Pentamethylcyclopentadienyl Molybdenum and Tungsten Carbene Complexes. *X*-Ray Crystal Structures of *cis*- and *trans*-$[MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$†

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Treatment of $[M(CO)_3(\eta\text{-}C_5Me_5)]^-$ (M = Mo or W) with $Br[CH_2]_3Br$ gives the metallapropanes $[M\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$. Reaction of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ with I^- provides *cis* and *trans* carbenes $[MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$. Crystallisation of the mixture gives two crystal forms, one of which consists of pure *trans* isomer while the second consists of a mixture of predominantly two *cis* components (68.5 and 7.1%) with some *trans* isomer (24.4%) incorporated in the crystal. For the *trans* isomer, orthorhombic, *a* = 15.38(6), *b* = 15.65(8), *c* = 14.78(6) Å, *R* 0.0665 for 1 335 independent reflections. For the *cis* isomer, monoclinic, *a* = 12.73(4), *b* = 9.26(3), *c* = 16.09(4) Å, β = 108.68(9)°, *R* 0.0908 for 974 independent reflections. In tetrahydrofuran solution the two isomers slowly interconvert at ambient temperature. The reaction of Br^- with $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ gives the carbene $[MoBr(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ as predominantly the *cis* isomer. The reaction of CN^- with $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ gives the *trans* carbene $[Mo(CN)(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ while reaction with SCN^- gives the *cis* carbene $[Mo(NCS)(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$. Reaction of $[W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ with I^- affords the iodo carbene $[WI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ as predominantly the *trans* isomer. Reaction of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ results in elimination of Br^- and formation of the heterodimetalla-alkane species $[(\eta\text{-}C_5Me_5)(OC)_3Mo(CH_2)_3Fe(CO)(\eta\text{-}C_5H_5)]$.

The cyclopentadienyl ligand is somewhat ubiquitous in organotransition-metal chemistry. It can frequently be relied upon to block formally three co-ordination sites on a metal and therefore allow study of reactions proceeding at remaining co-ordination sites. It is recognised that although the cyclopentadienyl group is generally unreactive while co-ordinated, it does exert an influence on the chemistry at the other co-ordination sites. Varying the nature of the cyclopentadienyl group therefore sometimes alters the chemistry at the remaining co-ordination sites. The methylcyclopentadienyl group is a common cyclopentadienyl derivative but the single methyl group generally has little effect on the chemistry of a compound. However, the pentamethylcyclopentadienyl ligand is clearly very different. In addition to quite markedly increasing electron density at the metal, the five methyl groups exert a strong steric effect at the metal. As a consequence, pentamethylcyclopentadienyl metal chemistry is often quite different from the corresponding cyclopentadienyl chemistry.

We are interested in carbene complexes, and have shown that metallahalogenoalkanes (**1**)—(**4**) are good precursors to carbene complexes such as (**5**)—(**9**) through their reactions with anionic nucleophiles (Scheme 1).[1-8] We are using carbene complexes of this type as vehicles for the study of migration reactions to carbene ligands.[9,10] In this paper, we report our examination of the syntheses of the corresponding pentamethylcyclopentadienyl complexes and contrast results for the two ligand systems.

Results and Discussion

The metallabromoalkanes (**1**) and (**3**) are made in the reaction of the appropriate anion $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) with $Br[CH_2]_3Br$.[11] For molybdenum, it is necessary to control the reaction conditions with some care in order to prevent side reactions.[2] The corresponding reactions of $[Mo(CO)_3(\eta\text{-}C_5Me_5)]^-$ (**10**) or its tungsten analogue (**11**) with $Br[CH_2]_3Br$ proceed quite smoothly to the expected complexes (**12**) and (**13**). The reactions appear rather cleaner than the corresponding formations of (**1**) and (**3**) and it is clear that the anions $[M(CO)_3(\eta\text{-}C_5Me_5)]^-$ (M = Mo or W) are more nucleophilic than the C_5H_5 analogues. The spectroscopic properties of (**12**) and (**13**) are given in Table 1 and relate closely to those of (**1**) and (**3**).[2]

The reaction of complex (**12**) with LiI is completed within 1 h at ambient temperature in tetrahydrofuran (thf). The i.r. spectrum of the reaction mixture suggests the formation of an initial *cis*-dicarbonyl (ν_{CO} 1 949s and 1 864s cm^{-1}).[12] These are assigned to (**14c**). On continued stirring a new band (ν_{CO} 1 894 cm^{-1}) appears. This subsequently proved attributable to (**14t**), the high-frequency signal of (**14t**) being obscured by the band of (**14c**) at 1 949 cm^{-1}. The *cis–trans* isomerisation does not proceed to completion; a 'steady-state' i.r. spectrum is achieved in about 2 h.

Chromatography on alumina gives only a single brown band but crystallisation of this band results in two distinct crystal types. The large, very dark red crystals can be manually separated from the smaller red-brown plates. The solution i.r. spectrum of the red-brown plates, recorded promptly after dissolution, is consistent with a *trans* dicarbonyl and their elemental analysis, mass, ^1H and ^{13}C n.m.r. spectra are all consistent with structure (**14t**). In particular, the high-frequency signal at δ 316.3 in the ^{13}C n.m.r. spectrum indicates a carbene atom.[13] This signal corresponds to the carbene signal at δ 316.6 in the ^{13}C n.m.r. spectrum of complex (**5**).[2] The carbonyl resonances are found about 5 p.p.m. to higher frequency compared with (**5**) while the CO stretching frequencies in the i.r. spectrum are a few wavenumbers lower.

The spectroscopic properties of the large dark red crystals are interesting. The solution i.r. spectra of a number of batches are

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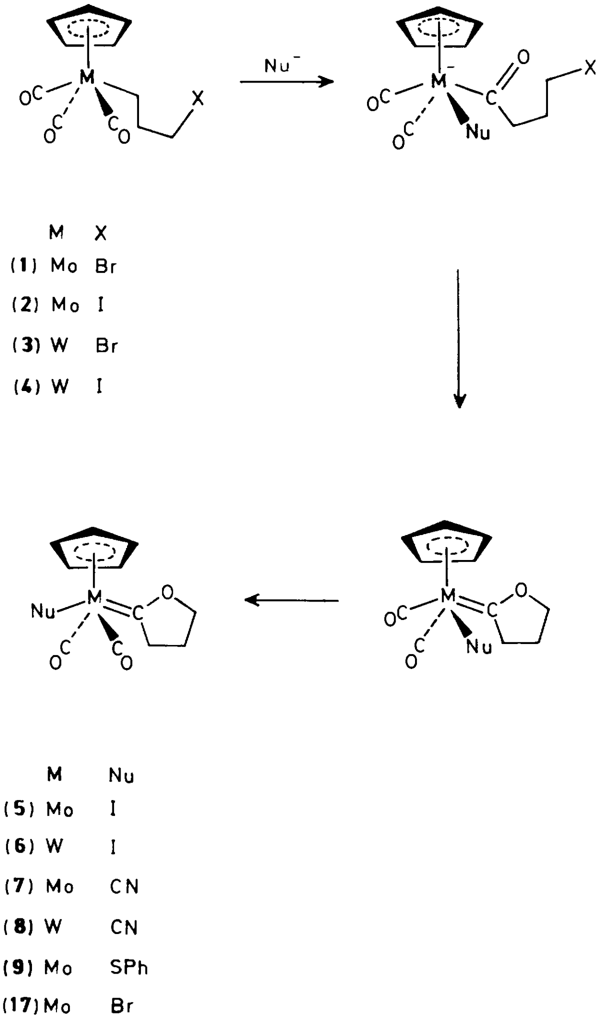
† *cis*- and *trans*-Dicarbonyliodo(2-oxacyclopentylidene)(η-pentamethylcyclopentadienyl)molybdenum.

