

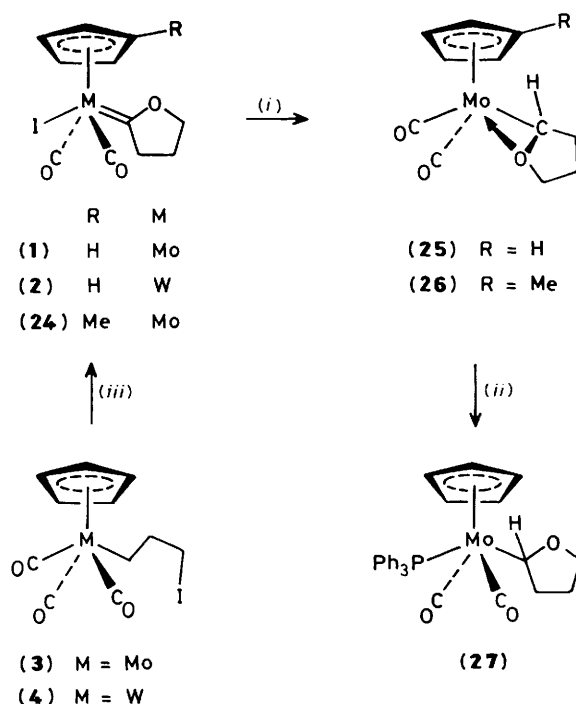
Syntheses and Reactions of Acyclic and Cyclic Carbene Complexes *cis*-[MI(=CMeNHMe)(CO)₂(η-C₅H₅)] (M = Mo or W) and *cis*-[MI{=C(CH₂)_nNMe}(CO)₂(η-C₅H₅)] (M = Mo, n = 3 or 4; M = W, n = 3) obtained through Alkyl Migration to Methyl Isocyanide co-ordinated to Molybdenum or Tungsten. X-Ray Structure of *cis*-[MoI{=C(CH₂)₃NMe}(CO)₂(η-C₅H₅)][†]

Harry Adams, Neil A. Bailey,* Valerie A. Osborn, and Mark J. Winter*
Department of Chemistry, The University, Sheffield S3 7HF

Reaction of the isonitrile anion [M(CNMe)(CO)₂(η-C₅H₅)]⁻ (M = Mo or W) with I(CH₂)₃I in tetrahydrofuran solution results in good yields of the carbene complexes *cis*-[MI{=C(CH₂)₃NMe}(CO)₂(η-C₅H₅)]. The structure of the molybdenum compound was studied by X-ray crystallography. It crystallises as red needles, triclinic, *a* = 7.824(3), *b* = 13.363(6), *c* = 14.559(6) Å, α = 78.62(4), β = 77.37(3), and γ = 80.99(4)°; *R* converged to 0.0385 for 2 378 independent reflections. There are two essentially similar independent molecules within the asymmetric unit. The cyclic carbene ligand and the iodine atom are mutually *cis*. The carbene ligand adopts a reverse orientation relative to the cyclopentadienyl ring in that the NMe substituent is orientated below the basal plane away from the cyclopentadienyl ring in contrast to the O substituent in related oxacyclopentylidene complexes. The molecule fails to interconvert from the observed *cis* configuration to the expected *trans* complex. An important feature of the formation of this molecule is a facile migration reaction of the alkyl chain to an isonitrile ligand. The six-membered carbene ring complex *cis*-[MoI{=C(CH₂)₄NMe}(CO)₂(η-C₅H₅)] is formed in the analogous reaction of [Mo(CNMe)(CO)₂(η-C₅H₅)]⁻ with I(CH₂)₄I. Both molybdenum carbene complexes react with Li(BEt₃H) by attack at the carbene affording [Mo{CH(CH₂)_nNMe}(CO)₂(η-C₅H₅)] (*n* = 3 or 4). Treatment of these complexes with acid results in the evolution of the organic heterocycle *N*-methylpyrrolidine (*n* = 3) or *N*-methylpiperidine (*n* = 4). The acyclic carbene compounds *cis*-[MI(=CMeNHMe)(CO)₂(η-C₅H₅)] (M = Mo or W) are formed in high yield in the reaction of the corresponding anion [M(CNMe)(CO)₂(η-C₅H₅)]⁻ with MeI followed by MeCO₂H and LiI.

