordination polyhedra, each of which can be described as having the

Table 1. Analytical [a] and other data for the new compounds

Complex	Colour	$\nu_{max.}$(CO)/cm^{-1}	M.p. (°C)	Analysis (%) C	Analysis (%) H
(13)	Maroon	[b] 1 977m, 1 918m, 1 897s, 1 853w	215 (decomp.)	42.5 (42.9)	3.2 (3.0)
(14)	Maroon	[b] 1 976m, 1 913m, 1 893s, 1 847w	168 (decomp.)	37.8 (37.4)	3.0 (2.6)
(18)	Yellow	[c] 2 015m, 1 915s	150 (decomp.)	31.8 (32.2)	2.3 (2.3)
(19)	Yellow	[c] 2 015m, 1 915s	164 (decomp.)	32.8 (33.2)	2.2 (2.5)
(20)	Yellow	[c] 2 015m, 1 919s	150—152 (decomp.)	43.7 (44.0)	3.5 (3.3)

[a] Calculated values are given in parentheses. [b] In methylcyclohexane. [c] In dichloromethane.

Table 2. Hydrogen-1 and carbon-13 n.m.r. data for the new complexes; solvent is $CDCl_3$ unless stated otherwise, *J* values are in Hz

Complex	^{1}H	^{13}C
(13)	5.35 (s, 5 H, C_5H_5), 5.32 (s, 5 H, C_5H_5), 4.62 [t, 2 H, OCH_2, *J*(HH) 7], 3.31 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 1.92 [quintet, 2 H, CH_2, *J*(HH) 7]	316.2 (Mo=C), 236.2 (CO *trans* to Mo–Mo), 230.1 (2 CO), 228.1 (2 CO), 97.0 (C_5H_5), 92.0 (C_5H_5), 80.6 (OCH_2), 56.3 (Mo*C*CH_2), 22.8 (CH_2)
(14)	5.39 (s, 5 H, C_5H_5), 5.35 (s, 5 H, C_5H_5), 4.51 [t, 2 H, OCH_2, *J*(HH) 7], 3.00 [t, 2 H, $WCCH_2$, *J*(HH) 7], 1.90 [quintet, 2 H, CH_2, *J*(HH) 7]	290.4 [W=C, *J*(WC) 173], 236.2 [Mo–CO *trans* to Mo–W], 226.6 (2 MoCO), 220.3 [2 WCO, *J*(WC) 120], 96.1 (C_5H_5), 92.3 (C_5H_5), 79.9 (OCH_2), 57.4 (W*C*CH_2), 23.8 (CH_2)
(18)	5.26 (s, 10 H, $2C_5H_5$), 1.69 (m, 2 H, CH_2), 1.45 (m, 4 H, WCH_2)	
(19)	* 4.48 (s, 10 H, $2C_5H_5$), 1.77 (m, 4 H, CH_2), 1.67 (m, 4 H, 2 WCH_2)	* 91.9 (C_5H_5), 44.3 (CH_2), −9.7 (WCH_2)
(20)	* 4.50 (s, 10 H, 2 C_5H_5), 1.83 (m, 4 H, CH_2), 1.68 (m, 4 H, 2 $MoCH_2$)	92.8 (C_5H_5), 42.6 (CH_2), 2.3 ($MoCH_2$)

* In C_6D_6.

Table 3. Bond lengths (Å) and bond angles (°) with estimated standard deviations for $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$ (14) [a]

(*a*) Bond lengths

W(1)–C(1)	1.98(4)	O(2)–C(2)	1.15(6)	Mo(1)–C(5)	1.91(5)	W(1) · · · C(3)	3.18(4)
W(1)–C(2)	1.96(5)	O(6)–C(6)	1.32(3)	Mo(1)–C(15)	2.26(4)	W(1) · · · C(5)	3.10(5)
W(1)–C(6)	1.977(17)	C(6)–C(7)	1.46	Mo(1)–C(16)	2.21(4)	Mo(1) · · · C(1)	3.17(4)
W(1)–C(10)	2.44(3)	C(7)–C(8)	1.52	Mo(1)–C(17)	2.27(4)	Mo(1) · · · C(2)	3.18(5)
W(1)–C(11)	2.48(3)	C(8)–C(9)	1.50(6)	Mo(1)–C(18)	2.35(4)		
W(1)–C(12)	2.41(3)	C(9)–O(6)	1.53(6)	Mo(1)–C(19)	2.34(4)	C–C (ring 1) [b]	1.40
W(1)–C(13)	2.32(3)	W(1)–Mo(1)	3.239(4)	O(3)–C(3)	1.21(6)	C–C (ring 2) [c]	1.40
W(1)–C(14)	2.34(3)	Mo(1)–C(3)	1.99(4)	O(4)–C(4)	1.15(5)		
O(1)–C(1)	1.13(6)	Mo(1)–C(4)	1.97(4)	O(5)–C(5)	1.25(7)		

