Cyclic Carbene Complexes of Molybdenum and Tungsten. Crystal and Molecular Structure of [MoI(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)] †

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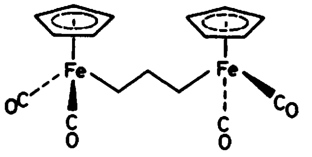
The cyclic carbene complex [MoI(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)] is formed during reaction of [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$ with I[CH$_2$]$_3$I or of [Mo{(CH$_2$)$_3$Br}(CO)$_3$(η-C$_5$H$_5$)] with LiI. Crystals of this complex are Monoclinic, space group $P2_1/c$, with a = 6.372(2), b = 14.168(5), c = 14.390(3) Å, β = 98.12(2)°, and Z = 4. The molecule contains mutually *trans* carbonyl ligands and a cyclic carbene ligand in which all but one of the ring carbon atoms are coplanar with the metal. Similarly, reactions of [Mo{(CH$_2$)$_3$Br}(CO)$_3$(η-C$_5$H$_5$)] with SPh$^-$ or CN$^-$ provide [MoX(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)] (X = SPh or CN). The cyclisation is tolerant to functionality on the cyclopentadienyl ring, thus reaction of [Mo(CO)$_3$(η-C$_5$H$_4$R)]$^-$ with I[CH$_2$]$_3$I produces [MoI(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_4$R)] [R = Me, C(O)Me, or SiMe$_3$]. The tungsten analogue [W{(CH$_2$)$_3$Br}(CO)$_3$(η-C$_5$H$_5$)] undergoes carbene formations with I$^-$ and CN$^-$ to form [WX(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)] (X = I or CN). Formation of the carbene complexes is likely to proceed by migration of the (CH$_2$)$_3$Br alkyl group to an adjacent CO group together with co-ordination of the incoming anion. This is followed by a ring closure reaction eliminating Br$^-$ and isomerisation so that in all cases the two CO groups are mutually *trans* in the isolated products. While [MoI(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)] does not react with transition-metal anions to form dinuclear carbene complexes by elimination of I$^-$, the salt [Mo(CO)$_2$(PPh$_3$)-{CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)]Br reacts with [W(CO)$_3$(η-C$_5$H$_5$)]$^-$ to give the unusual acyl complex [(η-C$_5$H$_5$)(Ph$_3$P)(OC)$_2$MoC(O)(CH$_2$)$_3$W(CO)$_3$(η-C$_5$H$_5$)].

Several years ago a series of papers described reactions of α,ω-dibromoalkanes with various transition-metal anionic nucleophiles.[1-4] The products isolated from these reactions are highly dependent on the metal involved. This paper describes some reactions of 1,3-di-iodopropane with the molybdenum nucleophile [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$ and other related species. Some aspects of this work have been the subject of preliminary communication.[5]



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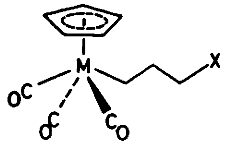

(2) M = Mo, X = Br
(3) M = W, X = Br
(4) M = Mo, X = I

Results and Discussion

The reaction of Br[CH$_2$]$_3$Br at ambient temperatures with the powerful nucleophile [Fe(CO)$_2$(η-C$_5$H$_5$)]$^-$ leads to nucleophilic displacement of both bromides resulting in the dimetallapentane [(η-C$_5$H$_5$)(OC)$_2$Fe(CH$_2$)$_3$Fe(CO)$_2$(η-C$_5$H$_5$)] (1)[1] while in the presence of excess Br[CH$_2$]$_3$Br at low temperatures the monosubstituted [Fe{(CH$_2$)$_3$Br}(CO)$_2$(η-C$_5$H$_5$)][6] is isolable. Reaction of the less nucleophilic [M(CO)$_3$(η-C$_5$H$_5$)]$^-$ (M = Mo or W) anions with Br[CH$_2$]$_3$Br is reported to result in replacement of a single bromide group and isolation of [M{(CH$_2$)$_3$Br}(CO)$_3$(η-C$_5$H$_5$)] [M = Mo (2) or W (3)] as the only identified product in moderate yield.[2]

Reaction of I[CH$_2$]$_3$I with [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$ proceeds rapidly to a yellow solution containing the expected [Mo{(CH$_2$)$_3$I}(CO)$_3$(η-C$_5$H$_5$)] (4) [on the basis of i.r. monitoring, ν(CO) (tetrahydrofuran) at 2 018m and 1 921s cm^{-1}] but prolonged stirring or a brief reflux results in darkening of the solution and the clean formation of a new dicarbonyl [ν(CO) (tetrahydrofuran) at 1 981m and 1 909s cm^{-1}] identified as a complex of oxacyclopentylidene, [MoI(CO)$_2${CO(CH$_2$)$_2$CH$_2$}(η-C$_5$H$_5$)] (5) and routinely isolated in better than 90% yields. The partially decoupled ^{13}C n.m.r. spectrum contains a doublet assignable to the cyclopentadienyl group together with three triplets corresponding to CH$_2$ groups, and two singlets at δ 316.6 and 223.4 p.p.m. assignable to a carbene carbon atom and two equivalent, mutually *trans* carbonyl groups respectively. The equivalence of the carbonyl groups is supported by the relative intensities of the carbonyl stretching bands in the i.r. spectrum which by analogy to related systems with this geometry suggest a *trans* configuration.[7] We have neither detected nor isolated an isomeric *cis* complex from the reaction. The relative orientation of the carbonyl groups and the nature of the carbene ligand have been confirmed by an *X*-ray crystallographic study.

The molecular structure of (5) is illustrated in the Figure 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 1 and 2.

The molecule comprises an MoI(CO)$_2$(η-C$_5$H$_5$) fragment of

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† Dicarbonyl(η^5-cyclopentadienyl)iodo(1-oxacyclopent-2-ylidene)-molybdenum.