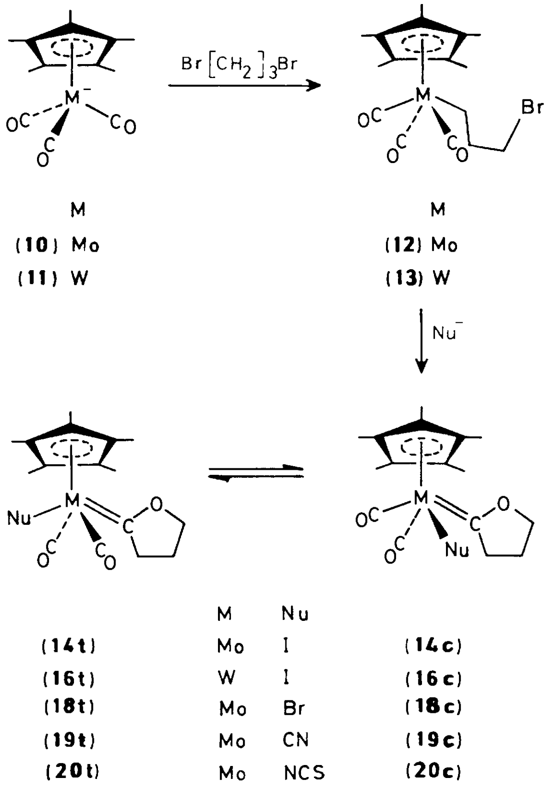
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



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

	M	Nu
(5)	Mo	I
(6)	W	I
(7)	Mo	CN
(8)	W	CN
(9)	Mo	SPh
(17)	Mo	Br

Scheme 1. Nu = Nucleophile

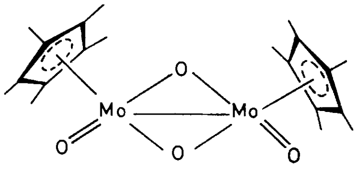


	M
(10)	Mo
(11)	W

	M
(12)	Mo
(13)	W

	M	Nu	
(14t)	Mo	I	(14c)
(16t)	W	I	(16c)
(18t)	Mo	Br	(18c)
(19t)	Mo	CN	(19c)
(20t)	Mo	NCS	(20c)

Scheme 2.



(15)

consistent with them being a mixture of a predominant *cis* dicarbonyl and (**14t**). The ^{1}H and ^{13}C n.m.r. spectra suggest the *cis* dicarbonyl to be (**14c**) and confirm the presence of small amounts of (**14t**). A carbene is indicated by the very high-frequency signal at δ 331.4,[13] while the *cis* stereochemistry is further indicated by the lack of symmetry within the ^{1}H n.m.r. spectrum for the ring protons and the observation of two CO signals in the ^{13}C n.m.r. spectrum.

On some occasions a faint, strongly retained orange band is observed on the column. It is eluted by CH_2Cl_2 and crystallises to give well formed orange crystals without any carbonyls evident in the i.r. spectrum. The elemental analysis, i.r., mass, and ^{1}H n.m.r. spectra are consistent with the oxide structure (**15**). This compound tends to arise in small quantities in most of the reactions discussed in this paper if any manipulation is carried out in the open atmosphere. The *cis* isomer of this complex has been structurally characterised.[14] The compound isolated here is the same species, preliminary *X*-ray data[14b] showing the same unit-cell constants. Our i.r. data for (**15**) [ν(Mo=O) 917 cm^{-1}, ν(MoOMo) 715 cm^{-1} (KBr)] are slightly at variance with that published for (**15**) and resemble similar data for related complexes *cis*-[{Mo(O)(μ-O)(η-C_5H_5)}$_2$] [ν(Mo=O) 925 and 901 cm^{-1}, ν(MoOMo) 710 cm^{-1}, ref. 15] and *trans*-[{Cr(O)(μ-O)(η-C_5Me_5)}$_2$] [ν(Cr=O) 910 cm^{-1}, ν(CrOCr) 715 cm^{-1}].[16]

The small brown needles consisting of pure (**14t**) and the large dark red crystals apparently containing both (**14t**) and (**14c**) were analysed by *X*-ray crystallography. Figure 1 shows the structure of the *trans* isomer and Figure 2 shows the major component *cis* isomer, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) are listed in Tables 2 and 3.

The molecular structure of the *trans* isomer is very similar to that of the corresponding cyclopentadienyl complex (**5**). The *trans*-basal angle for (**14t**) between iodine and the oxacyclopentylidene ring is 6.4° less, while the second such angle for the carbonyl ligands is 6.8° greater than for (**5**). This reflects the adjustments necessary for the more bulky basal ligands in order to recognise the C_5Me_5 ring. Otherwise, the patterns of bond lengths and bond angles are very similar. The oxacyclopentylidene is again hinged (23.1°) with the molybdenum atom coplanar with the fragment to which it is bonded, although the Mo–C distance is 0.046 Å shorter. The molybdenum atom is 2.032 Å away from the mean plane through the cyclopentadienyl ring carbon atoms and the methyl groups are displaced to various extents from the C_5 plane in a direction away from the metal. The angle between the cyclopentadienyl ring and the approximately planar fragment of the oxacyclopentylidene ring (74.3°) is 13° less close to 90° than in the case of the