(*b*) Bond angles

Mo(1)–W(1)–C(1)	70.3(12)	W(1)–C(6)–C(7)	126.0(19)	C(3)–Mo(1)–C(4)	79.6(16)
Mo(1)–W(1)–C(2)	70.5(13)	O(6)–C(6)–C(7)	109.9(23)	C(3)–Mo(1)–C(5)	107.6(18)
Mo(1)–W(1)–C(6)	136.1(5)	C(6)–C(7)–C(8)	105.7	C(4)–Mo(1)–C(5)	75.1(18)
C(1)–W(1)–C(2)	99.5(18)	C(7)–C(8)–C(9)	104(3)	Mo(1)–C(3)–O(3)	171(4)
C(1)–W(1)–C(6)	84.4(13)	C(8)–C(9)–O(6)	102(3)	Mo(1)–C(4)–O(4)	174(3)
C(2)–W(1)–C(6)	79.5(14)	C(9)–O(6)–C(6)	111(3)	Mo(1)–C(5)–O(5)	169(4)
W(1)–C(1)–O(1)	172(4)	W(1)–Mo(1)–C(3)	70.5(12)	C–C–C (ring 1) [b]	108.0
W(1)–C(2)–O(2)	168(4)	W(1)–Mo(1)–C(4)	121.9(11)	C–C–C (ring 2) [c]	108.0
W(1)–C(6)–O(6)	124.1(17)	W(1)–Mo(1)–C(5)	68.7(14)		

[a] Values quoted without estimated standard deviations were constrained at the quoted magnitudes during refinement. [b] Mean value for C_5H_5 ring C(10)—C(14). [c] Mean value for C_5H_5 ring C(15)—C(19).

shape of an irregular four-legged stool (square-based pyramid), are mutually staggered. The whole molecule has approximate C_s symmetry with the two metal atoms, one carbonyl [C(4)-O(4)], and the carbene ligand lying in this approximate plane; however, the orientation of this plane is not such as might raise the space group symmetry to $P2_1/m$. The molybdenum–tungsten bond length of 3.239 Å is comparable to the metal–metal distances in $[\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W),[12] to which compounds the overall molecular conformation is similar. Further detailed discussion of the molecular geometry is necessarily limited by the constraints applied during refinement. However, it may be noted that neither cyclopentadienyl ring is entirely symmetrically bonded, that to tungsten adopting a 'cocked-hat' conformation. The tungsten-carbon bond to the carbene [W(1)–C(6)] and the adjacent C(6)–O(6) lengths indicate some electron delocalisation, as does the coplanarity of the tungsten atom with atoms O(6), C(6), and C(7). The tungsten-carbon bond is markedly shorter than the comparable molybdenum-carbon bond in the related complex $[MoI(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$[6,7] and more

Table 4. Details of planar fragments of the two molecules. The equations of the mean planes are of the form: $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to orthogonal crystal axes a, b^*, c'. Deviations (Å) of atoms from the mean planes are given in square brackets

	p	*q*	*r*	*d*
(*a*) $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$ (14)				
Plane A: C(10)—C(14) R.m.s. deviation 0.00 Å	0.2742	−0.8024	0.5301	3.5866
[W(1) −2.074]				
Plane B: C(15)—C(19) R.m.s. deviation 0.00 Å	0.2027	−0.7697	0.6053	−1.8766
[Mo(1) 1.947]				
Plane C: O(6), C(6), C(7), C(9) R.m.s. deviation 0.013 Å	−0.7904	0.2545	0.5573	0.5654
[W(1) 0.113, C(8) −0.410]				
Plane D: W(1), O(6), C(6), C(7) R.m.s. deviation 0.004 Å	−0.7645	0.2859	0.5778	0.7449
[C(8) −0.334, C(9) 0.092]				