Supplementary data available (No. SUP 23700, 19 pp.): structure factors, anisotropic thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

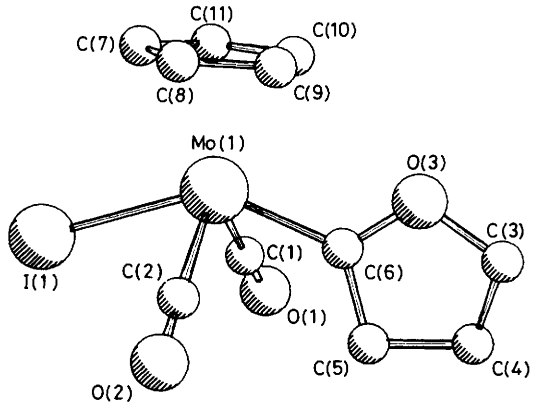


Figure. Molecular structure of [MoI$(CO)_2$\{$CO(CH_2)_2CH_2$\}(η-C_5H_5)] (5) with atom labelling

Table 1. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [MoI$(CO)_2$\{$CO(CH_2)_2CH_2$\}(η-C_5H_5)] (5)

Mo(1)–I(1)	2.862(1)	O(3)–C(3)	1.454(15)
Mo(1)–C(1)	1.991(9)	O(3)–C(6)	1.337(11)
Mo(1)–C(2)	2.007(9)	C(3)–C(4)	1.448(18)
Mo(1)–C(6)	2.086(8)	C(4)–C(5)	1.507(16)
Mo(1)–C(7)	2.392(11)	C(5)–C(6)	1.453(13)
Mo(1)–C(8)	2.378(11)	C(7)–C(8)	1.415(16)
Mo(1)–C(9)	2.326(10)	C(8)–C(9)	1.381(15)
Mo(1)–C(10)	2.315(11)	C(9)–C(10)	1.426(15)
Mo(1)–C(11)	2.366(11)	C(10)–C(11)	1.410(15)
O(1)–C(1)	1.150(12)	C(11)–C(7)	1.395(16)
O(2)–C(2)	1.137(12)		
I(1)–Mo(1)–C(1)	78.3(3)	C(6)–O(3)–C(3)	111.2(8)
I(1)–Mo(1)–C(2)	77.9(3)	O(3)–C(3)–C(4)	105.2(10)
I(1)–Mo(1)–C(6)	140.3(2)	C(3)–C(4)–C(5)	103.1(10)
C(1)–Mo(1)–C(2)	98.5(4)	C(4)–C(5)–C(6)	105.2(8)
C(1)–Mo(1)–C(6)	75.0(4)	O(3)–C(6)–C(5)	108.1(7)
C(2)–Mo(1)–C(6)	77.7(3)	Mo(1)–C(6)–O(3)	123.7(6)
cp–Mo(1)–I(1)	110.1	Mo(1)–C(6)–C(5)	128.2(6)
cp–Mo(1)–C(1)	131.1	C(11)–C(7)–C(8)	108.9(10)
cp–Mo(1)–C(2)	130.4	C(7)–C(8)–C(9)	107.6(9)
cp–Mo(1)–C(6)	109.6	C(8)–C(9)–C(10)	108.5(9)
Mo(1)–C(1)–O(1)	176.7(8)	C(9)–C(10)–C(11)	107.5(9)
Mo(1)–C(2)–O(2)	177.7(8)	C(10)–C(11)–C(7)	107.5(10)

cp represents the position of the centroid of the cyclopentadienyl ring C(7)–C(11): no estimated standard deviations are quoted for bond angles involving this site.

Table 2. Details of planar fragments of [MoI$(CO)_2$\{$CO(CH_2)_2CH_2$\}(η-C_5H_5)] (5). Equations of mean planes are of the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to axes a, b, c *. Deviations (Å) of atoms from the mean planes are given in square brackets

	p	*q*	*r*	*d*
Plane A: C(7)—C(11)				
	−0.3714	−0.8097	−0.4545	−0.2312
[C(7) −0.000, C(8) −0.001, C(9) 0.001, C(10) −0.002, C(11) 0.001, Mo(1) −2.028]				
Plane B: Mo(1), O(3), C(3), C(5), C(6)				
	−0.8945	0.1089	0.4336	1.0096
[Mo(1) −0.002, O(3) 0.004, C(3) −0.004, C(5) 0.001, C(6) 0.001, C(4) −0.406]				
Plane C: C(3)—C(5)				
	−0.7768	0.5345	0.3330	3.8502
[O(3) −0.595, C(6) −0.606]				

Angles (°) between planes: A–B 87.3
B–C 26.2

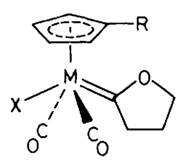
substantially conventional geometry with a planar, symmetric cyclopentadienyl ring and linear metal–carbonyl linkages. The oxacyclopentylidene ligand is bonded to the molybdenum atom *via* a formal double bond which is rather longer than those to the carbonyl carbon atoms, suggesting some degree of π-electron delocalisation into the carbon–oxygen bond which is intermediate in length between single and double. The oxacyclopentylidene has an envelope conformation with atom C(4) lying out of the mean plane through the remaining atoms and with which the molybdenum atom is also approximately coplanar. The co-ordination polyhedron of the molybdenum atom is intermediate in geometry between square pyramidal and trigonal bipyramidal (the position of the cyclopentadienyl ring being approximated by its centroid).

