Reactions of the Metallabromoalkane $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ and the Carbene Complexes *trans*-$[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H or Me) with $Li(BEt_3H)$. The Synthesis (R = H or Me) and *X*-Ray Structure (R = Me)† of $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4R)]$ containing an Unusual Oxygen–Molybdenum Donor Interaction

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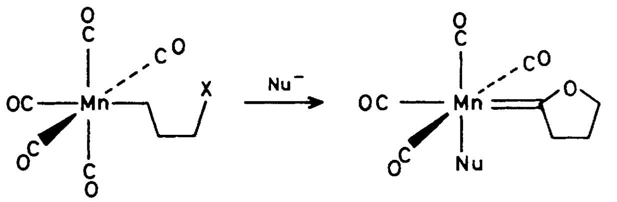
The reaction of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ with $Li(BEt_3H)$ leads to the spectroscopically characterised $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$. This compound is also formed in the reaction of the carbene complex *trans*-$[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ with $Li(BEt_3H)$. In both reactions small quantities of the known η^3-allyl $[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)]$ are also isolated. The methylcyclopentadienyl analogues are available through reaction of *trans*-$[MoI\{=C(CH_2)_3O\}(CO)_2\text{-}(\eta\text{-}C_5H_4Me)]$ with $Li(BEt_3H)$ and the resulting molecule $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4Me)]$ is the subject of an *X*-ray crystal structure determination. It crystallises as irregular red lumps, *a* = 8.416(9), *b* = 11.541(12), *c* = 7.063(3) Å, α = 105.23(3), β = 105.71(3), and γ = 104.938(12)°; *R* converged to 0.0299 for 1 805 independent reflections for which $I > 3.0\sigma(I)$. The bonding of the C_4H_7O ring is unusual and formulated as a metal–alkyl interaction adjacent to a O→Mo bond. The molybdenum–oxygen bond is labile, thus $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ reacts readily with PPh_3 to give the phosphine complex *trans*-$[Mo\{CH(CH_2)_3O\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ in good yield. Formation of $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ from the alkyl complex proceeds by the initial formation of a metal formyl complex $[Mo(CHO)\{(CH_2)_3Br\}(CO)_2(\eta\text{-}C_5H_5)]^-$ which rearranges through two further intermediates to the ultimate product. Formation of $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4R)]$ from the appropriate carbene complex is apparently by direct attack of the hydride reagent at the carbene atom. Reaction of the alkyl *trans*-$[Mo\{(CH_2)_3Br\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ with $Li(BEt_3H)$ leads only to the η^3-allyl $[Mo(CO)(PPh_3)(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)]$.

Neutral complexes (1)—(8) of the carbene ligand $=C(CH_2)_3O$ are formed in the reactions of $[Mn\{(CH_2)_3X\}(CO)_5]$, X = Cl (9) or Br (10), with I^- (ref. 1) or $[Mn(CO)_5]^-$ (ref. 2) (Scheme 1), or $[M\{(CH_2)_3X\}(CO)_3(\eta\text{-}C_5H_5)]$ (11)—(14) with anionic nucleophiles such as I^-, CN^-, SPh^-, and $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ (Scheme 2).[3] The mechanism of formation of the carbene ligand is common to these systems and involves a nucleophile-induced migratory insertion reaction, illustrated in Scheme 2 for the cases of Mo and W. The *trans* isomers are probably formed *via* the corresponding *cis* complexes. Perhaps naively, we reasoned that a nucleophilic hydride source might induce a similar insertion reaction leading to a neutral hydrido carbene complex with formula (15). Such a molecule, especially if in equilibrium with its *cis* isomer (16), could subsequently undergo hydride to carbene migrations in the presence of a two-electron donor ligand, L, as shown, which are of interest since such migrations are implicated in metal-assisted C–H bond formations during the reduction of CO.[4]

In this paper we examine the reactions of compound (11) with $Li(BEt_3H)$, which is a strongly nucleophilic hydride donor, carried out in the hope of synthesising (15). We also examine the reaction of the iodo carbene (3) with $Li(BEt_3H)$ in the expectation of forming the same compound. Parts of this work formed the subject of a preliminary communication.[5]



(9) X = Cl
(10) X = Br

(1) Nu = I
(2) Nu = $Mn(CO)_5$

Scheme 1. Nu = Nucleophile

Results and Discussion

The Complexes $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H *or* Me).—The hydrido carbene (15) is not isolable from the

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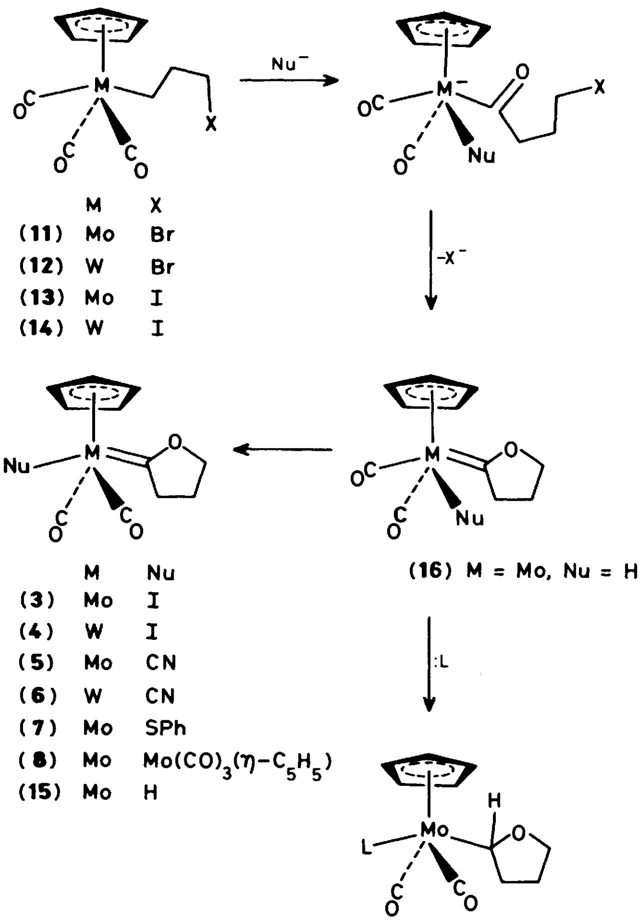
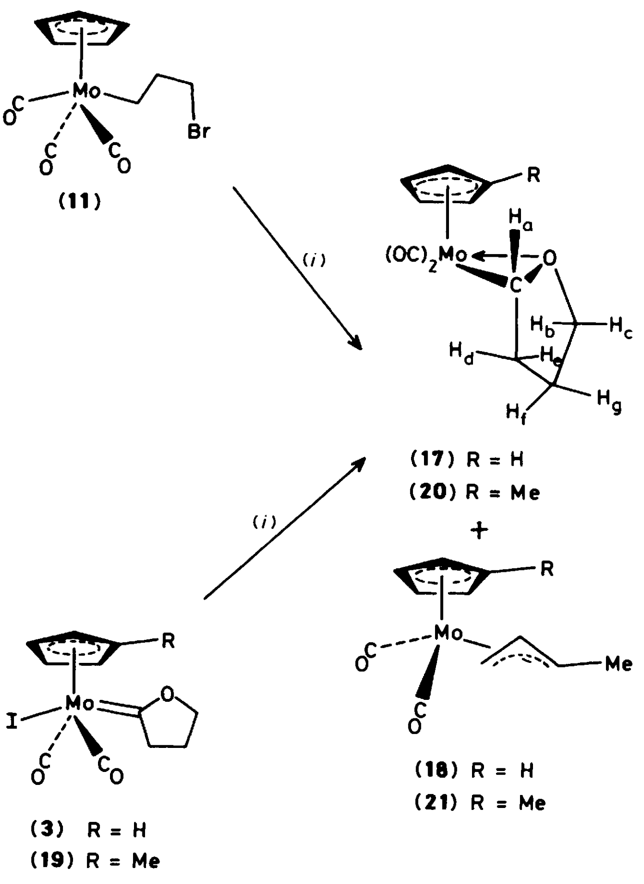
† Dicarbonyl(η-methylcyclopentadienyl)(oxolan-2-yl-C^2O)molybdenum.