Selected angles (°) between planes: A–B 6.2
A–C 97.2
B–C 91.1

	p	*q*	*r*	*d*
(*b*) $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ (20)				
Plane: C(4)—C(8) R.m.s. deviation 0.003 Å	0.2204	−0.8341	0.5058	2.1857
[C(4) −0.004, C(5) 0.004, C(6) −0.001, C(7) −0.001, C(8) 0.004, Mo(1) −2.019]				

Torsion angle (°): Mo(1)–C(9)–C(10)–C(10′) +174.4

comparable to various metal–carbon (cyclic carbene) lengths in other related complexes.[13–16] The principal non-planarity of the carbene ring involves a displacement of atom C(8) (0.41 Å) from the mean plane. The carbonyl ligands are all close to linear (within the rather high e.s.d.s) but four are 'semi-bridging' with short contacts between the carbon atom and the other metal of 3.10—3.18 Å.

From a chemical point of view the significant feature of this structure is that the carbene is bonded to the tungsten atom. Of relevance to this observation is the reaction of $[MnMe(CO)_5]$ with $[Re(CO)_5]^-$ followed by alkylation which leads to complex (16) in which the carbene ligand is bonded to rhenium rather than manganese.[9] The authors feel that ligand transfer takes place after alkylation, corresponding in the present case to carbene transfer after ring closure and bromide loss. We find that the tungsten complex (3) does not react with $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ to form (14). This removes the possibility of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ reacting with complex (1) to eliminate $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ so forming the tungsten alkyl (3) which subsequently reacts with the molybdenum anion thus generated, leading ultimately to (14). This observation does not preclude ligand transfer in an intermediate acyl resulting from attack of the tungsten anion upon (1). With our data it is not possible to say whether ligand transfer occurs before or after cyclisation, indeed both processes may conceivably occur.

Unfortunately, reaction of (1) with transition metal nucleophiles does not lead to a general synthetic method for heterodimetallic carbene complexes, thus reaction with $[Mn(CO)_5]^-$ leads exclusively to the dimanganese species (7)[3,4] while the strong nucleophile $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ produces (5),[1] both reactions proceeding by elimination of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$.

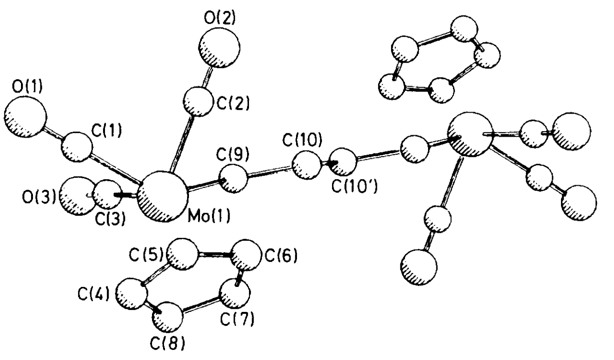
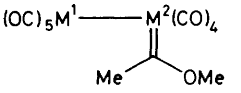
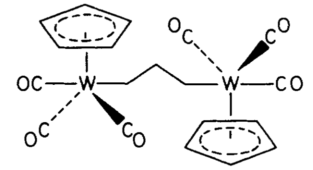


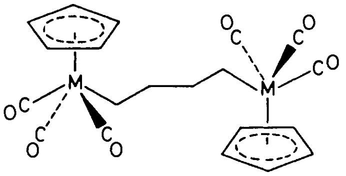
Figure 2. The molecular structure with atom labelling for $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ (20). The molecule possesses an inversion centre at the centre of the C(10)–C(10′) bond



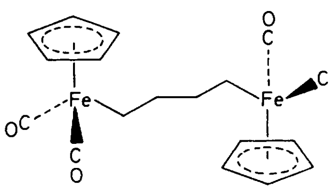
(16) M¹ = Mn, M² = Re
(17) M¹ = Re, M² = Mn



(18)



(19) M = W
(20) M = Mo



(21)

Neither does the anion $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ react with $[W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (3) at the tungsten atom. Instead, bromide is replaced and the dimetallapropane (18) is isolable in moderate yield. This is an extremely insoluble pale yellow complex which contrasts with the ready solubility of the related iron species (5). The i.r. spectrum is qualitatively very similar to that of any other species $[WR(CO)_3(\eta\text{-}C_5H_5)]$ (R = alkyl). The closely related complex (19) is obtained from reaction of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ with $I[CH_2]_4I$, proceeding *via* the intermediate $[W\{(CH_2)_4I\}(CO)_3(\eta\text{-}C_5H_5)]$, while the dimolybdenum complex (20) is similarly obtained from $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and $I[CH_2]_4I$. The latter reaction does not produce any species containing Mo–Mo bonds or carbene ligands. Physical and spectroscopic data for the new compounds (18)—(20) are presented in Tables 1 and 2; complex (20) has been studied by *X*-ray diffraction in order to relate its structure to that of the iron complex (21)[17] previously characterised.