In the structures of two other complexes involving this ligand its geometry is described as planar; in [MnPt(μ-I)\{$CO(CH_2)_2CH_2$\}$(CO)_4(PBu^t_2Me)$] [8] the oxacyclopentylidene ligand contains a very short carbon–carbon single bond, while that in [PtMe$(PMe_2Ph)_2$\{$CO(CH_2)_2CH_2$\}] [9] adopts an envelope conformation similar to that observed here but the out-of-plane deviation of C(4) is of much lesser magnitude. In the structures of two complexes containing the related 1,3-dioxacyclopentylidene ligand [10,11] no reference is made to the planarity of the ligand. In all cases the lengths of the various transition metal–carbon bonds suggest higher bond orders than in the present molybdenum complex in which a greater degree of π-electron delocalisation into the oxacyclopentylidene ligand occurs. In order to preserve optimum conjugation the out-of-plane deviations for the ligand are confined to atom C(4).

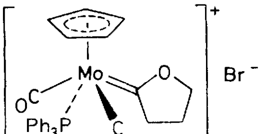
Complex (5) can also be prepared from the reaction of iodide ion (Li^+ or $Bu^n{}_4{}^+$ salt) with the metallabromoalkane (2). In tetrahydrofuran (thf) at reflux the reaction again proceeds in routinely better than 90% isolated yields. No other species were detected during monitoring of the i.r. spectrum. The starting material was recovered unchanged from analogous reactions employing bromide ion. This confirms that I^- but not Br^- is required for the ring closure stage under our reaction conditions.

It turns out that other anions induce analogous carbene complex formations. Complex (2) reacts with either CN^- or SPh^- in methanol producing moderate isolated yields of (6) and (7) respectively, again *cis* dicarbonyl species were not detected in these cases. Failure to detect *cis* dicarbonyl complexes during these reactions does not imply they are not formed during reaction; monitoring by i.r. spectroscopy would probably not allow detection of initially formed but short-lived *cis* dicarbonyl complexes since the i.r. stretching frequencies of both isomers are expected to be similar.

Reaction of the neutral nucleophile PPh_3 with (2) under concentrated conditions causes rapid precipitation of the *cis* dicarbonyl cation (8) whereas a solution of (8) undergoes *cis*–*trans* isomerisation to the thermodynamically favoured *trans* species (9).[12,13] The related iron complex [Fe\{$(CH_2)_3Br$\}$(CO)_2$(η-C_5H_5)] undergoes a similar reaction with PPh_3 but requires more forcing conditions, the products are the cation (10) and



	M	X	R
(5)	Mo	I	H
(6)	Mo	CN	H
(7)	Mo	SPh	H
(11)	Mo	I	Me
(12)	Mo	I	SiMe$_3$
(13)	Mo	I	C(O)Me
(17)	W	I	H
(18)	W	CN	H



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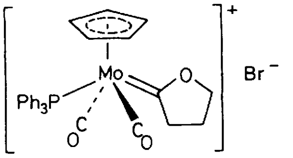

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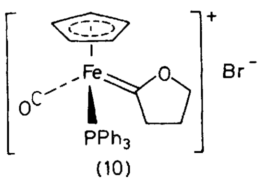
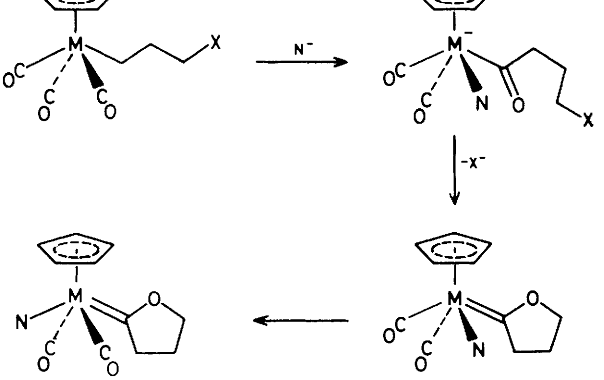


(10)

an acyl species [Fe{C(O)(CH$_2$)$_3$PPh$_3$}(CO)(PPh$_3$)(η-C$_5$H$_5$)]$^+$, the former being the precursor to the latter.[6]

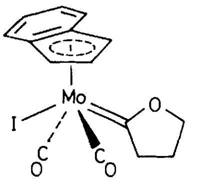
Based on these observations a plausible mechanism for carbene formation in the present system is given in the Scheme.



Scheme. N$^-$ = nucleophile

The key initial step is migration of the alkyl chain to an adjacent carbonyl group and co-ordination of the nucleophile at the metal atom. This forms an anionic acyl intermediate which undergoes a ring forming elimination of Br$^-$ by virtue of the nucleophilicity of the acyl oxygen atom. With our present data we cannot exclude *cis–trans* isomerisation of the acyl species prior to ring closure.

The system is tolerant to functionalisation of the cyclopentadienyl ring. Thus complexes (11)—(13) are all produced in good yield from reaction of the appropriate anion [Mo(CO)$_3$(η-C$_5$H$_4$R)]$^-$ [R = Me, SiMe$_3$, or C(O)Me] with I[CH$_2$]$_3$I. We have never obtained analytically pure samples of (12), ^{1}H n.m.r. spectra always indicate contamination by the unsubstituted complex (5). This appears to be a result of desilylation during routine handling. The indenyl complex (14) is made in a similar manner from [Mo(CO)$_3$(η^5-C$_9$H$_7$)]$^-$ and I[CH$_2$]$_3$I but in moderate isolated yields. Reaction times did not appear appreciably faster than for formation of (5). The ions [MoL(CO)$_2$(η-C$_5$H$_5$)]$^-$ [L = PPh$_3$ or P(OMe)$_3$] are readily available from sodium amalgam cleavage of the appropriate dimer [{MoL(CO)$_2$(η-C$_5$H$_5$)}$_2$][14] [L = PPh$_3$ or P(OMe)$_3$]. They react smoothly with Br[CH$_2$]$_3$Br with loss of a single bromide ion affording (15) and (16) as the only isolated products. In both cases the *trans* isomers are isolated exclusively. I.r. and ^{1}H n.m.r. spectroscopy show no sign of *cis* structures. Neither of the complexes (15) and (16) reacts with iodide ion in thf at reflux to produce carbene complexes, the former produces small quantities of *trans*-[MoI(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] together with starting material, while no reaction is evident at all for the latter.