We recently presented the synthesis of the cyclic carbene complexes [MI{=C(CH₂)₃O}(CO)₂(η-C₅H₅)] (1) and (2) (Scheme 1)¹ through the reaction of [M{(CH₂)₃I}(CO)₃(η-C₅H₅)] (3) and (4) with I⁻. Other anionic nucleophiles such as CN⁻, SPh⁻, and [M(CO)₃(η-C₅H₅)]⁻ (M = Mo or W) lead to related products.^{1,2} A crucial first step is the migration of the (CH₂)₃I function to an adjacent carbonyl group as the nucleophile co-ordinates to the metal. While alkyl to carbonyl migrations are fundamental within organotransition-metal chemistry,³ several other migration types are known. In particular, there are examples of alkyl to isonitrile insertions;⁴ the relative paucity of documented cases is probably a consequence of the lack of suitable subject molecules. However, it is apparent that these processes do occur more readily than corresponding carbonyl reactions; in fact there are examples of multiple insertions⁵ which is not the case for carbonyls.

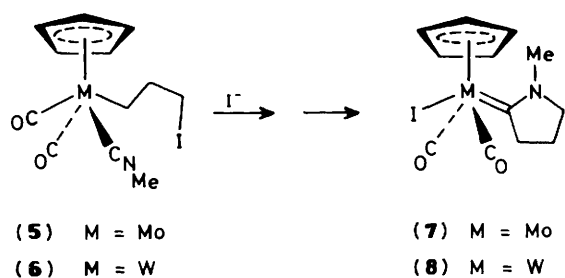
We reasoned that if complexes of formula *cis*-[M{(CH₂)₃I}(CNMe)(CO)₂(η-C₅H₅)] (5) or (6) (Scheme 2) were available, migration of the (CH₂)₃I to isonitrile might occur more rapidly than the competing migration to carbonyl, in which case the cyclic carbenes [MI{=C(CH₂)₃NMe}(CO)₂(η-C₅H₅)] (7) and (8) should result by a process analogous to the



* *cis*-Dicarbonyl(η-cyclopentadienyl)iodo(*N*-methyl-1-azolidin-2-ylidene)molybdenum.

Supplementary data available (No. SUP 56591, 4 pp.): thermal parameters, H-atom parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Scheme 1. (i) Li(BEt₃H); (ii) PPh₃, R = H; (iii) I⁻



Scheme 2.

formation of (1) and (2) (Scheme 1).¹ This paper describes the syntheses of complexes of the cyclic carbene $=\text{C}(\text{CH}_2)_3\text{NMe}$, and some related compounds, together with the reactivity of some of the complexes towards the hydride source $\text{Li}(\text{BEt}_3\text{H})$. Part of this work formed the subject of preliminary communications.⁶