The structure of the molecule is illustrated in Figure 2 with the atom labelling used in the corresponding Tables. Bond

Table 5. Bond lengths (Å) and bond angles (°) with estimated standard deviations for $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ (20)

(*a*) Bond lengths

C(10)–C(10′)	1.533(6)	Mo(1)–C(3)	1.987(4)	Mo(1)–C(8)	2.354(6)	C(5)–C(6)	1.378(9)
C(9)–C(10)	1.531(6)	Mo(1)–C(4)	2.314(7)	O(1)–C(1)	1.156(7)	C(6)–C(7)	1.369(8)
Mo(1)–C(9)	2.356(4)	Mo(1)–C(5)	2.321(7)	O(2)–C(2)	1.140(6)	C(7)–C(8)	1.366(8)
Mo(1)–C(1)	1.977(5)	Mo(1)–C(6)	2.345(6)	O(3)–C(3)	1.144(6)	C(8)–C(4)	1.403(9)
Mo(1)–C(2)	1.996(5)	Mo(1)–C(7)	2.359(5)	C(4)–C(5)	1.413(10)		

(*b*) Bond angles

C(10′)–C(10)–C(9)	111.7(4)	C(1)–Mo(1)–C(3)	78.56(20)	C(8)–C(4)–C(5)	107.1(6)
Mo(1)–C(9)–C(10)	116.7(3)	C(2)–Mo(1)–C(3)	104.81(19)	C(4)–C(5)–C(6)	107.4(6)
C(9)–Mo(1)–C(1)	131.90(18)	Mo(1)–C(1)–O(1)	179.3(5)	C(5)–C(6)–C(7)	108.3(5)
C(9)–Mo(1)–C(2)	73.90(17)	Mo(1)–C(2)–O(2)	178.6(4)	C(6)–C(7)–C(8)	109.8(5)
C(9)–Mo(1)–C(3)	71.57(16)	Mo(1)–C(3)–O(3)	177.0(4)	C(7)–C(8)–C(4)	107.4(5)
C(1)–Mo(1)–C(2)	78.56(20)				

lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables 4 and 5. The molecule possesses a crystallographically imposed inversion centre of symmetry at the middle of the tetramethylene chain which links the molybdenum atoms: each molybdenum co-ordination polyhedron can be viewed as a square-based pyramid, with the centroid of the cyclopentadienyl ring occupying the axial site. Three of the basal sites are occupied by linear carbonyl groups of conventional geometry; the fourth site is filled by the alkyl chain which has an antiperiplanar conformation. The cyclopentadienyl ring is planar and is almost symmetrically bonded to the molybdenum atom, with the carbon atoms which lie most nearly *trans* to the alkyl chain being slightly closer (0.04 Å, 7σ) than those lying *trans* to the strongly π-accepting carbonyl groups. The molecular structure may be compared to that of the iron complex (21)[17] where a similar *trans* conformation with approximate inversion symmetry is found.

The products formed in these systems are a result of an apparently rather delicate balance of attack by anions at the three conceivable positions, that is the tendencies for X^- to leave forming a dimetalla-alkane, for a metal anion to be eliminated and for attack to occur at the metal during a migratory insertion reaction.

Insertion reactions are sluggish for tungsten complexes and the trimethylene systems lead to dimetalla-alkanes whereas molybdenum systems will either undergo insertion with subsequent carbene ligand formation or lose the molybdenum as $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$. However the tetramethylene systems show no tendency to form six-membered carbene ligand rings, even for molybdenum, which is a consequence of the difficulty of ring closing to form a six-membered ring relative to direct replacement of the second halide.

Experimental

General techniques and instrumentation were as described recently.[7] The complexes $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$, $[W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$,[2] and the anions $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ [18] were prepared by methods similar to literature preparative procedures.