Supplementary data available (No. SUP 56590, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



Scheme 2. Nu = Nucleophile; L = CO, phosphine, *etc.*



Scheme 3. (*i*) Li(BEt$_3$H)

reaction of the bromometalla-alkane (**11**)[6] with Li(BEt$_3$H). Treatment of a solution of (**11**) in tetrahydrofuran (thf) with a solution of Li(BEt$_3$H) at ambient temperature results in rapid darkening of the solution to deep orange and replacement of the two carbonyl stretching bands of (**11**) [ν(CO)(thf) 2 015m and 1 923s cm^{-1}] by two predominant bands [ν(CO)(thf) 1 925s and 1 829s cm^{-1}] shown after work-up to correspond to the major product (**17**) (Scheme 3). Rather low yields of the known η^3-allyl (**18**)[7] are also formed; this result is considered later.

Complex (**17**) is an orange reasonably air-stable microcrystalline material that is somewhat air sensitive in solution. Isolated yields are rather variable and up to 35%; this would appear to be a consequence of decomposition during work-up rather than an inherent low yield for the reaction.

Complex (**17**) is fully spectroscopically characterised. The solution i.r. spectrum in the carbonyl region consists of two strong bands of comparable intensity, consistent with a *cis* dicarbonyl, assuming a square-based pyramidal geometry ('four-legged piano stool') at molybdenum. The partially decoupled ^{13}C n.m.r spectrum displays two carbonyl signals, an intense doublet assignable to the cyclopentadienyl group together with three triplets and a doublet attributable to the four carbon atoms of the ring system. The multiplicity of the latter four signals is indicative of three CH$_2$ and a single CH environment. The ^{1}H n.m.r. spectrum at 400 MHz consists of a singlet for the cyclopentadienyl group together with seven complex multiplets, each corresponding to a single hydrogen. A detailed analysis of the spectrum is consistent with structure (**17**) and the assignments are given in Scheme 3.

In addition to the above data a prominent ion pattern in the mass spectrum assignable to [C$_{11}$H$_{12}$MoO$_3$]$^+$ and the elemental analysis are consistent with the formulation [Mo(C$_4$H$_7$O)(CO)$_2$(η-C$_5$H$_5$)]. Vapour-pressure osmometry indicates a monomeric structure in chloroform solution. Elemental analysis and the n.m.r. spectra clearly show that there is no incorporated solvent molecule, co-ordinated to the metal or otherwise.

All the data suggest the complex has a C$_4$H$_7$O ring; the only way to maintain an 18-electron count at the metal is for the ether oxygen to donate a lone pair to the metal as in the representation (**17**). Ether–metal bonds are known, for instance in [Cr(CO)$_5$(thf)][8] and [Mn(CO)$_2$(thf)(η-C$_5$H$_5$)],[9] but they are generally too labile to allow isolation of the complexes. The stability in the present case relies upon the adjacent alkyl–metal interaction maintaining the ether oxygen within the bonding vicinity of the metal.

In addition to this route leading to (**17**), the reaction of the carbene complex (**3**) with Li(BEt$_3$H) under similar reaction conditions also produces (**17**) (Scheme 3). Again the η^3-allyl (**18**) is a by-product. Spectroscopic data for the two complexes are identical.

The reaction of Li(BEt$_3$D) (minimum 94% deuteride with the difference made up by hydride) with carbene (**3**) gives deuteriated (**17**) and (**18**); again, the latter η^3-allyl complex is considered below.

The 400-MHz ^{1}H n.m.r. spectrum of deuteriated compound (**17**) is consistent with it being a mixture of [^{2}H$_1$]-(**17**) and some unlabelled (**17**). The position of deuteriation is at H$_a$. A doublet at δ 4.22 is assigned to H$_a$ itself. The signals at δ 2.60 and

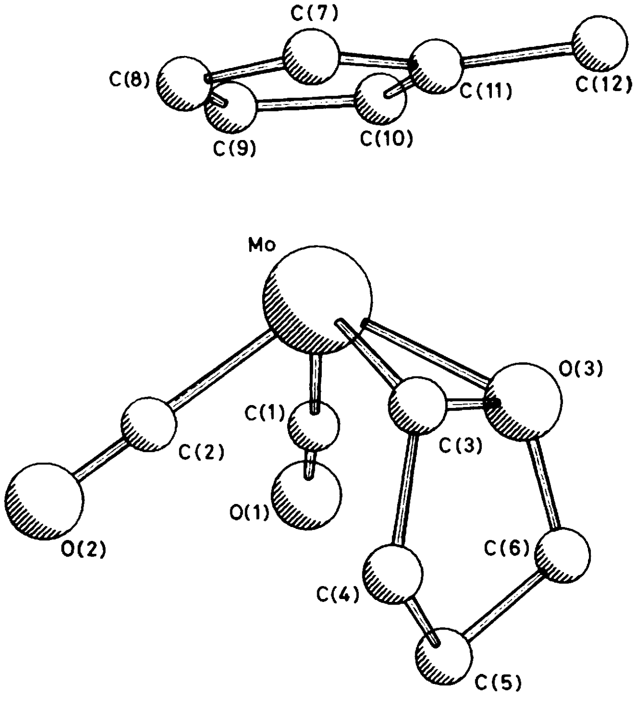


Figure. The molecular structure and atom labelling for $[\mathrm{Mo}\{\overline{\mathrm{CH(CH_2)_3O}}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})]$ (**20**)

Table 1. Atomic positional parameters with estimated standard deviations for $[\mathrm{Mo}\{\overline{\mathrm{CH(CH_2)_3O}}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})]$ (**20**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.235 18(5)	0.251 95(4)	0.016 49(6)
O(1)	0.355 2(6)	0.543 3(4)	0.262 3(7)
O(2)	−0.080 3(5)	0.288 5(4)	0.134 5(6)
O(3)	0.223 1(5)	0.284 2(3)	−0.274 1(5)
C(1)	0.313 8(6)	0.435 4(5)	0.169 0(8)
C(2)	0.037 1(6)	0.273 5(4)	0.088 6(7)
C(3)	0.059 1(6)	0.196 3(4)	−0.304 3(7)
C(4)	−0.081 9(7)	0.248 0(5)	−0.377 0(8)
C(5)	0.017 3(8)	0.390 9(5)	−0.305 0(8)
C(6)	0.196 3(8)	0.398 9(5)	−0.314 0(9)
C(7)	0.255 2(7)	0.045 1(4)	−0.041 8(8)
C(8)	0.248 9(7)	0.092 7(5)	0.157 1(9)
C(9)	0.400 8(7)	0.201 1(5)	0.279 8(8)
C(10)	0.501 4(6)	0.221 9(5)	0.151 4(8)
C(11)	0.409 3(6)	0.122 6(5)	−0.049 8(8)
C(12)	0.467 2(9)	0.104 0(7)	−0.236 6(10)