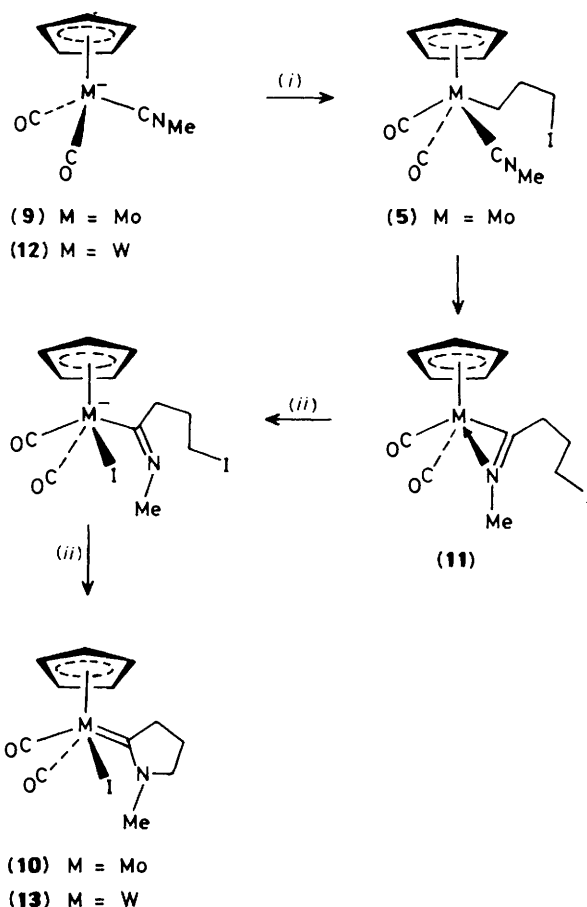
Results and Discussion

The anion $[\text{Mo}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ (9) is available through the sodium reduction of $[\text{MoCl}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$.⁷ Addition of $\text{I}(\text{CH}_2)_3\text{I}$ to a solution of (9) in tetrahydrofuran (thf) followed by a short period of stirring at ambient temperature results in a dark red solution whose i.r. spectrum contains two predominant carbonyl stretching bands [$\nu(\text{CO})$ 1946s and 1861s cm^{-1}] corresponding to the carbene complex $\text{cis-}[\text{MoI}\{\text{C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (10) (62%) which is the sole isolable product. The postulated mechanism of formation of (10) is indicated in Scheme 3 and parallels that of Scheme 1 but for the intermediate (11) (see later).

Compound (10) is fully spectroscopically characterised (Tables 1 and 2). The intensities of the two i.r. stretching bands are indicative of a *cis* dicarbonyl in a $[\text{MoX}(\text{CO})_2\text{L}(\eta\text{-C}_5\text{H}_5)]$ system based upon a square basal pyramidal ('four-legged piano stool') geometry.⁸ The same configuration is also indicated by the evident lack of symmetry for the six multiplets in the ^1H n.m.r. spectrum assigned to the carbene ring protons. Three high-frequency signals (δ 254.3, 253.2, and 247.2) in the ^{13}C n.m.r. spectrum are particularly important. Since mass spectrometry and the i.r. spectrum both indicate the product to be a dicarbonyl, the three signals are assigned to two inequivalent carbonyls, as expected for a *cis* but not a *trans* geometry, and a carbene.⁹ The assignment of a specific signal to the carbene is considered below, but it is notable here that the carbene resonance is shifted considerably to low frequency as compared to those for corresponding oxacyclopentylidene resonances.^{1,2} We have not detected or isolated the expected *trans* compound (7), which is at first sight surprising in view of the fact that no *cis* isomer of (1) has yet been observed¹ and that the *trans* geometry for $[\text{Mo}\{\text{C}(\text{CH}_2)_3\text{O}\}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ is thermodynamically more favourable than the *cis* form.¹⁰

Insertion reactions for tungsten systems of the type $[\text{WR}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (R = alkyl) are rather slower than for molybdenum¹¹ but we find that there is a pronounced tendency for the corresponding alkyl to isonitrile insertions for $[\text{WR}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ to proceed.

Addition of $\text{I}(\text{CH}_2)_3\text{I}$ to a solution of $[\text{W}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ (12)⁵ results in the ready formation of $\text{cis-}[\text{WI}\{\text{C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (13) whose spectroscopic properties (Tables 1 and 2) are essentially similar to those of its molybdenum analogue (10). Again there is no sign of the corresponding *trans* isomer.

Scheme 3. (i) $\text{I}(\text{CH}_2)_3\text{I}$, $-\text{I}^-$; (ii) I^-

In common with other compounds, the chemical shifts in the ^{13}C n.m.r. spectrum of the carbene and carbonyls occur to rather lower frequencies than for the molybdenum analogues. In this case, the ^{183}W satellites are resolved for the three signals assigned to the carbene and carbonyls and allow unambiguous assignment of these three resonances. Two of the $^1J(^{13}\text{C}^{183}\text{W})$ values are very similar (146 and 154 Hz) and the associated signals [$\delta(\text{C}_6\text{D}_5\text{CD}_3)$ 245.1 and 237.1 respectively] are therefore assigned to the two carbonyls while the third $^1J(^{13}\text{C}^{183}\text{W})$ value is rather smaller (101 Hz) and therefore assigned as the carbene signal [$\delta(\text{C}_6\text{D}_5\text{CD}_3)$ 240.9]. The shift for the carbene atom therefore is between those of the two carbonyl signals. It is tempting but not justified to assume this also to be the case for the molybdenum analogue.