Table 1. Proton and ^{13}C n.m.r. (δ) data for the complexes^{a}

Complex	^{1}H	^{13}C
(12)	3.43 (t, 2 H, *J* 7, CH_2Br), 2.15 (m, 2 H, central CH_2), 1.92 (s, 15 H, C_5Me_5), 0.86 (m, 2 H, $MoCH_2$)	
(13)	3.37 (t, 2 H, *J* 7, CH_2Br), 2.10 (m, 2 H, central CH_2), 2.00 (s, 15 H, C_5Me_5), 0.78 (m, 2 H, WCH_2)	
(14t)	4.73 (t, 2 H, *J* 7, OCH_2), 3.67 (t, 2 H, *J* 7, CH_2), 2.03 (s, 15 H, C_5Me_5), 1.88 (qnt, 2 H, central CH_2)	^{b} 316.3 (Mo=C), 228.2 (2CO), 108.2 (C_5Me_5), 82.7 (OCH_2), 60.4 (CH_2), 22.5 (central CH_2), 11.9 (C_5Me_5)
(14c)	4.93 (d of t, 1 H, *J* 9.0, 7.5, OCH_2), 4.83 (d of t, 1 H, *J* 9.0, 7.5, OCH_2), 4.40 (d of t, 1 H, *J* 19.5, 7.5, CH_2), 3.68 (d of t, *J* 19.5, 7.5, CH_2), 1.99 (s, 15 H, C_5Me_5), 1.86 (qnt, 2 H, *J* 7.5, central CH_2)	^{b} 331.4 (Mo=C), 248.7 (CO), 236.4 (CO), 107.3 (C_5Me_5), 86.1 (OCH_2), 63.9 (CH_2), 22.5 (central CH_2), 11.2 (C_5Me_5)
(15)	2.01 (s, 30 H, $2C_5Me_5$)	
(16t)	4.66 (t, 2 H, *J* 7, OCH_2), 3.52 (t, 2 H, CH_2), 2.13 (s, 15 H, C_5Me_5), 1.88 (qnt, 2 H, *J* 7, central CH_2)	^{b} 292.0 (W=C), 221.4 (2CO), 107.0 (C_5Me_5), 81.8 (OCH_2), 61.1 (CH_2), 23.4 (central CH_2), 12.0 (C_5Me_5)
(16c)	4.91 (d of t, 1 H, *J* 9, 7, OCH_2), 4.75 (d of t, 1 H, *J* 10, 7, OCH_2), 4.27 (d of t, 1 H, *J* 20, 7, CH_2), 3.71 (d of t, 1 H, *J* 20, 7, CH_2), 2.10 (s, 15 H, C_5Me_5), 1.85, (qnt, 2 H, *J* 7, central CH_2)	^{b} 312.6 (W=C), 240.4 (CO), 227.6 (CO), 105.8 (C_5Me_5), 85.0 (OCH_2), 64.6 (CH_2), 23.4 (central CH_2), 11.4 (C_5Me_5)
(18t)	4.67 (t, 2 H, *J* 7, OCH_2), 3.79 (t, 2 H, *J* 7, CH_2), 1.90 (s + overlapping multiplet, 17 H, C_5Me_5 + central CH_2)	
(18c)	5.06 (d of t, 1 H, *J* 9, 5, OCH_2), 4.67 (d of t, 1 H, *J* 9, 7, OCH_2), 3.99 (d of t, 1 H, *J* 21, 9, CH_2), 3.81 (d of d of d, 1 H, *J* 21, 9, 5, CH_2), 1.87 (s + overlapping multiplet, 17 H, C_5Me_5 + central CH_2)	^{c} 273.5 (Mo=C), 249.3 (CO), 236.4 (CO), 107.0 (C_5Me_5), 85.5 (OCH_2), 58.2 (CH_2), 21.8 (central CH_2), and 10.6 (C_5Me_5)
(19t)	4.87 (t, 2 H, *J* 7, OCH_2), 3.71 (t, 2 H, *J* 7, CH_2), 2.03 (s, 15 H, C_5Me_5), 1.94 (qnt, 2 H, central CH_2)	^{d} 322.3 (Mo=C), 230.6 (2CO), 106.8 (C_5Me_5), 84.9 (OCH_2), 60.3 (CH_2), 21.4 (central CH_2), 10.7 (C_5Me_5)
(20c)	5.14 (t of d, 1 H, *J* 9, 3, OCH_2), 4.68 (t of d, 1 H, *J* 8, 10, OCH_2), 4.01 (d of d of d, 1 H, *J* 21, 8, 3, CH_2), 3.49 (d of t, 1 H, *J* 21, 10, CH_2), 2.0 (m, 2 H, central CH_2), 1.89 (s, 15 H, C_5Me_5)	^{e} 328.5 (Mo=C), 247.4 (CO), 236.1 (CO), 146.6 (SCN), 106.4 (C_5Me_5), 85.0 (OCH_2), 54.3 (CH_2), 21.1 (central CH_2), 10.4 (C_5Me_5)
(21)	^{f} 4.18 (s, 5 H, C_5H_5), 2.21 (m, 2 H, central CH_2), 1.81 (d of d, 2 H, *J* 8, 7, CH_2), 1.60 (s, 15 H, C_5Me_5), and 1.33 (d of d, 2 H, *J* 8, 7, CH_2)	^{f} 243.5 (Fe–CO), 232.4 (Mo–CO *trans* to CH_2), 218.7 (2Mo–CO, mutually *trans*), 104.6 (C_5Me_5), 85.8 (C_5H_5), 45.9 (CH_2), 18.4 (CH_2), 10.8 (central CH_2), 10.7 (C_5Me_5)

^{a} In $CDCl_3$ at ambient temperature unless stated otherwise; *J* in Hz. ^{b} At 223 K. The data for *cis* complexes are extracted from spectra of *cis–trans* mixtures (about 50:50). The *trans* data are from pure samples of the *trans* isomer. ^{c} At 233 K. No *trans* isomer is visible at the signal to noise ratio of the spectrum. ^{d} In CD_2Cl_2 at 203 K. ^{e} At 223 K. ^{f} In C_6D_6.

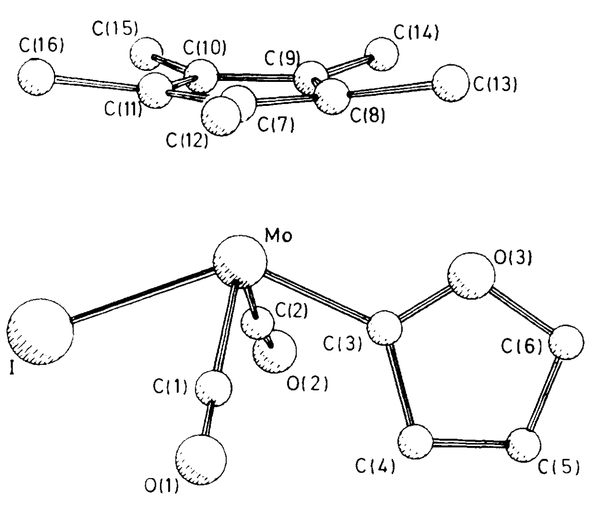


Figure 1. The molecular structure of *trans*-$[\mathrm{MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$ **(14t)**

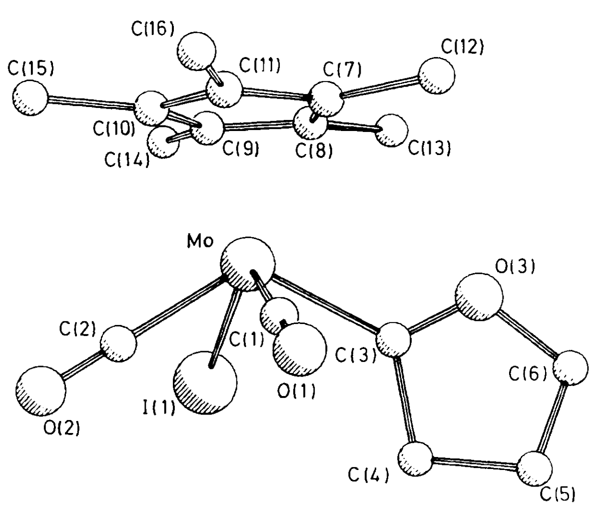


Figure 2. The molecular structure of the major component of *cis*-$[\mathrm{MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$ **(14c)**

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for the *trans* isomer of $[MoI(CO)_2\{=C(CH_2)_3O\}(\eta\text{-}C_5Me_5)]$