1.90 are more complex than those of pure (**17**). This is due to an isotopic shift of about 2.5 Hz to low frequency for these signals in $[^2H_1]$-(**17**) as compared to (**17**) itself, resulting in overlapping multiplets for the H_d and H_e protons. No couplings less than 1 Hz are resolved in this spectrum, the H_d signal for both (**17**) and $[^2H_1]$-(**17**) being essentially a doublet of doublets. Integration of the components of this signal allows an estimate of the ratio $[^2H_1]$-(**17**):(**17**) as 62:38. The change in multiplicity of the H_e signal (δ 1.90) makes the analysis of the overall overlapped multiplets intractable. A statistical analysis of the isotope patterns in the mass spectrum of deuteriated (**17**) and comparison with computer-simulated spectra gives a similar estimate of the ratio $[^2H_1]$-(**17**):(**17**). There are no other resolved n.m.r. isotope shifts for the more remote protons. One would expect this experiment to lead to pure $[^2H_1]$-(**17**); it appears that some loss of label occurs during the reaction or work-up.

In analogous fashion the methylcyclopentadienyl complex (**19**) reacts with $Li(BEt_3H)$, to give (**20**) as the major product; again small quantities of an η^3-allyl complex, (**21**), are observed. Comparison of the i.r., ^1H, and ^{13}C n.m.r. spectra shows the nature of the C_4H_7O ligands in (**17**) and (**20**) to be essentially identical.

Clearly compounds (**17**) and (**20**) are unusual. We were unable to prepare suitable samples of (**17**) for *X*-ray crystallographic analysis, but suitable samples of (**20**) form by crystallisation from pentane. The structure of compound (**20**) is illustrated in the Figure, while atomic positional parameters, bond lengths, angles, and details of planar fragments are in Tables 1—3.

The most significant feature of the molecule is the bonding mode of the C_4H_7O ligand. While the molybdenum–oxygen and molybdenum–carbon bonds are indistinguishable in length (2.161 Å), the assignment of the two atoms is made unambiguous by the clear detection of the hydrogen atom bonded to C(3). Although not refined, the position of this hydrogen atom is optimised from electron difference syntheses at a final position only 2.55 Å from the molybdenum atom. The MoC_4H_7O ring system is very non-planar, being cumulatively hinged about the C(3)–O(3) and C(4)···C(6) vectors by 58.7 and 31.1° respectively. The C(3)–O(3) bond length [1.409(6) Å] is close to that of a single bond. This is expected however one represents the bonding for the C_4H_7O ring to molybdenum. The two possibilities are a π donation from a carbon–oxygen double bond (pseudo-olefinic) as in structure (**22**), or directed valence bonds from essentially sp^3-hybridised carbon and oxygen atoms as in (**17**) and (**20**), which we use throughout this paper.

The bonding of the planar C_5H_4Me ring is slightly asymmetric with the distances to atoms C(7) and C(11) being the greatest; these lie above the C_4H_7O ring and approximately

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations for $[\mathrm{Mo}\{\overline{\mathrm{CH(CH_2)_3O}}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})]$ (**20**)

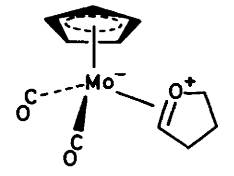
Mo–C(1)	1.943(6)	O(3)–C(3)	1.409(6)	C(1)–Mo–C(2)	76.37(22)	C(4)–C(5)–C(6)	103.7(5)
Mo–C(2)	1.925(5)	O(3)–C(6)	1.482(8)	C(1)–Mo–C(3)	112.14(21)	C(5)–C(6)–O(3)	104.8(5)
Mo–C(3)	2.161(5)	C(3)–C(4)	1.491(8)	C(1)–Mo–O(3)	90.89(19)	Mo–O(3)–C(3)	70.97(25)
Mo–O(3)	2.161(4)	C(4)–C(5)	1.515(9)	C(2)–Mo–C(3)	84.61(19)	Mo–O(3)–C(6)	123.31(33)
Mo–C(7)	2.372(5)	C(5)–C(6)	1.505(9)	C(2)–Mo–O(3)	110.32(18)	C(3)–O(3)–C(6)	109.0(4)
Mo–C(8)	2.321(6)	C(7)–C(8)	1.389(8)	C(3)–Mo–O(3)	38.05(16)	C(11)–C(7)–C(8)	109.4(5)
Mo–C(9)	2.310(6)	C(8)–C(9)	1.399(8)	Mo–C(1)–O(1)	117.4(5)	C(7)–C(8)–C(9)	108.4(5)
Mo–C(10)	2.338(5)	C(9)–C(10)	1.422(8)	Mo–C(2)–O(2)	178.8(4)	C(8)–C(9)–C(10)	107.7(5)
Mo–C(11)	2.393(5)	C(10)–C(11)	1.422(8)	Mo–C(3)–O(3)	70.98(25)	C(9)–C(10)–C(11)	107.5(5)
O(1)–C(1)	1.152(7)	C(11)–C(7)	1.398(8)	Mo–C(3)–C(4)	126.24(36)	C(10)–C(11)–C(7)	107.1(5)
O(2)–C(2)	1.160(6)	C(11)–C(12)	1.509(9)	O(3)–C(3)–C(4)	108.9(4)	C(10)–C(11)–C(12)	126.5(5)
				C(3)–C(4)–C(5)	103.6(5)	C(7)–C(11)–C(12)	126.4(5)

Table 3. Details of planar fragments of $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4Me)]$ (**20**). Equations of least-squares planes are of the form $pX + qY + rZ = d$ where p, q, and r are direction cosines referred to orthogonal crystal axes a, b^*, and c'. Deviations (Å) of atoms from mean planes are given in parentheses

Plane	*p*	*q*	*r*	*d*	Root mean square deviation
A C(7)—C(11)					0.005
	−0.6126	0.5744	−0.5429	−0.7598	
[C(7) −0.001, C(8) 0.005, C(9) −0.007, C(10) 0.006, C(11) −0.003, Mo 2.017, C(12) −0.016]					
B Mo, O(3), C(3)					
	−0.6525	0.7577	0.0099	1.1974	
[C(4) 1.185, C(5) 2.134, C(6) 1.218]					
C O(3), C(3), C(4), C(6)					0.014
	−0.2851	0.4289	0.8572	−1.7260	
[O(3) −0.017, C(3) 0.017, C(4) −0.010, C(6) 0.010, Mo 1.745, C(5) 0.482]					
D C(4)—C(6)					
	0.0594	0.0430	0.9973	−3.4734	
[O(3) 0.705, C(3) 0.747]					

Angles (°) between planes:

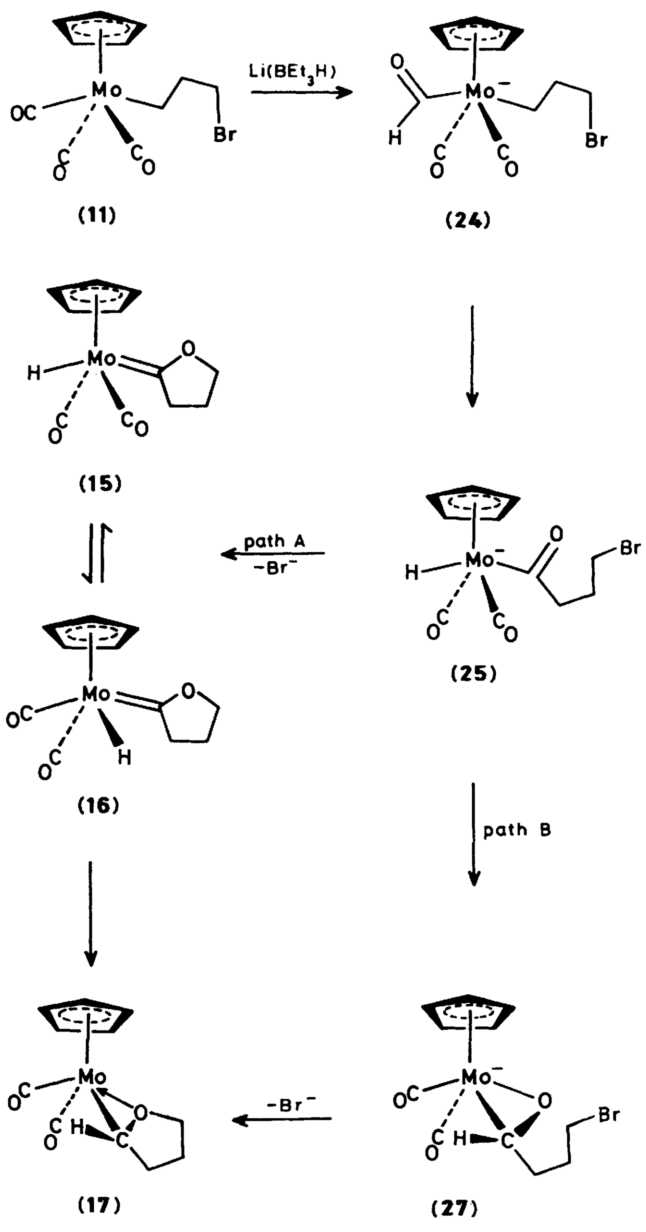
A–B	33.9	B–C	58.7
A–C	92.5	B–D	89.8
A–D	123.6	C–D	31.1



(22)

trans to the pair of linear carbonyl ligands, so this small asymmetry may have both steric [*via* atom H(3)] and electronic (through competitive back donation) origins. The methyl substituent on the cyclopentadienyl ring is almost coplanar with the ring, deviating very slightly (0.016 Å) in a direction away from the metal.

Mechanism of Formation of $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**17**) *from* $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (**11**).—The postulated mechanism for the formation of compound (**17**) from (**11**) is presented in Scheme 4; it is based partly on the results of a study into the reaction of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ with $Li(BEt_3H)$ discussed elsewhere[10] and summarised in Scheme 5. The ^1H n.m.r. spectra obtained after by mixing (**11**) and $Li(BEt_3H)$ in thf at −78 °C are complex and not entirely satisfactory; in part they are complicated by the large thf and ethyl resonances. However, the spectrum does show a clear, very high-frequency signal at δ 14.1 indicative of a metal formyl,[11] and very similar in position to the three related molybdenum formyls $[Mo(CHO)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$,[12] $[Mo(CHO)(COCO_2Me)(CO)_2(\eta\text{-}C_5H_5)]^-$,[13] and $[Mo(CHO)Me(CO)_2(\eta\text{-}C_5H_5)]^-$ (**23**) [δ(thf) 14.3].[10] The last of these formyls is the initial product formed in Scheme 5. This new species is therefore, by analogy with Scheme 4, assigned the structure (**24**). The presence of compound (**24**) indicates that the hydride *does not* promote an insertion reaction in a direct manner as in Scheme 2.

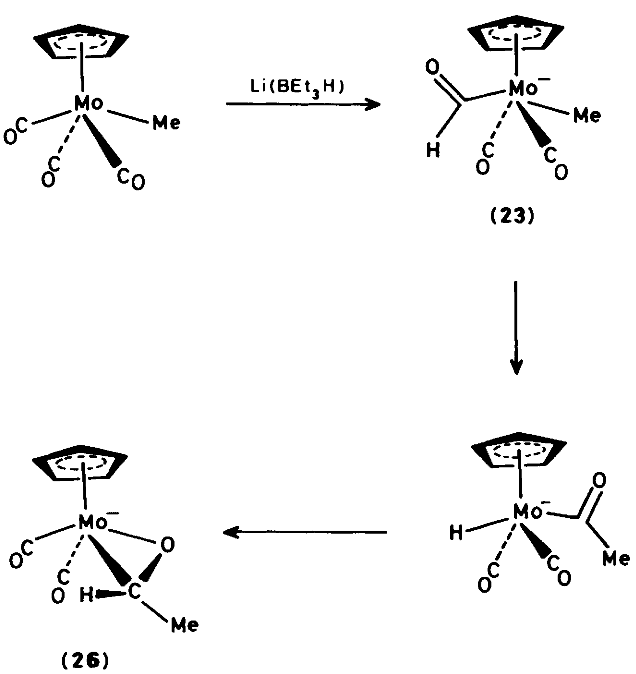


Scheme 4.

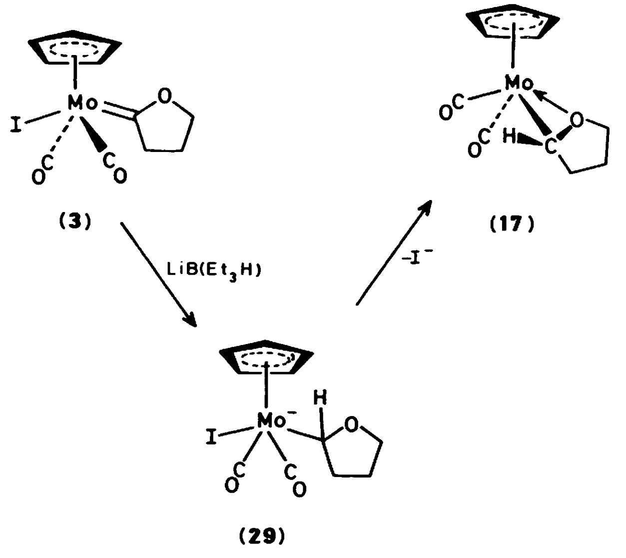
By analogy with the reaction in Scheme 4, the formyl (**24**) should then rearrange to the hydrido acyl (**25**) (Scheme 4). This is apparently the case; the formyl signal is replaced, upon warming to approximately −40 °C, by a hydride signal in some spectra [δ(thf) −6.5], but this is the present extent of the evidence for (**25**).

At this point, there are two possibilities for the eventual formation of (**17**), denoted A and B in Scheme 4. Either ring closure to the hydrido carbene (**15**) (path A) followed by hydride migration, or hydride to acyl migration (path B) followed by ring closure will result in (**17**).