The *trans* form is the thermodynamically more favoured for the several complexes of type $[\text{MX}(\text{=CR}^1\text{OR}^2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [$\text{X} = \text{halide, CN, SPh, SnPh}_3, \text{GeCl}_3, \text{ or } \text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$; $\text{R}^1 = \text{Me or Ph, R}^2 = \text{Me or Et, or } \text{R}^1\text{R}^2 = (\text{CH}_2)_3$; $\text{M} = \text{Mo or W}$],^{1,12} which may in principle exist as either *cis* or *trans* isomers. Compound (10) was analysed by *X*-ray crystallography in order to confirm its *cis* configuration and to gain insight as to why only the *cis* isomer is observed.

The crystal structure (Figure, Tables 3–5) comprises two independent but structurally almost identical molecules, denoted 1 and 2, per equivalent position. The iodine and the *N*-methyl-1-azacyclopent-2-ylidene ligands occupy mutually *cis* basal sites of an essentially square-based pyramidal molybdenum co-ordination system in which the axial site is occupied by the centroid of the η -cyclopentadienyl ring while the remaining two basal sites are occupied by CO groups. Both

Table 1. Analytical^a and other data for the complexes

Complex	Colour	M.p./°C	<i>M</i> ^b	$\nu_{\max}(\text{CO})^c/\text{cm}^{-1}$	Analysis		
					C	H	N
(10)	Maroon	129–131	429 (429)	1 950s, 1 860s	33.4 (33.7)	3.2 (3.3)	3.3 (3.3)
(13)	Orange	138–140	516 (516)	1 938s, 1 844s	28.3 (28.0)	2.8 (2.7)	2.5 (2.7)
(15)	Maroon	117–119	443 (443)	1 944s, 1 852s	35.5 (35.4)	3.7 (3.6)	3.2 (3.2)
(17)	Maroon	121–123	403 (403)	1 952s, 1 863s	30.3 (29.9)	3.1 (3.0)	3.3 (3.5)
(21)	Orange	131–133	488 (488)	1 940s, 1 846s	24.5 (24.6)	2.5 (2.5)	2.6 (2.9)
(22)	Yellow	69–71	303 (303)	1 932s, 1 840s ^d	47.7 (47.8)	5.3 (5.0)	4.4 (4.7)
(23)	Yellow	70–72	317 (317)	1 937s, 1 841s ^d	49.7 (49.5)	5.4 (5.4)	4.1 (4.5)

^a Calculated values are in parentheses. ^b From molecular ion in mass spectrum using ⁹⁸Mo or ¹⁸⁴W isotopes. ^c In CH₂Cl₂ solution unless stated otherwise. ^d In light petroleum.