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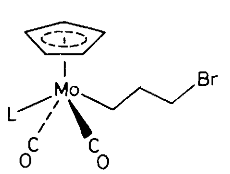


(15) L = PPh$_3$
(16) L = P(OMe)$_3$

The related tungsten systems display a closely related chemistry. Thus complex (3) reacts with nucleophiles, although rather more sluggishly. For instance, reaction with iodide to produce (17) requires overnight in 1,2-dimethoxyethane or 5 d in thf (at reflux) while reaction with CN$^-$ requires a 4 d period in methanol at reflux to form (18). In both cases the yields are lower than for the molybdenum cases owing to the appearance of some decomposition. Again *cis* dicarbonyl complexes were not detected. In the case of SPh$^-$ none of the expected product was obtained owing to extensive decomposition.

The ^{1}H n.m.r. spectrum of each of the cyclic carbene complexes (Table 3) shows a characteristic first-order triplet, triplet quintet pattern for the carbene ligands. The ^{13}C n.m.r. spectra of the molybdenum carbene complexes display signals in the region δ 315—317 p.p.m. to high frequency of SiMe$_4$ while the signal for complex (6) containing the more electron withdrawing cyanide ligand appears at δ 325.1 p.p.m. The observed signal for the tungsten complex (17) appears at δ 292.5 p.p.m., that is, to somewhat lower frequency than for the molybdenum complex (5).

In the ^{13}C-{^{1}H} spectrum of (17) tungsten satellites are clearly visible for several signals. The observed J(WC) coupling constants (Table 3) are of a similar order of magnitude to those of carbon atoms in similar environments in related systems.[15] On the basis of an observed J(WC) coupling constant of 16 Hz, the signal at 59.5 p.p.m. is assigned to the carbon atom α to carbene, the coupling for the other signals being too fine to resolve. The observed J(WH) couplings for both (17) and (18) in the ^{1}H spectra are all 3 Hz or less and are tabulated when resolved.

We have undertaken a study of some reactions of these carbene complexes. However we have been unable to displace the

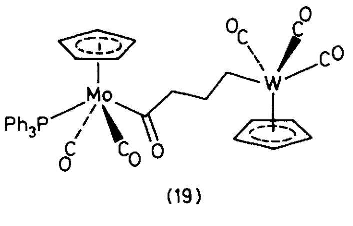
Table 3. N.m.r. data for the new complexes [a]

Complex	^{1}H (δ/p.p.m.)	^{13}C (δ/p.p.m.)
(5)	5.57 (s, 5 H), 4.60 [t, 2 H, OCH_2, *J*(HH) 7], 3.60 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 1.92 [quintet, 2 H, CH_2, *J*(HH) 7]	316.6 (Mo=C), 223.4 (CO), 96.9 (C_5H_5), 82.0 (OCH_2), 58.8 ($MoC\mathit{C}H_2$), and 22.5 (CH_2)
(6)	5.52 (s, 5 H), 4.76 [t, 2 H, OCH_2, *J*(HH) 7], 3.69 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 1.94 [quintet, 2 H, CH_2, *J*(HH) 7]	325.1 (Mo=C), 225.6 (CO), 95.0 (C_5H_5), 83.9 (OCH_2), 59.5 ($MoC\mathit{C}H_2$), 22.0 (CH_2)
(7)	7.43 [d, 2 H, *o*-Ph, *J*(HH) 7], 7.11 [t, 2 H, *m*-Ph, *J*(HH) 7], 7.00 [d, 1 H, *p*-Ph, *J*(HH) 7], 5.47 (s, 5 H, C_5H_5), 4.60 [t, 2 H, OCH_2, *J*(HH) 7], 3.70 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 1.87 [quintet, 2 H, CH_2, *J*(HH) 7]	
(11)	5.44 [m, 2 H, $C_5\mathit{H}_4Me$], 5.35 [m, 2 H, $C_5\mathit{H}_4Me$], 4.62 [t, 2 H, OCH_2, *J*(HH) 7], 3.56 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 2.18 [s, Me, 3 H], 1.91 [quintet, 2 H, CH_2, *J*(HH) 7]	316.9 (Mo=C), 224.1 (CO), 111.7 (*C*–Me), 100.6 [CH (C_5 ring)], 94.0 [CH (C_5 ring)], 81.7 (OCH_2), 59.0 ($MoC\mathit{C}H_2$), 22.6 (CH_2), 14.5 (CH_3)
(12)	5.47 (m, 2 H, $C_5\mathit{H}_4SiMe_3$), 5.31 (m, 2 H, $C_5\mathit{H}_4SiMe_3$), 3.54 [t, 2 H, OCH_2, *J*(HH) 7], 3.04 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 0.94 [quintet, 2 H, CH_2, *J*(HH) 7], 0.37 (s, 9 H, $SiMe_3$) [b]	315.6 (Mo=C), 224.1 (CO), 107.8 [CH (C_5 ring)], 100.6 ($\mathit{C}SiMe_3$), 96.6 [CH (C_5 ring)], 81.3 (OCH_2), 58.6 ($MoC\mathit{C}H_2$), 24.3 (CH_2), 0.3 ($SiMe_3$) [b]
(13)	5.89 [m, 2 H, $C_5\mathit{H}_4C(O)Me$], 5.59 [m, 2 H, $C_5\mathit{H}_4C(O)Me$], 4.68 [t, 2 H, OCH_2, *J*(HH) 7], 3.57 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 3.36 [s, 3 H, C(O)Me], 1.94 [quintet, 2 H, CH_2, *J*(HH) 7]	316.3 (Mo=C), 221.8 (CO), 193.6 [*C*(O)Me], 104.6 [*C*C(O)Me], 102.3 [CH (C_5 ring)], 96.1 [CH (C_5 ring)], 83.0 (OCH_2), 59.3 ($MoC\mathit{C}H_2$), 27.6 [C(O)*Me*], 22.3 (CH_2)
(14)	7.50 [d of d, 2 H, CH (C_6 ring), *J*(HH) 7 and 3], 7.16 [d of d, 2 H, CH (C_6 ring), *J*(HH) 7 and 3], 4.05 [d, 2 H, CH (C_5 ring), *J*(HH) 3], 5.77 [t, 1 H, CH, *J*(HH) 3], 4.75 [t, 2 H, OCH_2, *J* 7], 3.45 [t, 2 H, $MoCCH_2$, *J*(HH) 7], 1.91 [quintet, 2 H, CH_2, *J*(HH) 7]	315.7 (Mo=C), 223.9 (Mo=C), 125.9 [CH (C_6 ring)], 112.4 (C), 95.0 [CH (unique, C_5 ring)], 92.0 [CH (C_5 ring)], 82.2 (OCH_2), 58.9 ($MoC\mathit{C}H_2$), 22.7 (CH_2)
(17)	5.67 [s, 5 H, C_5H_5, *J*(^{183}WH) 1.5], 4.52 [t, 2 H, OCH_2, *J*(HH) 7.2, *J*(WH) 0.9], 3.42 [t, 2 H, $W{=}CCH_2$, *J*(HH) 7.6, *J*(WH) 3.0], 1.90 [m, 2 H, CH_2]	292.5 (W=C), 216.5 (CO), 96.1 (C_5H_5), 81.5 (OCH_2), 59.5 [*J*(WC) 16, $WC\mathit{C}H_2$], 23.8 (CH_2) [c]
(18)	5.62 [s, 5 H, C_5H_5], 4.65 [t, 2 H, OCH_2, *J*(HH) 7], 3.54 [t, 2 H, $W{=}CCH_2$, *J*(HH) 7, *J*(WH) 2.5], 1.92 [quintet, 2 H, CH_2, *J*(HH) 7]	
(19)	7.01 (m, 15 H, Ph), 4.89 [d, 5 H, Mo(η-C_5H_5), *J*(PH) 1], 4.64 [s, 5 H, W(η-C_5H_5)], 3.57 [t, 2 H, $C(O)CH_2$, *J*(HH) 7], 2.05 (m, 2 H, CH_2), 1.77 (m, 2 H, CH_2) [b]	261.2 (C=O), 239.2 [d, Mo–CO, *J*(PC) 24], 230.1 (W–CO *trans*), 217.5 (W–CO), 136.6 [d, *i*-Ph, *J*(PC) 43], 133.4 [d, *o*-Ph, *J*(PC) 10], 130.3 (*p*-Ph), 128.6 [d, *m*-Ph, *J*(PC) 9], 96.6 (C_5H_5), 91.5 (C_5H_5), 71.5 [$C(O)\mathit{C}H_2$], 33.9 (CH_2), −9.4 (WCH_2) [b]