Mo–I	2.864(17)	Mo–C(7)	2.409(23)
Mo–C(1)	2.057(22)	Mo–C(8)	2.348(20)
C(1)–O(1)	1.072(28)	Mo–C(9)	2.339(24)
Mo–C(2)	2.015(22)	Mo–C(10)	2.346(21)
C(2)–O(2)	1.115(29)	Mo–C(11)	2.366(22)
Mo–C(3)	2.040(20)	C(7)–C(8)	1.343(31)
O(3)–C(3)	1.325(25)	C(8)–C(9)	1.459(32)
C(3)–C(4)	1.530(31)	C(9)–C(10)	1.439(32)
C(4)–C(5)	1.500(35)	C(10)–C(11)	1.381(31)
C(5)–C(6)	1.489(35)	C(11)–C(7)	1.443(32)
C(6)–O(3)	1.494(28)	C(7)–C(12)	1.484(36)
I···C(11)	3.501(22)	C(8)–C(13)	1.561(33)
I···C(16)	3.509(26)	C(9)–C(14)	1.462(37)
O(3)···C(8)	3.049(26)	C(10)–C(15)	1.523(35)
O(3)···C(13)	2.877(30)	C(11)–C(16)	1.515(34)

I–Mo–C(1)	76.0(6)	C(11)–C(7)–C(8)	105.6(20)
I–Mo–C(2)	76.0(6)	C(11)–C(7)–C(12)	127.2(21)
I–Mo–C(3)	133.9(6)	C(8)–C(7)–C(12)	127.0(22)
C(1)–Mo–C(2)	105.3(9)	C(7)–C(8)–C(9)	111.5(19)
C(1)–Mo–C(3)	80.0(8)	C(7)–C(8)–C(13)	125.8(20)
C(2)–Mo–C(3)	73.3(8)	C(9)–C(8)–C(13)	121.5(19)
Mo–C(1)–O(1)	178.2(20)	C(8)–C(9)–C(10)	105.1(19)
Mo–C(2)–O(2)	173.7(20)	C(8)–C(9)–C(14)	129.1(22)
Mo–C(3)–O(3)	123.8(14)	C(10)–C(9)–C(14)	125.3(22)
Mo–C(3)–C(4)	129.8(15)	C(9)–C(10)–C(11)	106.8(19)
O(3)–C(3)–C(4)	106.1(17)	C(9)–C(10)–C(15)	126.8(20)
C(3)–C(4)–C(5)	107.1(19)	C(11)–C(10)–C(15)	126.1(20)
C(4)–C(5)–C(6)	103.5(20)	C(10)–C(11)–C(7)	111.1(20)
C(5)–C(6)–O(3)	104.4(18)	C(10)–C(11)–C(16)	127.9(21)
C(6)–O(3)–C(3)	113.4(16)	C(7)–C(11)–C(16)	120.2(20)

cyclopentadienyl complex, suggesting that steric interactions are reduced by a twisting of the oxacyclopentylidene ring as well as by a reduction in the I–Mo–C angle. The shortest contact between ligands is 2.88 Å and the out-of-plane deviations of the methyl groups reflect the steric interactions with the basal ligands. The largest deviations are 0.27 Å for C(13) which is closest to O(3), 0.18 Å for C(14), which is also adjacent, and 0.22 Å for C(16) which lies almost above the iodine. Although atom C(12) is precisely eclipsed by the carbonyl group, its out-of-plane displacement is the smallest at 0.10 Å.

In view of the extensive disorder in the structure of the *cis* isomer and the geometric constraints that were necessarily applied, it is not possible to discuss the details of the geometries of any of the components. The apparent envelope conformation of the oxacyclopentylidene ring gives a hinge angle of 22.1° which is essentially the same, although in the opposite sense (relative to the Figures), to that seen in the two *trans* complexes. In the *trans* component, the pattern of *trans*-basal angles is very similar to that seen in the pure *trans* crystal structure. However, in the *cis* components, the *trans*-basal angles are much more equal and intermediate between the values seen in the *trans* isomers (as would be expected now that the most bulky ligands lie mutually *cis*). In the small *trans* component (24.4%) in the crystal structure of the predominantly *cis* compound, O(3) makes a slightly shorter contact (2.83 Å) to the lower-occupancy component of the C_5Me_5 ring than the shortest such distance in the crystal structure of the purely *trans* isomer. However a short iodine–methyl contact (3.32 Å) would inhibit the occurrence of the *trans* isomer with a C_5Me_5 rotational orientation corresponding to the higher occupancy, and the population parameters determined support the view that this 68.5% occupancy is entirely associated with the predominant *cis* component, which is illustrated in Figure 2 and for which there are no contacts less than those found in the crystal structure of the purely *trans* isomer. There are no intramolecular interactions involving I(3) (7.1% occupancy, second *cis* component) which would favour either rotamer of the C_5Me_5 ring over the other, but the population of at least 31.5% for the lower-occupancy component supports our suggestion that it is this rotamer which should be associated with the 7.1% occupancy *cis* component, as well as with the 24.4% occupancy *trans* component. Low-occupancy *cis* components present in both sites related by inversion symmetry through (0.5, 0, 0) would suffer a slightly short iodine–methyl contact of 3.32 Å, but this occurrence is statistically improbable and would be unlikely to lead to any ordering of the site occupancies.

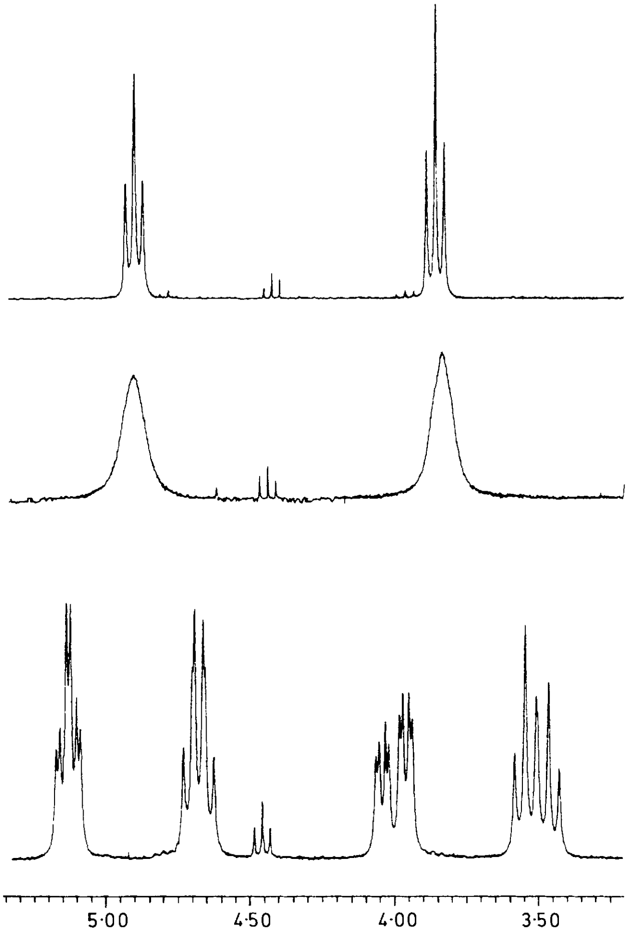
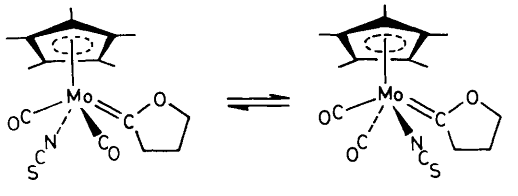


Figure 3. Sections of the ^1H n.m.r. spectra (250 MHz) of $[Mo(NCS)(CO)_2\{=C(CH_2)_3O\}(\eta\text{-}C_5Me_5)]$ (**20**) at 317 (top), 297 (middle), and 223 K (bottom). The small triplet at the centre is due to an impurity

The two isomeric carbenes (**14c**) and (**14t**) interconvert in solution. The i.r. spectrum of a sample of pure (**14t**) in thf changes over 6 h into one containing bands due to both (**14c**) and (**14t**) in the same proportions as indicated in the i.r. spectrum of the original reaction mixture. Similarly a thf solution of crystals originally consisting of predominantly (**14c**) changes into a mixture of (**14c**) and (**14t**) with the same (**14c**):(**14t**) ratio. A similar phenomenon is observed while recording n.m.r. data. Thus, the ^1H n.m.r. spectrum of initially pure (**14t**) changes into an equilibrium mixture of (**14c**) and (**14t**) with a (**14c**):(**14t**) ratio of 40:60 as determined by integrations within the final spectrum measured after 24 h. A



Scheme 3.

little decomposition is also evident in the n.m.r. spectrum of the sample measured after this time. These results indicate that the two isomers interconvert rather easily and that there is very little difference in energy between them.