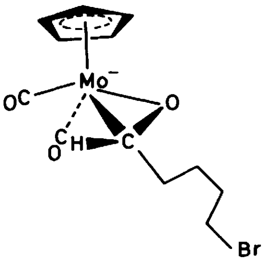
The results of an i.r. monitoring experiment indicate that path B is followed. Monitoring a reaction in which the reactants were mixed at −78 °C and allowed to warm towards ambient temperature gave a mixture which at about −5 °C contains bands assignable to compound (**17**), and two other absorptions



Scheme 5.



Scheme 6.



(28)

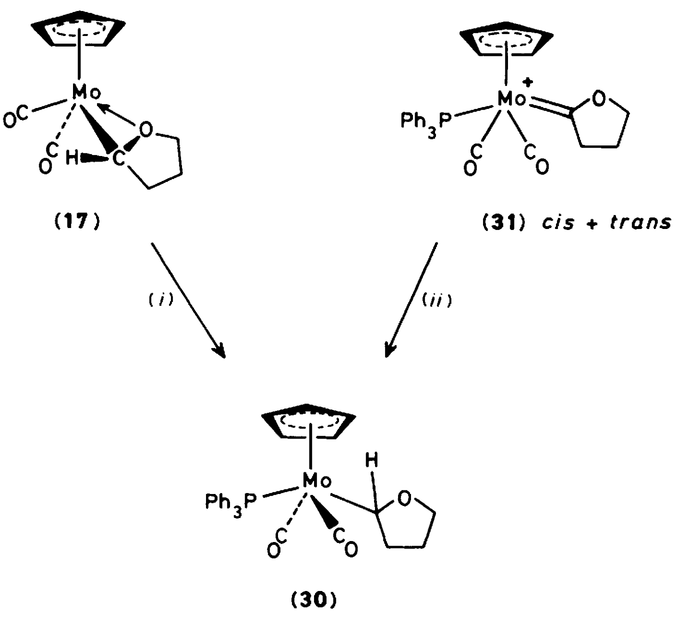
[ν(CO) (thf) 1 877s and 1 773s cm^{-1}] which diminish in favour of the two main product bands. The i.r. bands of the intermediate correspond very closely to those (1 870s and 1 776 cm^{-1})[10] of the η^2-acetaldehyde anion [Mo(CO)$_2$(η^2-MeCHO)(η-C$_5$H$_5$)]$^-$ (**26**) (Scheme 5) and therefore suggest that the aldehyde anion (**27**) is an intermediate as required by path B. These i.r. stretching frequencies indicate an anion rather than a neutral species. There are no signs in the i.r. spectrum at any stage of a species that could be accorded the structure [MH(CO)$_2$(carbene)(η-C$_5$H$_5$)] whose i.r. absorptions would occur at much higher frequency.[14] It is therefore apparent that hydrogen migration in (**25**) to form (**27**) proceeds more rapidly than ring closure to form (**15**).

The facility with which compound (**11**) reacts with Li(BEt$_3$H) to give (**17**) indicated that it might be possible to synthesise a six-membered ring analogue by use of [Mo{(CH$_2$)$_4$Br}(CO)$_3$(η-C$_5$H$_5$)] in place of (**11**). This is not so. Treatment of a solution of [Mo{(CH$_2$)$_4$Br}(CO)$_3$(η-C$_5$H$_5$)] with Li(BEt$_3$H) results in changes in the i.r. spectrum which suggest an anionic dicarbonyl [ν(CO) 1 878s and 1 774s cm^{-1}]. This spectrum is similar to those of (**26**) and (**27**) and therefore is probably due to the anion [Mo{η^2-OCH(CH$_2$)$_4$Br}(CO)$_2$(η-C$_5$H$_5$)]$^-$ (**28**). Prolonged stirring does not result in any change in the i.r. spectrum, indicating that ring closure does not take place. Heating the reaction mixture results in some decomposition and gives a solution whose i.r. spectrum shows it to contain [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$.[15] It is not unreasonable that excess of Li(BEt$_3$H) will replace the terminal Br by H rendering the ring closure impossible, but this was not examined.

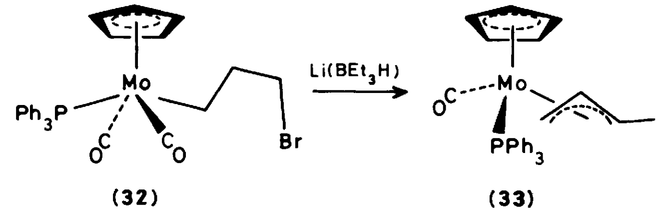
Mechanism of Formation of [Mo{CH(CH$_2$)$_3$O}(CO)$_2$(η-C$_5$H$_4$R)] (**17**) *and* (**20**) *from* [MoI{C(CH$_2$)$_3$O}(CO)$_2$(η-C$_5$H$_4$R)] (**3**) *and* (**19**).—The mechanism of formation of compound (**17**) from (**3**) is different from that in its synthesis from (**11**). Monitoring the reaction between (**3**) and Li(BEt$_3$H) by low-temperature ^{1}H n.m.r. spectroscopy does not result in the direct observation of any formyl or molybdenum hydride intermediates. This suggests that attack of hydride directly at the carbene atom (Scheme 6) provides the intermediate represented as (**29**) which loses I$^-$ upon co-ordination of the ring oxygen atom to provide the observed product (**17**). A similar process will clearly operate for the formation of (**20**). This n.m.r. evidence is negative rather than positive, however, therefore this hypothesis remains a suggestion only. Nevertheless, attack of hydride at carbene centres is well documented. Direct attack of hydride at the metal with loss of I$^-$ to provide the neutral hydrido carbene (**15**) cannot be ruled out if hydride to carbene migration proceeds sufficiently rapidly to preclude detection by the n.m.r. methods employed.

Cleavage of the Mo←O *Bond by* PPh$_3$.—One expects the Mo←O interaction in (**17**) to be labile owing to a lack of available oxygen orbitals to stabilise the low-oxidation-state molybdenum through a back-bonding interaction. This lack is reflected in the relatively low carbonyl stretching frequencies indicating they accommodate more than the usual charge density. This hypothesis is borne out. The Mo←O lability is illustrated in the reaction of compound (**17**) with PPh$_3$ (Scheme 7); rapid reaction ensues at ambient temperatures and good yields of the *trans*-phosphine complex (**30**) result. The ^{1}H n.m.r. spectrum of (**30**) is again quite complex but consistent with the postulated structure. The hydrogen atoms situated on carbon atoms alpha to the oxygen atom resonate at considerably higher frequency than those of (**17**), as a consequence of the removal of oxygen from the co-ordination sphere of molybdenum. One interesting feature of the ^{13}C n.m.r. spectrum is that the two carbonyls are prochiral; each appears as a doublet because of coupling to ^{31}P.

By way of chemical corroboration of the structure of (**30**), a mixture of *cis* and *trans* isomers of the cationic carbene (**31**)[16] upon treatment with Li(BEt$_3$H) at ambient temperature also



Scheme 7. (*i*) PPh_3; (*ii*) $Li(BEt_3H)$



Scheme 8.

leads to a high yield of (**30**) (Scheme 7). The latter reaction probably proceeds by direct attack of the hydride at the carbene. It is likely that the *cis* isomer of (**30**) is also formed, but undergoes *cis–trans* isomerisation to the thermodynamically preferred *trans* product.