Reaction of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ *with* $Br[CH_2]_3Br$.—A solution of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ (20 mmol) in thf (50 cm³) was treated with $Br[CH_2]_3Br$ (2.02 g, 10 mmol) and stirred (3 d) at ambient temperature. Removal of solvent and extraction into dichloromethane gave a deep red solution. Rapid chromatography on alumina (10 × 2.5 cm column) gave a single maroon fraction providing $[(\eta\text{-}C_5H_5)(OC)_3MoMo(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$ (13) (1.56 g, 30%). The compound tends to undergo a complex decomposition reaction affording $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ if chromatography is too slow; rapid elution is attainable by careful application of reduced pressure and the whole chromatography step should be completed within 15 min.

Reaction of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ *with* $[W(CO)_3(\eta\text{-}C_5H_5)]^-$.—A solution of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ (1 mmol) and $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (0.369 g, 1 mmol) was stirred in thf (1 cm³; 19 h) and solvent removed from the resulting deep red solution. Extraction of the mixture into dichloromethane followed by filtration through alumina and crystallisation from dichloromethane–light petroleum (b.p. 40–60 °C) provided maroon crystalline $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$ (14) (0.26 g, 43%).

Reaction of $I[CH_2]_4I$ *with* $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$.—A solution of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ (20 mmol) and $I[CH_2]_4I$ (3.10 g, 10 mmol) was heated in thf (100 cm³) at reflux (2 h). Removal of solvent under reduced pressure, extraction into dichloromethane and filtration through alumina gave a yellow solution which provided yellow microcrystalline $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ (20) (3.44 g, 63%).

Reaction of $I[CH_2]_4I$ *with* $[W(CO)_3(\eta\text{-}C_5H_5)]^-$.—A solution of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ (5 mmol) and $I[CH_2]_4I$ (0.8 g, 2.5 mmol) was heated in 1,2-dimethoxyethane–thf (50 cm³, approx. 4 : 1) at reflux (12 h). Removal of solvent under reduced pressure, extraction into dichloromethane and filtration through alumina gave a yellow solution which provided yellow microcrystalline $[(\eta\text{-}C_5H_5)(OC)_3W\{(CH_2)_4\}W(CO)_3(\eta\text{-}C_5H_5)]$ (19) (1.95 g, 54%).

Reaction of $I[CH_2]_3I$ *with* $[W(CO)_3(\eta\text{-}C_5H_5)]^-$.—The method used is similar to the previous preparation and results in yellow microcrystalline $[(\eta\text{-}C_5H_5)(OC)_3W\{(CH_2)_3\}W(CO)_3(\eta\text{-}C_5H_5)]$ (18) (61%).

Crystallographic Studies.—Crystal data for (14). $[(C_5H_5)(OC)_3MoW(CO)_2(C_4H_6O)(C_5H_5)]$: $C_{19}H_{16}MoO_6W$, M = 620.03, crystallises from dichloromethane–light petroleum (b.p. 40–60 °C) as maroon needles; crystal dimensions 0.215 × 0.05 × 0.08 mm; Monoclinic, a = 8.017(6), b = 15.026(16), c = 7.981(3) Å, β = 92.88(5)°, U = 960.2(13) Å³, D_m = 2.10, Z = 2, D_c = 2.145 g cm^{-3}, $F(000)$ = 588, space group $P2_1$ (C_2^2, no. 4), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 67.85 cm^{-1}.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffracto-

Table 6. Atomic positional parameters with estimated standard deviations for $[(\eta\text{-}C_5H_5)(OC)_3MoW(CO)_2(C_4H_6O)(\eta\text{-}C_5H_5)]$ (14) *

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
W(1)	0.115 19(17)	−0.002 7(3)	0.298 05(16)	C(7)	0.261(5)	0.186(2)	0.315(6)
Mo(1)	−0.182 7(4)	−0.026 7(3)	0.012 3(4)	C(8)	0.414(2)	0.230(2)	0.399 0(2)
O(1)	0.248(4)	0.063(3)	−0.038(4)	C(9)	0.440(7)	0.181(4)	0.561(7)
O(2)	−0.145(4)	0.142(2)	0.373(4)	C(10)	0.249(4)	−0.148(3)	0.304(4)
O(3)	0.098(4)	−0.168(3)	−0.074(4)	C(11)	0.084(4)	−0.165(2)	0.344(4)
O(4)	−0.392(5)	−0.201(3)	−0.037(5)	C(12)	0.055(3)	−0.119(3)	0.493(4)
O(5)	−0.316(5)	−0.083(4)	0.361(5)	C(13)	0.202(5)	−0.075(2)	0.545(4)
O(6)	0.359(4)	0.091(2)	0.520(3)	C(14)	0.322(3)	−0.093(2)	0.428(5)
C(1)	0.194(5)	0.034(3)	0.078(5)	C(15)	−0.278(5)	0.024(2)	−0.241(4)
C(2)	−0.055(6)	0.089(3)	0.326(6)	C(16)	−0.126(4)	0.065(3)	−0.194(5)
C(3)	0.002(5)	−0.111(3)	−0.032(5)	C(17)	−0.151(4)	0.119(2)	−0.054(5)
C(4)	−0.308(5)	−0.139(3)	−0.015(4)	C(18)	−0.318(5)	0.111(3)	−0.015(4)
C(5)	−0.258(6)	−0.053(3)	0.230(6)	C(19)	−0.397(4)	0.053(3)	−0.130(5)
C(6)	0.256(2)	0.097(2)	0.385 2(2)				