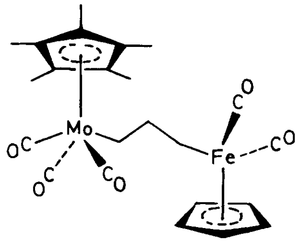
As with the C_5H_5 systems, carbene formation is also observed for the analogous tungsten system. Thus, reaction of (**13**) with I^- gives the expected carbene complexes (**16c**) and (**16t**). The reaction is considerably slower than for the molybdenum case, requiring overnight warming. Again, there are two isomers and two crystal forms. The *trans* form predominates over the *cis* form although not by much; the ^1H n.m.r. spectrum of a solution at equilibrium shows a *trans*:*cis* ratio of 63:37 in $CDCl_3$.

Complex (**1**) shows no sign of reacting with Br^- to form a bromo carbene complex (**17**).[2] This is presumably because the bromide ion is insufficiently nucleophilic to induce migration of the pendant $[CH_2]_3Br$ to an adjacent carbonyl (Scheme 1). However, bromide does induce carbene formation from (**12**). This reaction proceeds smoothly and in high yield at ambient temperature to form carbene (**18**). This complex exists as predominantly the *cis* isomer with a ratio (**18c**):(**18t**) of 88:12 (integration of the ^1H n.m.r. spectrum at 250 K), which is slightly higher than the corresponding ratio for the iodides. No pure *trans* complex (**18t**) has been isolated from this reaction. The isolated material is always a mixture of (**18c**) and (**18t**). We have not attempted the analogous reactions of LiBr with the tungsten compound (**13**).

Cyanide ion reacts with (**12**) to give the cyano carbene (**19**). The spectroscopic properties are very reminiscent of those for (**6**) formed in the analogous reaction of (**1**) with CN^-.[2] There is no sign of any *cis* isomer of (**19**).

The SCN^- ion does not promote carbene formation in its reaction with (**1**). However SCN^- reacts within 2 h at ambient temperature to give the carbene (**20**). In this case, only the *cis* isomer is detectable. The CN stretching frequency and intensity of 2 092s cm^{-1} is consistent with the NCS being nitrogen bonded,[17] but this is still not definitively proven. The *cis* stereochemistry is indicated very clearly by the carbonyl band intensities in the i.r. spectrum, and the two observed carbonyl signals in the ^{13}C n.m.r. spectrum.

The ^1H n.m.r. spectrum is temperature dependent. At 223 K the two protons α to the carbene and the two OCH_2 protons appear as four complex multiplets (Figure 3). At 297 K the four signals collapse into two broad humps which on further warming to 317 K appear as two sharp triplets. This is an averaging process of the two carbene α protons with each other and the two OCH_2 protons with each other. The central CH_2 proton signals are expected to undergo related changes but they are partially obscured by the C_5Me_5 signal and any temperature dependence in this part of the spectrum is not clear. One mechanism to account for this averaging is a *cis–cis* isomerisation, or racemisation, shown in Scheme 3. Such isomerisations are known for some $[MoX(CO)_2L(C_5H_5)]$ (X = halide, Me, or H; L = phosphine) systems.[18] The $\Delta G^\ddagger$ for complex (**20**) is calculated to be 57 kJ mol^{-1} which is comparable to the values for the $[MoX(CO)_2L(C_5H_5)]$ systems. There is no sign of the *cis* iodide undergoing any such isomerisation at ambient temperature but the ambient-temperature spectrum of the bromide (**18**) shows definite signs of broadening compared with that at 223 K.



(**21**)

In the above discussion it becomes clear that the stereochemistry of a number of complexes $[MX(CO)_2\{=C(CH_2)_3O\}(\eta\text{-}C_5Me_5)]$ (M = Mo or W; X = Br, I, NCS, or CN) can be *cis*, *trans*, or both. It is still not clear what all the factors are that determine which isomer is favoured in these C_5Me_5 complexes or the corresponding C_5H_5 species.

We note one further difference in the reactivity of the C_5Me_5 complexes. Complex (**1**) is known to react with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ by elimination of both Br^- and $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ to form the dimetalla-alkane $[(\eta\text{-}C_5H_5)(OC)_2Fe(CH_2)_3Fe(CO)_2(\eta\text{-}C_5H_5)]$.[11] However, treatment of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**12**) with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ leads to the heterodimetalla-alkane (**21**), isolated in reasonable yield. The only other product isolated is $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$. The i.r. spectrum of (**21**) is a straightforward overlapping of $[MoR(CO)_3(\eta\text{-}C_5Me_5)]$ and $[FeR(CO)_2(\eta\text{-}C_5Me_5)]$ (R = alkyl) type spectra. The central CH_2 signal in the ^{13}C n.m.r. spectrum (Table 1) has about the same shift as that in $[(\eta\text{-}C_5H_5)(OC)_2Fe(CH_2)_3Fe(CO)_2(\eta\text{-}C_5H_5)]$ (δ 47.4),[19] but the two MCH_2 shifts are at slightly higher frequency than those for $[(\eta\text{-}C_5H_5)(OC)_2Fe(CH_2)_3Fe(CO)_2(\eta\text{-}C_5H_5)]$ (δ 7.8)[19] or $[(\eta\text{-}C_5H_5)(OC)_3Mo(CH_2)_3Mo(CO)_3(\eta\text{-}C_5H_5)]$ (δ 2.3).[3]

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 Perkin-Elmer R34 (220 MHz), Bruker AM-250 (250.13 MHz), and WH-400 (400.13 MHz) instruments, carbon-13 n.m.r. spectra using a JEOL PFT-100 (25.15 MHz) or Bruker AM-250 (62.90 MHz) instrument. Mass spectra were obtained using a Kratos MS 25 instrument operating in electron impact or chemical ionisation (NH_3) modes.

The anions $[M(CO)_3(\eta\text{-}C_5Me_5)]^-$, (**10**) and (**11**),[20] and $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ (ref. 21) are available by literature methods. All reactions were performed under nitrogen or argon atmospheres using deoxygenated solvents dried with an appropriate reagent, thf from sodium–benzophenone and light petroleum (b.p. 40—60 °C throughout) from $LiAlH_4$. Alumina was neutral Brockmann Activity II or Activity I deactivated with water (5% w/w).