[a] Measured in $CDCl_3$ solution at ambient temperature unless stated otherwise, coupling constants in Hz. [b] Measured in C_6D_6 solution at ambient temperature. [c] Measured in CD_2Cl_2 solution at ambient temperature.

iodide ion from (5) by use of transition-metal anions, so forming dimetal carbene complexes. In the cases of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, $[W(CO)_3(\eta\text{-}C_5H_5)]$,$^-$ $[Mn(CO)_5]^-$, and $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ the reactions are complicated, no new complexes were isolated and generally extensive decomposition was evident. For instance, in the case of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ the only species we have been able to isolate are $[WI(CO)_3(\eta\text{-}C_5H_5)]$ and $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, both in rather low yield. The only species isolated from reaction with Zn–Hg is $[Hg\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, the main result being decomposition.

However, the cationic species (9) is reactive towards transition-metal nucleophiles. Thus reaction of (9) with $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ in thf proceeds in good yield to the unusual acyl species (19). This is a pale yellow air-stable microcrystalline



(19)

solid whose ^{13}C-$\{^1H\}$ n.m.r. spectrum shows several useful diagnostic features, although ^{183}W satellites were not visible even after overnight accumulation owing to its low solubility. A high-frequency signal at δ 261.2 is in the expected region for an acyl metal species,[15] this assignment is reinforced by the presence of a signal in the i.r. spectrum at 1 610 cm^{-1}. One carbonyl signal with appropriate intensity and which has the appropriate value of *J*(PC) is assigned to two mutually *trans* carbonyl ligands orientated *cis* to PPh_3. Of the three signals assigned to three CH_2 groups one is at a very low frequency (δ −9.4 p.p.m.) and characteristic of an alkyl carbon group bonded directly to a metal. The qualitative features of the CH_2 signals in the ^{1}H n.m.r. spectrum are similar to those of other $[Mo\{(CH_2)_3X\}L(CO)_2(\eta\text{-}C_5H_5)][X = \text{halogen}; L = CO, PR_3$, or $P(OR)_3]$ systems.