Table 2. N.m.r. data for the complexes^a

Complex	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
(10)	5.52 (s, 5 H, C ₅ H ₅), 3.86 [d of t of d, 1 H, Mo=CCH ₂ , <i>J</i> (HH) 11.7, 7.2, 1.4], 3.65 [d of t of t, 1 H, Mo=CCH ₂ , <i>J</i> (HH) 11.7, 8.6, 1.4], 3.53 [d of t of quintets, 1 H, MeNCH ₂ , <i>J</i> (HH) 18.3, 7.0, 1.4], 3.43 [d of t of sextets, 1 H, MeNCH ₂ , <i>J</i> (HH), 18.3, 7.0, 1.4], 3.32 [t, 3 H, Me, <i>J</i> (HH) 1.4 Hz], 2.00 (m, 2 H, central CH ₂)	^b 254.3 (CO or Mo=C), 253.2 (CO or Mo=C), 247.2 (CO or Mo=C), 95.4 (C ₅ H ₅), 60.3 (NCH ₂), 53.6 (Mo=CCH ₂), 42.9 (Me), 20.9 (CH ₂)
(13)	5.66 (s, 5 H, C ₅ H ₅), 3.95 [d of t, 1 H, W=CCH ₂ , <i>J</i> (HH) 12.0, 7.0], 3.75 [d of t, 1 H, W=CCH ₂ , <i>J</i> (HH), 12.0, 8.5], 3.51 [d of t of q, 1 H, MeNCH ₂ , <i>J</i> (HH) 18.0, 9.0, 1.0], 3.41 [d of t of q, 1 H, MeNCH ₂ , <i>J</i> (HH) 18.0, 7.0, 1.0 Hz], 3.36 (m, 3 H, Me), 1.98 (m, 2 H, central CH ₂)	^c 245.1 [¹ <i>J</i> (WC) 146, CO], 240.9 [¹ <i>J</i> (WC) 101, W=C], 237.1 [¹ <i>J</i> (WC) 154 Hz, CO], 94.0 (C ₅ H ₅), 60.7 (NCH ₂), 54.5 (W=CCH ₂), 43.9 (Me), 21.6 (CH ₂)
(15)	5.52 (s, 5 H, C ₅ H ₅), 3.62 [d of t, 1 H, Mo=CCH ₂ , <i>J</i> (HH) 14.0, 6.6], 3.54 [d of t of q, 1 H, MeNCH ₂ , <i>J</i> (HH) 19.0, 6.5, 1.0], 3.44 [t, 3 H, Me, <i>J</i> (HH) 1.0], 3.41 [d of t, 1 H, Mo=CCH ₂ , <i>J</i> (HH) 14.0, 6.0], 3.32 [d of t of q, 1 H, MeNCH ₂ , <i>J</i> (HH) 19.0, 6.0, 1.0 Hz], 1.85 (m, 2 H, Mo=CCH ₂ CH ₂), 1.61 (m, 2 H, MeNCH ₂ CH ₂)	^d 254.4 (2 CO or CO + Mo=C), 243.1 (CO or Mo=C), 96.1 (C ₅ H ₅), 54.1 (NCH ₂), 52.6 (Mo=CCH ₂), 48.0 (Me), 21.5 (CH ₂), 19.6 (CH ₂)
(17)	8.12 (s, br, 1 H, NH), 5.56 (s, 5 H, C ₅ H ₅), 3.25 [d of q, 3 H, NMe, <i>J</i> (HH) 5.0, 1.0], 2.93 [quintet, 3 H, Mo=CMe, <i>J</i> (HH) 1.0 Hz]	^e 263.7 (CO or Mo=C), 251.9 (CO or Mo=C), 246.1 (CO or Mo=C), 95.9 (C ₅ H ₅), 43.8 (Me), 40.4 (Me)
(21)	7.98 (s, br, 1 H, NH), 5.71 (s, 5 H, C ₅ H ₅), 3.28 [d of q, 3 H, NMe, <i>J</i> (HH) 5.0, 1.0], 2.95 [quintet, 3 H, W=CMe, <i>J</i> (HH) 1.0 Hz]	^f 249.6 (CO), 244.3 (W=C), 238.3 (CO), 94.7 (C ₅ H ₅), 44.4 (Me), 41.5 (Me)
(22) ^d	4.89 (s, 5 H, C ₅ H ₅), 2.86 [d of d, 1 H, MeNCH ₂ , <i>J</i> (HH) 10.0, 7.5], 2.69 [d, 1 H, MoCH, <i>J</i> (HH) 6.0], 2.41 [d of d, 1 H, MoCHCH ₂ , <i>J</i> (HH) 13.0, 7.0], 2.00 [d of d of d of d, 1 H, MoCHCH ₂ , <i>J</i> (HH) 13.0, 11.5, 7.0, 6.0], 1.92 [d of d of d, 1 H, MeNCH ₂ , <i>J</i> (HH) 12.0, 10.0, 7.0 Hz], 1.88 (s, 3 H, Me), 1.52 [q of t, 1 H, central CH ₂ , <i>J</i> (HH) 12.0, 7.0], 1.10 [d of t, 1 H, central CH ₂ , <i>J</i> (HH) 12.0, 7.0 Hz]	^g 253.1 (CO), 245.3 (CO), 92.6 (C ₅ H ₅), 63.2 (NCH ₂), 54.6 (Mo-CH), 52.9 (Me), 30.1 (MoCHCH ₂), 23.0 (CH ₂)
(23) ^d	4.90 (s, 5 H, C ₅ H ₅), 2.54 [d of d of d of d, 1 H, MoCHCH ₂ , <i>J</i> (HH) 13.4, 5.6, 2.6, 0.7], 2.36 [d of d, 1 H, MoCH, <i>J</i> (HH) 8.8, 6.0], 2.27 [d of d of d of d, 1 H, MeNCH ₂ , <i>J</i> (HH) 14.4, 6.0, 4.8, 3.7], 2.14 [d of d of d, 1 H, MeNCH ₂ , <i>J</i> (HH) 13.4, 11.8, 5.4], 1.87 (s, 3 H, Me), 1.79 (m, 1 H, MoCHCH ₂), 1.46 [d of d of d of d of d, 1 H, MoCHCH ₂ CH ₂ , <i>J</i> (HH) 13.3, 12.3, 7.4, 4.8, 3.2], 1.20 [d of d of d of d of d, 1 H, MeNCH ₂ CH ₂ , <i>J</i> (HH) 14.0, 11.8, 9.9, 5.6, 3.2], 1.05 [d of d of d of d of d, 1 H, MoCHCH ₂ CH ₂ , <i>J</i> (HH) 13.3, 12.3, 10.1, 9.9, 4.8], 0.78 [d of d of d of d of d, 1 H, MeNCH ₂ CH ₂ , <i>J</i> (HH) 14.0, 10.1, 7.4, 5.5, 2.6 Hz]	^h 252.6 (CO), 244.9 (CO), 92.4 (C ₅ H ₅), 60.4 (NCH ₂), 56.2 (Mo-CH), 51.4 (Me), 30.4 (MoCH-CH ₂), 20.8 (NCH ₂ CH ₂), 19.3 (MoCHCH ₂ CH ₂)