Preparations.—$[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**12**). Addition of $Br[CH_2]_3Br$ (4.04 g, 20 mmol) to a solution in thf (50 cm^3) of $[Mo(CO)_3(C_5Me_5)]^-$ (10 mmol) gave a yellow solution after stirring for 4 h. Removal of solvent under reduced pressure followed by filtration through an Al_2O_3 plug (light petroleum) gave a yellow solution from which yellow crystalline $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**12**) was obtained after crystallisation from light petroleum (2.8 g, 64%), m.p. 81—83 °C (Found: C, 44.3; H, 5.0%; M^+ 438. $C_{16}H_{21}BrMoO_3$ requires C,

Table 3. Bond lengths (Å) and angles (°) with e.s.d.s and constrained dimensions for the three components of the *cis* isomer of $[MoI(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$

Mo–I(1)	2.853(10)	Mo–C(3)	2.105(34)
Mo–C(7)	2.331(24)	O(3)–C(3)	1.24(5)
Mo–C(8)	2.354(24)	C(3)–C(4)	1.52(7)
Mo–C(9)	2.382(25)	C(4)–C(5)	1.50(8)
Mo–C(10)	2.376(24)	C(5)–C(6)	1.40(8)
Mo–C(11)	2.345(25)	C(6)–O(3)	1.51(6)
Mo–C(17)	2.31(5)	Mo–I(2 and 3)	2.85
Mo–C(18)	2.40(5)	Mo–C(carbonyl)	2.00
Mo–C(19)	2.39(5)	C–O(carbonyl)	1.15
Mo–C(20)	2.29(5)	C–C(cp ring)	1.40
Mo–C(21)	2.24(5)	C–C(methyl)	1.55
I(1)–Mo–C(1)	124.6(5)	Mo–C(3)–O(3)	124.5(27)
I(1)–Mo–C(2)	77.5(6)	Mo–C(3)–C(4)	130.2(29)
I(1)–Mo–C(3)	82.2(9)	O(3)–C(3)–C(4)	105(3)
C(1)–Mo–C(2)	72.6(8)	C(3)–C(4)–C(5)	107(4)
C(1)–Mo–C(3)	74.7(10)	C(4)–C(5)–C(6)	103(5)
C(2)–Mo–C(3)	120.4(11)	C(5)–C(6)–O(3)	106(4)
I(2)–Mo–C(1)	79.0(6)	C(6)–O(3)–C(3)	114(4)
I(2)–Mo–C(3)	129.0(10)	Mo–C–O(carbonyl)	180
I(2)–Mo–C(27)	83.5(15)	C–C–C(cp ring)	108
C(1)–Mo–C(3)	74.7(10)	C–C–C(cp exocyclic)	125.4—125.9
C(1)–Mo–C(27)	113.1(16)		
C(3)–Mo–C(27)	68.5(18)	I(1) ··· C(14)	3.50(4)
I(3)–Mo–C(2)	74.4(11)	I(2) ··· C(15)	3.32(4)
I(3)–Mo–C(3)	76.8(13)	I(3) ··· C(26^{I})	3.32(9)
I(3)–Mo–C(27)	117.5(17)	O(3) ··· C(12)	3.02(5)
C(2)–Mo–C(3)	120.4(11)	O(3) ··· C(24)	2.83(8)
C(2)–Mo–C(27)	80.7(16)		
C(3)–Mo–C(27)	68.5(18)		

Symmetry operation: I $1-x, -y, -z$. For convenience, the complete set of angles around the molybdenum is given for each disorder component, although this results in duplicate listing of three C(3)–Mo–C(carbonyl) angles. The values quoted in summary and without estimated standard deviations were constrained during refinement: the range of values for C–C–C(cp exocyclic) results from the various out-of-plane displacements of the methyl groups.

44.0; H, 4.8%; M^+ 438); ν_{CO}(max.) 2 003s and 1 909s, br cm^{-1} (CH_2Cl_2).

$[W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**13**). In a similar preparation to that above, $[W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**13**) was obtained in 67% yield starting from $[W(CO)_3(C_5Me_5)]^-$ (10 mmol, in thf, 50 cm^3) and $Br[CH_2]_3Br$ (4.04 g, 20 mmol), m.p. 80—82 °C (Found: C, 37.0; H, 4.1%; M^+ 526. $C_{16}H_{21}BrO_3W$ requires C, 36.6; H, 4.0%; M^+ 526); ν_{CO}(max.) 2 000s and 1 901s, br cm^{-1} (CH_2Cl_2).

cis- and trans-$[MoI(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ (**14**). Solid LiI (0.27 g, 2.0 mmol) was added to a solution of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**12**) (0.44 g, 1.0 mmol) in thf (10 cm^3) and the solution stirred at ambient temperature for 2 h. Removal of solvent and chromatography on a short Al_2O_3 column (8 × 2 cm) with dichloromethane–light petroleum (2:8) gave a brown fraction that yielded *cis-* and *trans-*$[MoI(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ (**14**) as a mixture of small red [pure (**14t**)] and large red-black [predominantly (**14c**)] crystals that are manually separable (0.32 g, 67%), m.p. of mixture 116—118 °C (Found: C, 40.0; H, 4.6%; M^+ 484. $C_{16}H_{21}IMoO_3$ requires C, 39.7; H, 4.4%; M^+ 484); ν_{CO}(max.) 1 957s and 1 867s (**14c**), 1 973m and 1 885s cm^{-1} (**14t**) (CH_2Cl_2).

On some occasions an orange band was eluted from the column using dichloromethane–acetone (80:20) containing variable amounts of *cis*-$[\{MoO(\mu\text{-}O)(\eta\text{-}C_5Me_5)\}_2]$ (**15**) (typically about 0.02 g, 8%), m.p. > 220 °C (Found: 45.9; H, 5.8%; M^+ 526. $C_{20}H_{30}Mo_2O_4$ requires C, 45.6; H, 5.7%; M^+ 526); ν_{MoO}(max.) 917s (KBr), ν_{MoOMo}(max.) 715m cm^{-1} (KBr).

Table 4. Atomic positional parameters with e.s.d.s for the *trans* isomer of $[MoI(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.212 83(10)	0.080 69(12)	0.250 99(12)
I	0.285 80(11)	−0.014 30(14)	0.103 79(10)
O(1)	0.320 1(11)	−0.062 9(12)	0.347 1(11)
O(2)	0.349 6(11)	0.209 4(15)	0.174 4(11)
O(3)	0.225 3(9)	0.212 6(11)	0.396 6(10)
C(1)	0.282 9(13)	−0.014 7(17)	0.313 2(12)
C(2)	0.302 4(12)	0.160 2(17)	0.198 1(13)
C(3)	0.264 7(12)	0.147 6(15)	0.356 5(12)
C(4)	0.355 4(14)	0.142 2(17)	0.398 8(15)
C(5)	0.367 9(15)	0.221 7(18)	0.454 0(16)
C(6)	0.277 5(14)	0.251 6(17)	0.471 1(15)
C(7)	0.072 7(12)	0.023 5(18)	0.291 5(15)
C(8)	0.077 5(12)	0.105 0(15)	0.319 8(13)
C(9)	0.086 7(11)	0.163 9(16)	0.243 9(19)
C(10)	0.088 5(12)	0.110 4(16)	0.164 7(12)
C(11)	0.079 7(12)	0.027 2(18)	0.194 2(13)
C(12)	0.056 7(17)	−0.053 2(20)	0.348 0(17)
C(13)	0.055 6(14)	0.137 6(21)	0.416 9(15)
C(14)	0.082 8(16)	0.257 3(17)	0.243 4(21)
C(15)	0.090 6(15)	0.139 9(24)	0.066 5(15)
C(16)	0.063 3(16)	−0.052 1(19)	0.137 9(16)