* The estimated standard deviations of atoms C(6)—C(8) and C(10)—C(19) are derived from the e.s.d.s of the group parameters which were used to refine these atoms.

Table 7. Atomic positional parameters with estimated standard deviations for $[(\eta\text{-}C_5H_5)(OC)_3Mo\{(CH_2)_4\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ (20)

Atom	X/a	Y/b	Z/c
Mo(1)	0.256 40(5)	0.226 54(5)	0.238 05(3)
O(1)	0.336 8(7)	0.235 6(7)	−0.028 4(3)
O(2)	−0.119 4(6)	0.336 5(7)	0.129 9(4)
O(3)	0.623 0(5)	0.627 1(5)	0.293 1(4)
C(1)	0.307 2(8)	0.230 9(8)	0.069 8(4)
C(2)	0.018 5(7)	0.299 3(7)	0.169 8(4)
C(3)	0.487 5(6)	0.481 6(7)	0.269 8(4)
C(4)	0.372 9(11)	−0.054 6(10)	0.228 0(6)
C(5)	0.159 7(12)	−0.128 6(7)	0.198 4(5)
C(6)	0.084 5(8)	−0.061 1(8)	0.302 1(6)
C(7)	0.244 4(8)	0.049 9(7)	0.394 1(5)
C(8)	0.422 0(8)	0.055 6(8)	0.351 8(6)
C(9)	0.204 7(6)	0.475 4(6)	0.397 5(4)
C(10)	0.003 5(6)	0.417 5(6)	0.444 2(4)

meter by the omega-scan method. The 1 256 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions (C–H 0.95 Å); their contributions were included in structure factor calculations (B = 8.0 Å^2) but no refinement of positional parameters was permitted. Owing to difficulties arising from pseudo-symmetry effects, conventional refinement produced unacceptable geometries in three regions of the molecule. Consequently constraints were applied to the geometries of the two cyclopentadienyl rings (D_{5h}, C–C 1.40 Å) and a three-atom fragment of the cyclic carbene ligand [C(6)—C(8)]. The absolute configuration of the molecule in the chosen crystal was confirmed from anomalous scattering results. Refinement converged at R = 0.0645 with allowance for anisotropic thermal motion of tungsten, molybdenum, and oxygen atoms and for the anomalous scattering of tungsten and molybdenum. Table 6 lists the atomic positional parameters with estimated standard deviations.

Crystal data for (20). $[\{(C_5H_5)(CO)_3Mo(CH_2)_2\}_2]$: $C_{20}H_{18}Mo_2O_6$, M = 546.16, crystallises from dichloromethane as yellow, elongated plates; crystal dimensions 0.24 × 0.31 × 0.10 mm; Triclinic, a = 6.9782(16), b = 7.0051(10), c = 11.3150(25) Å, α = 102.378(15), β = 95.806(18), γ = 105.909(15)°, U = 511.98(18) Å^3, D_m = 1.76, Z = 1, D_c = 1.771 g cm^{-3}, $F(000)$ = 270, space group $P\bar{1}$ (C_i^1, no. 2), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 12.27 cm^{-1}.

The data were collected ($3.5 < 2\theta < 50°$) and processed (1 646 independent reflections, absorption corrections not applied) and the structure solved and refined (R = 0.0263) as for the heterodimetallic complex above: no geometric constraints were applied during refinement; anisotropic thermal parameters were refined for all non-hydrogen atoms. Table 7 lists atomic positional parameters with estimated standard deviations.

Scattering factors were taken from ref. 19; unit weights were used throughout the refinement; computer programs form part of the Sheffield X-ray system.

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Received 19*th May* 1983; *Paper* 3/806