Formation of the η^3-*Allyl Complexes* $[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_4R)]$ (**18**) *and* (**21**).—The mechanism of formation of compound (**18**) or (**21**) in the above reactions is clearly complex. Clues are provided by ^2H- and ^{13}C-labelling experiments involving the carbene (**3**) as the precursor for (**18**). The arguments used below obviously may be applied for the formation of (**21**). Despite the resulting information there is not an unambiguous mechanism, but some interesting points arise from the spectroscopic data.

The allyl ligand contains a four-carbon chain whereas the aliphatic chain in the carbene (**3**) only has three. This implies the fourth carbon originates from the carbene atom. The seventh hydrogen atom comes from the hydride reagent. The positions of ^{13}C and ^2H incorporation are revealed by isotopic labelling experiments. These experiments show that (*i*) the carbene atom of (**3**) is transformed exclusively into the methyl group of (**18**) and (*ii*) deuteriated (**18**) incorporates some deuterium in *all* positions of the molecule, including the cyclopentadienyl ring, but the bulk of the label is in the methyl group. The methyl group contains an average of one deuterium atom but is a mixture of CH_3, CH_2D, CD_2H, and with a possibility of a little CD_3. Although the deuterium-isotope incorporation into the molecule is approximately 20:40:35:5 for $^2H_0$:$^2H_1$:$^2H_2$:$^2H_3$ overall, these numbers do not necessarily reflect the deuterium incorporation of the methyl group.

The labelled carbene (**3***) may be synthesised from $[\{Mo({}^*CO)_3(\eta\text{-}C_5H_5)\}_2]$ (enriched by ^{13}C at the carbonyl positions to an average of 10%) by sodium-amalgam cleavage to form $[Mo({}^*CO)_3(\eta\text{-}C_5H_5)]^-$ and subsequent treatment with $I(CH_2)_3I$. In this way the carbene atom is enriched to around 10% ^{13}C. Treatment of (**3***) with $Li(BEt_3H)$ under the above reaction conditions leads to (**17***) together with (**18***). The ^{13}C n.m.r. spectrum of (**18***) contains three signals enhanced as a result of ^{13}C enrichment; these are the two non-equivalent carbonyls and the signal assigned to the methyl group (a quartet in the partially proton-decoupled spectrum). Rather unexpectedly, it is clear that the original carbene atom is the only carbon atom no longer bonded to molybdenum. The overall formation of (**18**) from $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ therefore requires the complete cleavage of the CO triple bond. There is *no* indication of ^{13}C enrichment at any other site.

We have not carried out a similar labelling experiment using (**11***) as starting material but expect that a similarly labelled complex (**18***) would ensue.

The deuterium-labelling experiment is not as clear cut. Addition of $Li(BEt_3D)$ to a solution of compound (**3**) leads to deuteriated (**17**), as described above, in addition to deuteriated (**18**). A statistical analysis of the molecular ion isotope pattern of labelled (**18**) indicates that this material is a mixture of $^2H_0$, $^2H_1$, $^2H_2$, and perhaps $^2H_3$ complexes in the approximate ratio 20:40:35:5. The ^2H n.m.r. spectrum of this mixture indicates the bulk of this label is at the methyl position but that there is a quantity (total approximately 20% by integration of the ^2H n.m.r. spectrum) distributed between all other positions including the cyclopentadienyl ring. This is reinforced by the ^1H n.m.r. spectrum in which the methyl multiplet integrates only to approximately two protons relative to the other signals. The ^{13}C-$\{^1H\}$ n.m.r. spectrum (100 MHz, −70 °C) is rather interesting. The methyl region is complex and consists principally of a singlet (δ 21.1) assigned to the $^2H_0$ species and a 1:1:1 triplet $[{}^1J({}^{13}C{}^2H)$ 20 Hz$]$ assigned to $[{}^2H_1]$-(**18**) with an isotope shift of 26 Hz to low frequency as compared to the singlet. The carbon alpha to the methyl also appears as a multiplet owing to $^2J({}^{13}C{}^2H)$ coupling of 6 Hz. Other much lower-intensity signals might be attributed to $[{}^2H_2]$-(**18**) but not unambiguously owing to the quality of the spectrum. Since the initial $Li(BEt_3D)$ contained a minimum of 94% deuterium it is clear that considerable scrambling occurs.

In separate experiments treatment of a solution of compound (**17**) with $Li(BEt_3H)$ led to some (**18**) (i.r. spectrum) suggesting that (**17**) may be a precursor, though not necessarily unique, for (**18**) in the reactions involving (**3**) and (**11**). We also note that higher yields of (**18**) arise when higher molar excesses of $Li(BEt_3H)$ are employed.

The observation of some deuterium incorporation into the cyclopentadienyl ring suggests that metal deuterides might be involved at some stage. It is possible to write more than one mechanism for the formation of (**18**), but they must remain speculative despite all the available data.

Reaction of $[Mo\{(CH_2)_3Br\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ *with* $Li(BEt_3H)$.—Finally we note one further result. Addition of $Li(BEt_3H)$ to a solution of compound (**32**) results in a slow reaction and isolation of a single product, the monocarbonyl η^3-allyl (**33**) (Scheme 8). This compound was characterised by elemental analysis, mass spectrometry, and i.r. spectroscopy together with its ambient-temperature ^1H and ^{13}C n.m.r. spectra. Decoupling experiments allow full assignment of the ^1H n.m.r. spectrum. There is no indication of two isomers in either n.m.r. spectra. There is no sign in this reaction of the phosphine derivative $[Mo\{\overline{CH(CH_2)_3O}\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ although it could still be an intermediate.

Experimental

Infrared spectra were recorded using a Perkin-Elmer 257 spectrometer calibrated using the absorption of polystyrene film at 1 601.4 cm^{-1}. Proton n.m.r. spectra were recorded using Bruker WP-80SY (80.13 MHz), Bruker WH-400 (400.13 MHz), AM-250 (250 MHz), and Perkin-Elmer R34 (220 MHz) instruments. Carbon-13 n.m.r. spectra were recorded using a JEOL PFT-100 (25.15 MHz) or the WH-400 (100.62 MHz) instrument, ^2H n.m.r. spectra on the WH-400 instrument at 61.42 MHz. Mass spectra were obtained using a Kratos MS 25 instrument.

All reactions were performed under a nitrogen atmosphere. Solvents were used as supplied, except thf which was distilled from sodium–benzophenone immediately prior to use and light petroleum (b.p. 40—60 °C throughout) which was distilled from $LiAlH_4$. Alumina was Brockmann activity I deactivated with water (5% w/w) to activity II.