cis- and trans-$[WI(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ (**16**). Solid LiI (0.45 g, 3.6 mmol) was added to a solution of $[W\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**13**) (0.4 g, 0.76 mmol) in thf (5 cm^3) and the solution maintained at 58 °C for 19 h. Removal of solvent and chromatography on a short Al_2O_3 column (8 × 2 cm) with dichloromethane–light petroleum (2:8) gave a brown fraction that yielded two crops of crystals. The first consisted of predominantly *trans* material (orange) (0.18 g) and the second (brown, 0.058 g) was about a 50:50 mixture of (**16c**) and (**16t**) (low-temperature ^{13}C n.m.r. spectrum) (total yield 0.238 g, 55%), m.p. 152—154 °C (Found: C, 33.6; H, 3.9%; M^+, 572. $C_{16}H_{21}IO_3W$ requires C, 33.6; H, 3.7%; M^+ 572); ν_{CO}(max.) 1 947s and 1 853s (**16c**), 1 961m and 1 878s cm^{-1} (**16t**) (CH_2Cl_2).

cis- and trans-$[MoBr(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ (**18**). Solid LiBr (0.4 g, 4.5 mmol) was added to a solution of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**12**) (0.44 g, 1.0 mmol) in thf (4 cm^3). The mixture was stirred for 3 h during which time the colour of the solution became dark brown and the i.r. spectrum indicated the reaction to be complete. Solvent was removed under reduced pressure and the residue extracted into several portions of CH_2Cl_2 until the extracts were virtually colourless. Filtration of the extracts through Al_2O_3 (4 × 2 cm column) followed by crystallisation from a mixture of CH_2Cl_2 and light petroleum gave lustrous dark red crystals of $[MoBr(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ (**18**) as predominantly the *cis* isomer (0.36 g, 83%), m.p. 102 °C (Found: C, 44.0; H, 4.9%; $[M - CO - H]^+$ 410. $C_{16}H_{21}BrO_3W$ requires C, 44.0; H, 4.8%; M^+ 439); ν_{CO}(max.) 1 967s, 1 892(sh), and 1 871s cm^{-1} (CH_2Cl_2).

trans-$[Mo(CN)(CO)_2\{=\!\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)]$ (**19**). Solid KCN (**TOXIC!**) (0.08 g, 1.2 mmol) was added to a solution of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)]$ (**12**) (0.500 g, 1.14 mmol) in MeOH (30 cm^3). The mixture was stirred for 3 h during which time its colour became pale orange and the i.r. spectrum indicated the absence of starting material. Solvent was removed under reduced pressure and the residue filtered through a short Al_2O_3 column (8 × 2 cm) with dichloromethane–acetone

Table 5. Atomic positional parameters with e.s.d.s for the *cis* isomer of $[\mathrm{MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Occupancy
Mo	0.248 35(28)	0.229 19(33)	0.009 99(21)	1.000
I(1)	0.110 3(4)	0.254 3(7)	0.118 3(3)	0.685
I(2)	0.322 4(16)	−0.006 9(10)	0.128 3(8)	0.244
I(3)	0.252(5)	0.007(3)	−0.111 9(23)	0.071
O(1)	0.236 6(28)	−0.026 3(19)	−0.122 3(14)	0.929
O(2)	0.299 7(36)	−0.059 0(20)	0.120 2(19)	0.756
O(3)	0.078 6(26)	0.347 6(35)	−0.150 1(22)	1.000
O(4)	0.048(4)	0.232(12)	0.085(4)	0.315
C(1)	0.240 8(18)	0.066 8(12)	−0.074 0(9)	0.929
C(2)	0.280 9(23)	0.046 1(12)	0.080 0(12)	0.756
C(3)	0.096 1(25)	0.256(4)	−0.090 7(20)	1.000
C(4)	−0.012(4)	0.174(6)	−0.109(4)	1.000
C(5)	−0.084(4)	0.216(6)	−0.199(3)	1.000
C(6)	−0.038(4)	0.347(6)	−0.213(3)	1.000
C(7)	0.335 7(19)	0.401(3)	−0.051 4(14)	0.685
C(8)	0.291 5(18)	0.476(2)	0.005 3(16)	0.685
C(9)	0.347 1(20)	0.430(3)	0.091 0(14)	0.685
C(10)	0.425 6(19)	0.326(3)	0.087 3(15)	0.685
C(11)	0.418 5(19)	0.308(3)	−0.000 7(16)	0.685
C(12)	0.308 0(30)	0.429(4)	−0.151 0(14)	0.685
C(13)	0.206 7(27)	0.601(3)	−0.020 9(25)	0.685
C(14)	0.334 1(31)	0.495(4)	0.175 7(18)	0.685
C(15)	0.511 2(26)	0.254(4)	0.166 9(19)	0.685
C(16)	0.495 1(28)	0.213(4)	−0.035 1(24)	0.685
C(17)	0.389(4)	0.365(6)	0.104(3)	0.315
C(18)	0.307(4)	0.467(6)	0.065(4)	0.315
C(19)	0.291(4)	0.468(5)	−0.025(3)	0.315
C(20)	0.363(4)	0.367(6)	−0.042(3)	0.315
C(21)	0.424(4)	0.303(5)	0.038(4)	0.315
C(22)	0.442(7)	0.339(9)	0.204(3)	0.315
C(23)	0.251(7)	0.569(8)	0.114(5)	0.315
C(24)	0.224(6)	0.585(8)	−0.091(5)	0.315
C(25)	0.383(7)	0.343(9)	−0.131(4)	0.315
C(26)	0.522(6)	0.197(8)	0.052(6)	0.315
C(27)	0.120 8(23)	0.231(8)	0.0574(27)	0.315
H(4A)	−0.0017	0.0717	−0.1030	1.000
H(4B)	−0.0501	0.2014	−0.0661	1.000
H(5A)	−0.0785	0.1435	−0.2409	1.000
H(5B)	−0.1611	0.2226	−0.2035	1.000
H(6A)	−0.0415	0.3569	−0.2732	1.000
H(6B)	−0.0822	0.4266	−0.2013	1.000

The estimated standard deviations of all atoms with the exception of Mo, I(1), O(3), and C(3)—C(6) were derived from the e.s.d.s of the group parameters which were used to refine them. The six hydrogen atoms were not refined. Atoms Mo, O(3), and C(3)—C(6) are common to all disorder components. The remaining atoms of each disorder component are as follows: *cis* component, 68.5% occupancy, I(1), O(1), O(2), C(1), C(2), and C(7)—C(16); *trans* component, 24.4% occupancy, I(2), O(1), O(4), C(1), and C(17)—C(27); *cis* component, 7.1% occupancy, I(3), O(2), O(4), C(2), and C(17)—C(27).