This ring opening reaction is apparently related to the reaction of iodide with the cation $[Fe\{\overline{CO(CH_2)_2CH_2}\}(CO)_2(\eta\text{-}C_5H_5)]^+$ which produces the neutral acyl $[Fe\{C(O)(CH_2)_3I\}(CO)_2(\eta\text{-}C_5H_5)]$ [16] and that of PPh_3 with $[Fe\{\overline{CO(CH_2)_2CH_2}\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ which results in the cation $[Fe\{C(O)(CH_2)_3PPh_3\}(CO)_2(\eta\text{-}C_5H_5)]^+$.[6]

Experimental

I.r. spectra were recorded using a Perkin-Elmer 297 spectrometer and calibrated *via* the 1 601 cm^{-1} absorption of polystyrene. Proton and ^{13}C n.m.r. spectra were obtained using JEOL PFT-100, Perkin-Elmer R34, and Bruker WH-400 instruments while mass spectra were recorded using a Kratos MS 25 spectrometer. Reactions were normally performed under nitrogen atmospheres using solvents dried by distillation from Na–benzophenone (thf and dimethoxyethane) or LiAl-

Table 4. Analytical[a] and other data for the new complexes

Complex	Colour	M.p./°C	M[b]	$\nu_{\mathrm{max.}}$(CO)[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(5)	Orange	98—100	416 (416)	1 985m, 1 909s	32.4 (31.9)	2.4 (2.7)
(6)	Yellow	172—174[d]	315 (315)	1 998m, 1 919s[e]	46.1 (46.0)	4.2 (3.5)
(7)	Yellow-brown	93—96[d]	398 (398)	1 978m, 1 900s	51.8 (51.5)	4.2 (4.0)
(11)	Orange	94—96	430 (430)	1 988m, 1 909s	33.9 (33.6)	3.1 (3.1)
(12)	Orange	75—77	488 (488)	1 984m, 1 909s	33.6 (34.6)	3.9 (4.2)
(13)	Orange	119—120	458 (458)	1 998m, 1 924s, 1 678 (C=O)	34.2 (34.2)	2.9 (3.1)
(14)	Orange	84—86	466 (466)	1 987m, 1 912s	38.4 (38.8)	2.9 (2.8)
(17)	Orange	174—176	502 (502)	1 984m, 1 901s	26.6 (26.3)	2.5 (2.2)
(18)	Yellow	194—198[d]	401 (401)	1 998m, 1 910s[f]	36.3 (35.9)	3.1 (2.7)
(19)	Yellow	>124 darkens gas evolution >135	[g]	2 012s, 1 933 (sh), 1 912s, 1 851s, 1 610m (C=O)	50.7 (50.3)	3.3 (3.5)

[a] Calculated values are given in parentheses. [b] From molecular ion in mass spectrum. [c] In dichloromethane solution. [d] With decomposition. [e] $\nu_{\mathrm{max.}}$(CN) at 2 115 cm^{-1}. [f] $\nu_{\mathrm{max.}}$(CN) at 2 115 cm^{-1}. [g] Molecular ion *m/e* 882 not observed.

$\mathrm{H_4}$ [light petroleum, b.p. 40—60 °C (throughout)]. The alumina used throughout was Brockmann activity I deactivated by 5% w/w water. The complexes $[\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_2]$ (M = Mo or W),[17] $[\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}]^-$ (M = Mo or W),[18] and $[\mathrm{W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$[5] were prepared by literature procedures. Physical data for the new complexes are given in Table 4.

Preparation of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ (2).—An adaptation of the literature procedure[5] was used. A solution of $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}]^-$ (10 mmol) and $\mathrm{Br[CH_2]_3Br}$ (4.04 g, 20 mmol) was stirred in thf (250 cm^3) at room temperature (19 h) and finally heated (1 h). After removal of solvent the resulting solid was extracted into warm dichloromethane, the resulting solution filtered through alumina, concentrated and chromatographed on alumina. Elution with dichloromethane–light petroleum (1 : 19) gave a yellow fraction which provided $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ (yields 30—80%). Further elution with dichloromethane–light petroleum (4 : 6) gave a red band containing $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]$ in variable yields up to 10%.

Preparation of $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)}]$ (5).—(*a*) A mixture of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ (1.35 g, 3.7 mmol) and $\mathrm{LiI{\cdot}3H_2O}$ (0.75 g, 4 mmol) was heated in thf (30 cm^3, 1 h) at reflux. Removal of solvent from the resulting deep orange solution, extraction into dichloromethane, and filtration through alumina gave a solution which provided $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)}]$ (5) (1.38 g, 90%) as orange-brown crystals from a dichloromethane–light petroleum mixture.

(*b*) A solution of $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}]^-$ (10 mmol) was treated with $\mathrm{I[CH_2]_3I}$ (3.26 g, 11 mmol) and stirred overnight. Removal of solvent from the resulting deep brown solution, extraction into dichloromethane, and filtration through alumina gave a solution which provided $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)}]$ (5) (3.72 g, 90%).

Reaction of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ *with* KSPh.—A solution of benzenethiol (0.22 g, 2.0 mmol) in methanol (15 cm^3) was treated with KOH (0.12 g, 2.1 mmol) and stirred until the KOH had dissolved. A solution of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ (2) (0.367 1.0 mmol) in methanol (15 cm^3) was added to this and stirred at room temperature (3.5 h). The resulting yellow-brown solution was reduced in volume, extracted into dichloromethane, filtered through alumina, and chromatographed on alumina (20 × 2 cm). Elution with light petroleum gave PhSSPh and subsequent elution with dichloromethane gave a brown solution which eventually produced yellow crystals of $[\mathrm{Mo(SPh)(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)}]$ (7) (0.094 g, 24%) by crystallisation from dichloromethane–light petroleum.

Reaction of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ *with* KCN.—A solution of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)}]$ (0.25 g, 0.7 mmol) and KCN (0.065 g, 1.0 mmol) was heated in methanol (50 cm^3) at reflux (1.7 h). The resulting solution was evaporated to dryness, extracted into dichloromethane, and filtered through alumina. Crystallisation from light petroleum–dichloromethane produced $[\mathrm{Mo(CN)(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)}]$ (6) (0.045 g, 22%).