The compounds $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[17] $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (**11**),[6] $[Mo\{(CH_2)_3Br\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (**32**),[3a] and *trans*-$[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5R)]$ (**3**; R = H) and (**19**; R = Me)[3] were synthesised according to literature procedures. Complexes enriched with ^{13}C were prepared from $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ enriched with ^{13}C to approximately 10% at each of the carbonyl positions.[18]

The reagents $Li(BEt_3H)$ (Aldrich, 'Super Hydride') and $Li(BEt_3D)$ (Aldrich, 'Super Deuteride') were used as supplied. Measurement of the ^{11}B n.m.r. spectra for several batches of $Li(BEt_3H)$ indicates the reagent consists mainly of $Li(BEt_3H)$ [δ(thf) −12.5] together with small amounts (which vary with the batch number) of $Li(BEt_4)$ [δ(thf) −17.8] and $Li(BEt_2H_2)$ [δ(thf) −18.5, $^1J(BH)$ *ca.* 70 Hz], all shifts relative to $BF_3{\cdot}OEt_2$. Some consequences of this observation are reported elsewhere.[19]

Reactions.—$[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ (**11**) *with* $Li(BEt_3H)$. A solution of compound (**11**) (0.75 g, 2.04 mmol) in thf (50 cm^3, −78 °C) was treated dropwise with $Li(BEt_3H)$ (4.0 cm^3, 0.9 mol dm^{-3} in thf, 3.6 mmol). The resulting mixture was allowed to warm to ambient temperature after which the solvent was removed under reduced pressure. Extraction of the dark oily residue into light petroleum–dichloromethane (1:4) followed by chromatography (alumina, 25 × 2 cm, −25 °C) gave two fractions. Elution with light petroleum–dichloromethane (85:15) provided small quantities of $[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)]$ (**18**) which was followed by an orange fraction containing $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**17**) (0.125 g, 20%).

trans-$[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**3**) *with* $Li(BEt_3H)$. A solution of compound (**3**) (0.5 g, 1.21 mmol) in thf (50 cm^3, −78 °C) was treated dropwise with $Li(BEt_3H)$ (1.7 cm^3, 1.0 mol dm^{-3} in thf, 1.7 mmol) and allowed to warm towards ambient temperature. The solution darkened and then lightened to an orange colour. After filtration through alumina and removal of solvent the resulting dark oil was extracted into light petroleum, filtered through Kieselguhr, and chromatographed on a short alumina column (5 × 2 cm). Elution with light petroleum gave yellow $[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)]$ (**18**) (0.036 g, 11%) followed by orange $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**17**) (0.12 g, 31%), both of which crystallised from pentane.

$[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**17**): m.p. 69.5—70.5 °C [Found: C, 46.2; H, 3.9%; *M* 290 (^{98}Mo). $C_{11}H_{12}MoO_3$ requires C, 45.8; H, 4.2%; *M* 290 (^{98}Mo)]; ν(CO)(light petroleum) 1 937s and 1 845 cm^{-1}; ^1H n.m.r., $\delta(C_6D_6)$ 5.10 (s, 5 H, C_5H_5), 4.22 {1 H, H_a [H_b 0.5, H_c 0.5, H_d 0.5, H_e 6.5, and H_g 0.5]}, 3.33 {1 H, H_b [H_a 0.5, H_c 8.35, H_d 0.5, H_e 0.5, H_f 8.4, and H_g 0.9]}, 3.27 {1 H, H_c [H_a 0.5, H_b 8.35, H_d 0.5, H_e 0.3, H_f 7.4, and H_g 5.7]}, 2.60 {1 H, H_d [H_a 0.5, H_b 0.5, H_c 0.5, H_e 13.1, H_f 7.4, and H_g 0.7]}, 1.94 {1 H, H_e [H_a 6.5, H_b 0.5, H_c 0.3, H_d 13.1, H_f 11.9, and H_g 7.5]}, 1.59 {1 H, H_f [H_b 8.4, H_c 11.9, H_d 7.4, H_e 11.9, and H_g 12.5]}, and 1.07 {1 H, H_g [H_a 0.5, H_b 0.9, H_c 5.7, H_d 0.7, H_e 7.5, and H_f 12.5 Hz]}; ^{13}C n.m.r., $\delta(C_6D_6)$ 256.7 (s, CO), 246.7 (s, CO), 94.6 (d, C_5H_5), 79.9 (t, OCH_2), 75.6 (d, MoCH), 30.2 (t, $CHCH_2$), and 21.9 (t, central CH_2).

$[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)]$ (**18**), data as reported in the literature,[7] but in addition: ^{13}C n.m.r., $\delta(CD_2Cl_2$, −70 °C) 208.3 (s, CO), 205.1 (s, CO), 92.3 (d, C_5H_5), 69.3 (d, CH) 64.4 (d, *C*HMe), 34.1 (t, CH_2), and 21.1 (q, Me).

$[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4Me)]$ (**19**) *with* $Li(BEt_3H)$. The methylcyclopentadienyl compounds, orange $[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4Me)]$ (**20**) and yellow $[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_4Me)]$ (**21**) were prepared in a similar fashion and yields to those of (**17**) and (**18**) above from *trans*-$[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4Me)]$ (**19**). The C_5H_4Me complexes are more soluble than their C_5H_5 analogues.

$[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_4Me)]$ (**20**): m.p. 63—64 °C [Found: C, 47.7; H, 4.6%; *M* 304 (^{98}Mo). $C_{12}H_{14}MoO_3$ requires C, 47.7; H, 4.6; *M* 304 (^{98}Mo)]; ν(CO)(hexane) 1 939s and 1 844s cm^{-1}; ^1H n.m.r., $\delta(C_6D_6)$ 5.20 (m, 1 H, C_5H_4Me), 5.14 [t of d, 1 H, C_5H_4Me, *J*(HH) 2.6, 1.9], 4.80 (m, 2 H, C_5H_4Me), 4.05 {1 H, H_a [H_e 6.5 and H_f 0.5]}, 3.32 {1 H, H_b [H_c 8.3, H_f 8.2, and H_g 0.8]}, 3.23 {1 H, H_c [H_b 8.3, H_f 11.8, and H_g 5.7]}, 2.58 {1 H, H_d [H_e 12.9, H_f 7.4, and H_g 0.8]}, 1.92 {1 H, H_e [H_a 6.5, H_d 12.9, H_f 12.3, and H_g 7.4]}, 1.59 {1 H, H_f [H_a 0.5, H_b 8.2, H_c 11.8, H_d 7.4 H_e 12.3, and H_g 12.3]}, 1.52 [d, 3 H, Me, *J*(HH) 0.5], and 0.97 {1 H, H_g [H_b 0.8, H_c 5.7, H_d 0.8, H_e 7.4, and H_f 12.3 Hz]}; ^{13}C n.m.r., $\delta(C_6D_6)$ 256.4 (CO), 246.9 (CO), 113.4 (*C*Me), 96.1 (CH), 95.1 (CH), 90.6 (CH), 89.9 (CH), 79.7 (OCH_2), 77.6 (MoCH), 30.1 ($CHCH_2$), 21.8 (central CH_2), and 13.2 (Me).