(90:10) as solvent. Removal of solvent and crystallisation of the resulting oil from dichloromethane–light petroleum gave crystalline orange *trans*-$[\mathrm{Mo(CN)(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$ (**19**) (0.135 g, 31%), m.p. 102—104 °C (Found: C, 53.6; H, 5.7; N, 3.4%; $[M + \mathrm{H}]^+$ 386. $\mathrm{C_{17}H_{21}MoNO_3}$ requires C, 53.2; H, 5.5; N, 3.7%; M^+ 383); ν_{CO}(max.) 1 985s and 1 950s, ν_{CN}(max.) 2 102 cm^{-1} ($\mathrm{CH_2Cl_2}$).

cis-$[\mathrm{Mo(NCS)(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$ (**20**). Solid LiSCN (0.75 g, 10 mmol) was added to a solution of $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)}]$ (**12**) (0.44 g, 1.0 mmol) in thf (5 cm^3). The mixture was stirred for 60 min during which time its colour became dark red and the i.r. spectrum indicated the absence of starting material. Solvent was removed under reduced pressure and the residue extracted into $\mathrm{CH_2Cl_2}$ (about 100 cm^3). Filtration of the extract twice through $\mathrm{Al_2O_3}$ (3 × 2 cm column) followed by crystallisation from a mixture of $\mathrm{CH_2Cl_2}$ and hexane gave bright red crystals of $[\mathrm{Mo(NCS)(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$ (**20**) as the *cis* isomer (0.22 g, 54%), m.p. 85 °C (Found: C, 49.4; H, 5.0; N, 3.6%; M^+ 417. $\mathrm{C_{17}H_{21}MoNO_3S}$ requires C, 49.2; H, 5.1; N, 3.4%; M^+ 417); ν_{CO}(max.) 1 980s and 1 905s, ν_{CN}(max.) 2 092s cm^{-1} ($\mathrm{CH_2Cl_2}$).

$[\mathrm{(\eta\text{-}C_5H_5)(OC)_2Fe(CH_2)_3Mo(CO)_3(\eta\text{-}C_5Me_5)}]$ (**21**). Solid $[\mathrm{Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5Me_5)}]$ (**12**) (0.44 g, 1 mmol) was added to a solution of $[\mathrm{Fe(CO)_2(\eta\text{-}C_5H_5)}]^-$ (2 mmol) in thf (50 cm^3). After stirring for 2 h at ambient temperature, the solvent was removed from the brown reaction mixture and the residue was chromatographed on a short $\mathrm{Al_2O_3}$ column (10 × 2 cm). Elution with light petroleum provided a yellow fraction that yielded yellow crystalline $[\mathrm{(\eta\text{-}C_5H_5)(OC)_2Fe(CH_2)_3Mo(CO)_3(\eta\text{-}C_5Me_5)}]$ (**21**) on crystallisation from light petroleum (0.15 g, 28%), m.p. 94 °C {Found: C, 51.2; H, 4.8%; highest ion visible *m*/*z* 574 corresponding to $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2}]^+$. $\mathrm{C_{23}H_{26}FeMoO_5}$ requires C, 51.7; H, 4.9%; M^+ 536); ν_{CO}(max.) 2 009s, 1 999s, 1 953s, 1 919s, and 1 911s cm^{-1} (light petroleum).

Further elution with $\mathrm{CH_2Cl_2}$ provided a dark red fraction whose i.r. spectrum indicated it to contain $[\mathrm{\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2}]$ as the only carbonyl-containing species.

Crystallography.—Crystal data. *trans*-$[\mathrm{MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$, $\mathrm{C_{16}H_{21}IMoO_3}$, *M* 484.14, crystallises from $\mathrm{CH_2Cl_2}$–light petroleum as red hexagonal plates; crystal dimensions 0.614 × 0.346 × 0.185 mm, orthorhombic, a = 15.38(6), b = 15.65(8), c = 14.78(6) Å, U = 3 557(28) Å^3, Z = 8, D_c = 1.808 g cm^{-3}, space group *Pbca* (D_{2h}^{15}, no. 61), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 24.44 cm^{-1}, F(000) = 1 888.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method. The 1 335 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption: a correction was made for 50% intensity loss during the 250 h of data collection based on the monitoring of one reflection. 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 [C–H 0.96 Å, C–C–H(methyl) 111°] and their contributions were included in structure-factor calculations (B = 7.0 Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0665 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of iodine and molybdenum. Table 4 lists the atomic positional parameters with estimated standard deviations.

cis-$[\mathrm{MoI(CO)_2\{=\overline{C(CH_2)_3O}\}(\eta\text{-}C_5Me_5)}]$, crystallises from $\mathrm{CH_2Cl_2}$–light petroleum as very dark red polyhedral fragments which cocrystallise with the *trans* isomer, a crystal cut from a larger fragment had dimensions 0.135 × 0.246 × 0.438 mm, monoclinic, a = 12.73(4), b = 9.26(3), c = 16.09(4) Å, β = 108.68(9)°, U = 1 796(10) Å^3, Z = 4, D_c = 1.791 g cm^{-3}, space group $P2_1/c$ (C_{2h}^5, no. 14), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 24.20 cm^{-1}, F(000) = 944.

The data were collected and processed (974 independent reflections, again a correction was made for 50% decay) as for the *trans* isomer above. The structure was found to be extensively disordered with two different *cis* components (refined populations 68.5 and 7.1%) and a significant presence of the *trans* isomer (24.4%). The $\mathrm{C_5Me_5}$ ligand was also rotationally disordered in about 2:1 ratio and for tactical reasons the populations were set at 68.5 and 31.5%. The molybdenum and oxacyclopentylidene ring were deemed to be ordered and were unconstrained in their positional refinement. The highest-occupancy iodine atom was also permitted free positional refinement, but the two lower-occupancy iodines, in the remaining two basal sites, were constrained to be 2.85 Å from the molybdenum. The six carbonyl components, comprising two carbonyl ligands in total, were refined in pairs in three sites with constrained geometries (Mo–C 2.00 and C–O 1.15 Å, Mo–C–O 180°) and with occupancies optimised as the appropriate sums of overall molecular disorder component populations (92.9, 75.6, and 31.5%). This inevitably introduced approximations since the atom positions in carbonyl sites would differ for different molecular conformations, but further elaborations were impractical. The geometries of both components of the C_5Me_5 rings were also constrained (ring D_{5h}, C–C 1.40 and C–Me 1.55 Å); the methyl groups were situated external to the ring on the bisectors of the ring angles, with out-of-plane displacements away from the metal following the pattern (with respect to the basal ligands) determined in the *trans* isomer. Each whole C_5Me_5 disorder component was then refined as a rigid body. The molybdenum atom and the two highest-occupancy iodine components were permitted anisotropic thermal motion; the remaining iodine component and the atoms of the oxacyclopentylidene ligand were each permitted individual isotropic thermal parameters. One isotropic thermal parameter was refined for each carbonyl group with a differential of 0.4 $Å^2$ (in units of B) between the two atoms, in favour of the oxygen. An overall isotropic thermal parameter was refined for all ring-carbon atoms of both components of the C_5Me_5 group and two further such parameters, one for each set of five methyl-group carbon atoms, for the methyl groups. Hydrogens were positioned on the oxacyclopentylidene ring (C–H 0.97 Å, $B = 10.0$ $Å^2$) but no attempt was made to locate those of the disordered methyl groups. Allowance was made for the anomalous scattering of molybdenum and iodine. Refinement converged at R 0.0908. Table 5 lists atomic positional parameters with estimated standard deviations.

Scattering factors were taken from ref. 22. Unit weights were used throughout both refinements. Computer programs formed part of the Sheffield *X*-ray system.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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