Preparation of $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_4Me)}]$ (11).—A solution of $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_4Me)}\}_2]$[17] (2.59 g, 5.0 mmol) in thf (50 cm^3) was treated with an excess of Na–Hg amalgam until the red colour of the dimer had become discharged. The resulting virtually colourless solution of $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_4Me)}]^-$ was separated from excess amalgam, treated with $\mathrm{I[CH_2]_3I}$ (3.2 g, 11.0 mmol), and heated at reflux (45 min). Removal of solvent from the resulting deep orange solution, extraction into dichloromethane, and filtration through alumina provided an orange solution which yielded $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_4Me)}]$ (11) (2.50 g, 59%) from the first crop of crystals.

Preparation of $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_4SiMe_3)}]$ (12).—A mixture of $[\mathrm{Mo(CO)_6}]$ (2.64 g, 10 mmol) and $\mathrm{Na[SiMe_3(C_5H_4)]}$[19] (15 cm^3, 1.0 mol dm^{-3} in thf, 15 mmol) was heated at reflux until no $[\mathrm{Mo(CO)_6}]$ was present. After stirring the resulting solution with $\mathrm{I[CH_2]_3I}$ (3.2 g, 11.0 mmol, 19 h) the solvent was removed under reduced pressure; the resulting solid was extracted into dichloromethane and filtered through alumina. Red crystalline $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_4SiMe_3)}]$ (1.45 g, 15%) was obtained from this solution contaminated by some $[\mathrm{MoI(CO)_2\{\overline{CO(CH_2)_2CH_2}\}(\eta\text{-}C_5H_5)}]$ (5).

Preparation of [MoI(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}\{η-C$_5H_4$C(O)Me\}] (13).—A solution of [Mo(CO)$_3$\{η-C$_5$H$_4$C(O)Me\}]$^-$[20] (23 mmol) in thf (50 cm^3) was treated with I[CH$_2$]$_3$I (7.5 g, 25 mmol) and heated at reflux (1 h). Removal of solvent, extraction into dichloromethane, and filtration through alumina gave an orange solution which provided orange crystalline [MoI(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}\{η-C$_5H_4$C(O)Me\}] (13) (7.75 g, 73%).

Preparation of [MoI(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η^5-C$_9H_7$)] (14).—A mixture of [Mo(CO)$_6$] (2.64 g, 10 mmol) and NaC$_9$H$_7$ (15 cm^3, 0.76 mol dm^{-3} in thf, 11.4 mmol) was refluxed until [Mo(CO)$_6$] was no longer present. Treatment of the resulting green solution with I[CH$_2$]$_3$I (3.2 g, 11.0 mmol) at room temperature (19 h) provided a brown solution from which brown crystalline [MoI(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η^5-C$_9H_7$)] (301 mg, 7%) was isolated after rapid chromatography [dichloromethane–light petroleum (1 : 1)].

Reaction of [Mo(CO)$_2$(PPh$_3$)\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η-C$_5H_5$)]Br (9) *with* [W(CO)$_3$(η-C$_5H_5$)]$^-$.—A solution of [W(CO)$_3$(η-C$_5H_5$)]$^-$ (0.5 mmol) in thf (30 cm^3) was treated with [Mo(CO)$_2$(PPh$_3$)\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η-C$_5H_5$)]Br (9) (0.315 g, 0.5 mmol). The resulting yellow suspension was stirred (19 h) during which time several changes occurred in the i.r. spectrum of the solution. The solvent was removed and the resulting solid washed with light petroleum. The resulting solid was dissolved in dichloromethane, filtered through alumina, and crystallised from dichloromethane to give the brownish yellow solid [(η-C$_5$H$_5$)(Ph$_3$P)(OC)$_2$MoC(O)(CH$_2$)$_3$W(CO)$_3$(η-C$_5$H$_5$)] (19) (0.274 g, 62%).

Preparation of [Mo\{(CH$_2$)$_3$Br\}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] (15).—A suspension of [\{Mo(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)\}$_2$][14] (0.48 g, 0.50 mmol) in thf (30 cm^3) was stirred over Na–Hg amalgam until the pink colour of the dimer was replaced by the yellow colour of the anion [Mo(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]$^-$ [ν(CO) (thf) at 1 792s and 1 693s cm^{-1}]. After removal of the excess amalgam the anion solution was treated with Br[CH$_2$]$_3$Br and stirred (22 h). Removal of solvent, extraction into dichloromethane, rapid filtration through alumina and crystallisation from dichloromethane–light petroleum afforded yellow air stable [Mo\{(CH$_2$)$_3$Br\}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] (15) (0.360 g, 60%), m.p. 122—123 °C (Found: C, 55.5; H, 4.5. C$_{28}$H$_{26}$BrMoO$_2$P requires C, 55.9; H, 4.3%); $\nu_{\mathrm{max.}}$(CO) (thf) at 1 923m and 1 846s cm^{-1}. N.m.r. (CDCl$_3$): ^{1}H, δ 7.40 (m, 15 H, Ph), 4.76 (s, 5 H, C$_5$H$_5$), 3.40 [t, 2 H, CH$_2$Br, *J*(HH) 7 Hz], 2.24 (m, 2 H, CH$_2$), and 1.47 (m, 2 H, CH$_2$); ^{13}C, δ 238.0 [d, CO, *J*(PC) 23], 136.7 [d, *i*-Ph, *J*(PC) 42], 133.1 [d, *o*-Ph, *J*(PC) 9], 129.9 (s, *m*-Ph), 128.2 [d, *p*-Ph, *J*(PC) 10 Hz], 92.7 (s, C$_5$H$_5$), 39.6 (s, CH$_2$), 37.6 (s, CH$_2$), and 0.1 (s, MoCH$_2$).