$[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_4Me)]$ (**21**): m.p. 31—32 °C [Found: C, 50.7; H, 5.3%; *M* 288 (^{98}Mo). $C_{12}H_{14}MoO_2$ requires C, 50.3; H, 4.9; *M* 288 (^{98}Mo)]; ν(CO)(hexane) 1 957(sh), 1 954s, 1 893m, and 1 879s cm^{-1}; ^1H n.m.r., $\delta(CDCl_3)$ (major isomer) 5.19 (m, 2 H, C_5H_4Me), 5.11 (m, 1 H, C_5H_4Me), 5.07 (m, 1 H, C_5H_4Me), 3.80 [t of d, 1 H, *J*(HH) 10, 7 Hz, H_c], 2.30 [d of d, 1 H, *J*(HH) 7, 3, H_s], 1.96 (m, 3 H, C_5H_4Me), 1.76 (m, 3 H, $Me_{s'}$), 1.71 (m, 1 H, $H_{a'}$), and 0.76 [d of d, 1 H, *J*(HH) 10, 3 Hz, H_a] (hydrogen labels as in ref. 7).

$[Mo\{CH(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**17**) *with* PPh_3. Solid PPh_3 (0.317 g, 1.21 mmol) was added to a solution of compound (**17**) at ambient temperature prepared *in situ* as a thf solution from $[MoI\{=C(CH_2)_3O\}(CO)_2(\eta\text{-}C_5H_5)]$ (**3**) (1.0 mmol) in a similar way to that above. Stirring was continued for 2 h during which time the colour of the solution lightened to yellow. Filtration through alumina followed by removal of solvent gave a yellow oil which was taken up in dichloromethane, refiltered through alumina, and crystallised from dichloromethane–light petroleum to provide yellow crystalline *trans*-$[Mo\{CH(CH_2)_3O\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (**30**) (0.30 g, 55%): m.p. 152—154 °C {Found: C, 62.7; H, 4.7. $C_{29}H_{27}MoO_3P$ requires C, 63.3; H, 4.9%. The highest ion visible in the mass spectrum is at *m/e* 482 (^{98}Mo) which corresponds to the fragment $[MoH(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$}; $\nu(CO)(CH_2Cl_2)$ 1 934m and 1 850s cm^{-1}; ^1H n.m.r., $\delta(C_6D_6)$ 5.70 [d of d, 1 H, *J*(HH) 10.5, 5.5, MoCH], 4.83 (s, 5 H, C_5H_5), 4.08 [q, 1 H, *J*(HH) 7.5, OCH_2], 3.76 [t of d, 1 H, *J*(HH) 8.0, 4.5, OCH_2], 2.85 [d of d of d of d, 1 H, *J*(HH) 12.5, 8.0, 5.5, 2.5, $CHCH_2$], 2.53 [d of d of d of d, 1 H, *J*(HH) 12.5, 10.5, 9.5, 9.2, $CHCH_2$], 1.86

[d of d of d of d of d, 1 H, J(HH) 11.5, 9.0, 7.5, 4.5, 2.5, central CH_2], and 1.73 [d of d of q, 1 H, J(HH) 11.5, 9.5, 8.0 Hz, central CH_2]; ^{13}C n.m.r., δ($CDCl_3$) 240.1 [d, CO, J(PC) 25], 136.5 [d, Ph-*i*, J(PC) 43], 133.1 [d, Ph-*o*, J(PC) 11], 129.8 [d, Ph-*p*, J(PC) 2], 128.1 [d, Ph-*m*, J(PC) 9], 93.0 (s, C_5H_5), 75.3 [d, MoCH, J(PC) 11 Hz], 69.7 (s, OCH_2), 39.0 (s, CH*C*H_2), and 19.0 (s, central CH_2).

$[Mo\{{=}C(CH_2)_3O\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]Br$ (cis/trans) (**31**)[16] *with* Li(BEt_3H). A suspension of the cation (**31**) (0.41 g, 0.66 mmol) in thf (30 cm^3) was treated with Li(BEt_3H) (1.0 cm^3, 1.0 mol dm^{-3} in thf, 1.0 mmol) which resulted in a clear yellow solution. A similar work-up to that in the above experiment resulted in *trans*-$[Mo\{CH(CH_2)_3O\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (**30**) (0.075 g, 21%).

$[Mo\{(CH_2)_3Br\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (**32**) *with* Li(BEt_3H). A solution of Li(BEt_3H) (3.75 cm^3, 1.0 mol dm^{-3} in thf, 3.75 mmol) was added to a thf solution containing $[Mo\{(CH_2)_3Br\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (**32**) (0.75 g, 1.25 mmol) and the resulting mixture stirred (4 h) at the end of which the resulting yellow solution contained essentially no starting material (i.r. analysis). Removal of solvent under reduced pressure, followed by chromatography on alumina [9 × 2 cm, elution with light petroleum–diethyl ether (3:1)], provided a single yellow fraction containing yellow crystalline $[Mo(CO)(PPh_3)(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)]$ (**33**) (0.13 g, 21%); m.p. 149—152 °C [Found: C, 66.2; H, 5.6%; *M* 508 (^{98}Mo). $C_{28}H_{27}MoOP$ requires C, 66.4; H, 5.3; *M* 508 (^{98}Mo)]; ν(CO)(light petroleum) 1 846 cm^{-1}; ^1H n.m.r., δ($CDCl_3$) 7.32 (m, 15 H, Ph), 4.84 (s, 5 H, C_5H_5), 2.87 [d of t, 1 H, J(HH) 6, 9, H_c], 2.60 [d of q, 1 H, J(HH) 9, 6, $H_{a'}$], 1.88 [d, 3 H, J(HH) 6, $Me_{s'}$], 1.79 [d, J(HH) 10, H_a], and 1.61 [d of d, 1 H, J(HH) 14, 6 Hz, H_s]; ^{13}C n.m.r., δ($CDCl_3$) 254.3 [d, CO, J(PC) 22], 137.1 [d, Ph-*i*, J(PC) 36.5], 133.1 [d, Ph-*o* or -*m*, J(PC) 10], 129.2 (s, Ph-*p*), 127.7 [d, Ph-*o* or -*m*, J(PC) 9], 90.0 (s, C_5H_5), 87.4 (s, CH), 52.8 [d, CH, J(PC) 2.5], 35.4 [d, CH_2, J(PC) 6.5 Hz], and 21.2 (s, Me).

Crystallographic Studies.—Crystal data. $C_{12}H_{14}MoO_3$, (**20**), $M = 302.14$, crystallises from light petroleum as irregular red crystals, dimensions of crystal used 0.40 × 0.35 × 0.50 mm, triclinic, $a = 8.416(9)$, $b = 11.541(12)$, $c = 7.063(3)$ Å, $\alpha = 105.23(3)$, $\beta = 105.71(3)$, $\gamma = 104.938(12)^\circ$, $U = 595.9(9)$ Å^3, $Z = 2$, $D_c = 1.684$ g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2, assumed and confirmed by the successful analysis), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 10.62 cm^{-1}, $F(000) = 304$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50^\circ$ on a Stoe Stadi-2 diffractometer by the omega-scan method. The 1 805 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz, polarisation and absorption effects. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions after detection on an electron-density difference synthesis [C–H 0.96 Å, C–C–H(methyl) 111°]: the position of H(3) was optimised for best agreement with the difference synthesis, which resulted in a position intermediate between sp^2 and sp^3 hybridisation for atom C(3) at a distance C–H 0.98 Å. Once positioned, hydrogen-atom parameters were permitted no refinement ($B = 7.0$ Å^2). Refinement coverged at R 0.0299 with allowance for anisotropic thermal motion for all non-hydrogen atoms and for the anomalous scattering of molybdenum. Scattering factors were taken from ref. 20; unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

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