Preparation of [Mo\{(CH$_2$)$_3$Br\}(CO)$_2$\{P(OMe)$_3$\}(η-C$_5$H$_5$)] (16).—A suspension of [\{Mo(CO)$_2$[P(OMe)$_3$](η-C$_5$H$_5$)\}$_2$][14] (0.341 g, 0.5 mmol) in thf (30 cm^3) was stirred over Na–Hg amalgam until the maroon colour of the dimer was replaced by the very pale green colour of the anion [Mo(CO)$_2$\{P(OMe)$_3$\}(η-C$_5$H$_5$)]$^-$ [ν(CO) (thf) at 1 832 (sh), 1 810s, 1 759w, and 1 719s cm^{-1}]. After removal of excess amalgam the anion solution was treated with Br[CH$_2$]$_3$Br (0.4 g, 2.0 mmol) and stirred (19 h). Removal of solvent gave a yellow oil which was extracted into light petroleum and chromatographed rapidly on alumina. Elution with light petroleum removed excess Br[CH$_2$]$_3$Br while the product was eluted with dichloromethane and crystallised from dichloromethane–light petroleum to give low-melting-point yellow crystals of [Mo\{(CH$_2$)$_3$Br\}(CO)$_2$\{P(OMe)$_3$\}(η-C$_5$H$_5$)] (16) (0.25 g, 53%), m.p. 40—41 °C (Found: C, 33.6; H, 4.4. C$_{13}$H$_{20}$BrMoO$_5$P requires C, 33.7; H, 4.3%); $\nu_{\mathrm{max.}}$ (CO) (light petroleum) at 1 952m, and 1 879s cm^{-1}. N.m.r. (CDCl$_3$): ^{1}H, δ 5.05 (s, 5 H), 3.60 [d, 9 H, OMe, *J*(PH) 11], 3.37 [t, 2 H, CH$_2$Br, *J*(HH) 7 Hz], 2.15 (m, 2 H, CH$_2$), and 1.38 (m, 2 H, CH$_2$).

Table 5. Atomic positional parameters with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I(1)	0.095 39(12)	0.206 75(6)	0.131 90(5)
Mo(1)	−0.166 02(10)	0.251 58(5)	−0.040 91(5)
O(1)	0.255 2(10)	0.355 1(6)	−0.070 5(6)
O(2)	−0.334 0(12)	0.396 1(6)	0.097 1(5)
O(3)	−0.376 3(11)	0.360 2(5)	−0.211 1(5)
C(1)	0.104 2(13)	0.316 0(7)	−0.057 1(7)
C(2)	−0.269 8(14)	0.343 3(7)	0.048 7(6)
C(3)	−0.411 8(22)	0.452 3(9)	−0.255 1(8)
C(4)	−0.253 4(18)	0.513 5(8)	−0.204 3(9)
C(5)	−0.205 3(16)	0.466 1(7)	−0.109 9(7)
C(6)	−0.256 5(12)	0.367 1(6)	−0.127 3(5)
C(7)	−0.235 4(19)	0.086 0(7)	−0.034 5(8)
C(8)	−0.432 7(16)	0.133 4(7)	−0.047 9(8)
C(9)	−0.450 0(16)	0.179 4(7)	−0.133 3(7)
C(10)	−0.262 8(18)	0.161 4(7)	−0.174 2(7)
C(11)	−0.130 9(19)	0.102 8(7)	−0.111 8(8)

Reaction of [W\{(CH$_2$)$_3$Br\}(CO)$_3$(η-C$_5$H$_5$)] *with* LiI.—A solution of [W\{(CH$_2$)$_3$Br\}(CO)$_3$(η-C$_5$H$_5$)] (3) (0.39 g, 0.86 mmol) and LiI·3H$_2$O (0.2 g, 1.07 mmol) in 1,2-dimethoxyethane (50 cm^3) was refluxed for 30 h. Removal of solvent from the deep orange solution, extraction into dichloromethane and filtration through alumina gave an orange solution from which was obtained orange crystalline [WI(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η-C$_5H_5$)] (17) (0.22 g, 51%).

Reaction of [W\{(CH$_2$)$_3$Br\}(CO)$_3$(η-C$_5$H$_5$)] *with* KCN.—A solution of [W\{(CH$_2$)$_3$Br\}(CO)$_3$(η-C$_5$H$_5$)] (3) (0.5 g, 1.1 mmol) and KCN (0.1 g, 1.54 mmol) in methanol was refluxed for 4 d. Removal of solvent from the deep orange solution, extraction into dichloromethane, and filtration through alumina gave a yellow solution from which yellow crystalline [W(CN)(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η-C$_5H_5$)] (18) was isolated in low yield (0.010 g, 2.3%).

Crystal Structure Determination of [MoI(CO)$_2$\{$\overline{\mathrm{CO(CH_2)_2CH_2}}$\}(η-C$_5H_5$)] (5).—*Crystal data.* MoI(CO)$_2$(C$_4$H$_6$O)(C$_5$H$_5$), C$_{11}$H$_{11}$IMoO$_3$, *M* = 414.01, crystallises from dichloromethane–light petroleum (b.p. 40—60 °C) as thin, red needles (crystal dimensions 0.44 × 0.30 × 0.15 mm), Monoclinic, $a = 6.372(2)$, $b = 14.168(5)$, $c = 14.390(3)$ Å, $\beta = 98.12(2)°$, $U = 1\,286.0(6)$ Å^3, $D_m = 2.15$, $Z = 4$, $D_c = 2.138$ g cm^{-3}, space group $P2_1/c$ (from systematic absences), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 33.61 cm^{-1}, and $F(000) = 784$.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer by the ω-scan method. 1 726 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and, by the monitoring of two reflections, for 5% intensity loss during data collection. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were detected and 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 their positional parameters was permitted. Refinement converged at $R = 0.0355$ with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of iodine and molybdenum. Scattering factors were taken from ref. 21. Table 5 lists the atomic positional parameters with estimated standard deviations. Unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

Acknowledgements

We thank the S.E.R.C. for support.

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Received 17*th January* 1983; *Paper* 3/062