^a Recorded in CDCl₃ and at ambient temperature unless stated otherwise. ^b Recorded in C₆D₅CD₃ at -60 °C. ^c Recorded in C₆D₅CD₃. ^d Recorded in C₆D₆. ^e Recorded at -50 °C. ^f Recorded in C₆D₅CD₃ at -50 °C.

cyclopentadienyl rings are planar [root mean square (r.m.s.) deviation 0.006 Å] and although η⁵ in nature there is a variation in molybdenum-carbon distances which is consistent for both molecules. The most remote carbon atom lies above the iodine atom (I...C 3.47 and 3.53 Å) suggesting the origin of the asymmetry is steric.

The molybdenum-carbene distance is shorter than expected for a purely single bonded carbon but longer than that of complex (1) (2.08 Å).¹ Similarly, the adjacent carbon-nitrogen bond is shorter than the corresponding carbon-oxygen bond in (1) suggesting a greater contribution from a Zwitterionic resonance form (14) (Scheme 4) than is the case for (1).

The methyl substituent on the heteroatom of the carbene ring necessitates the ring to be bonded in the reverse orientation to that of (1), thus minimising steric interactions between the methyl and cyclopentadienyl ring hydrogen atoms. As a consequence the methyl group partially blocks the metal site below the basal plane although there is no evidence for any

advantageous interaction between the methyl group and molybdenum; in fact the large bond angles Mo(1)-C(3)-N(1) and C(3)-N(1)-C(7) for both molecules suggest any interaction to be repulsive.

In both molecules the carbene ring has an envelope conformation with C(5) deviating from the mean plane through the remaining ring atoms and molybdenum. A related envelope configuration is also apparent for (1) and other molecules.^{1,3} The closeness of this coplanarity is less precise for molecule 2 and the folding greater. These features may be associated with the only short intermolecular contact of 3.44 Å between C(6') and C(8) of a symmetry-related molecule (1 - *x*, 1 - *y*, 1 - *z*). The rather short C(5)-C(6) bond results from the much higher thermal motion of these atoms than the corresponding more closely packed atoms in molecule 2.

There is now the question as to why the products of these reactions are *cis* rather than *trans*. Some possible mechanisms for the *cis-trans* isomerisation of [MoX(CO)₂L(η-C₅H₅)]

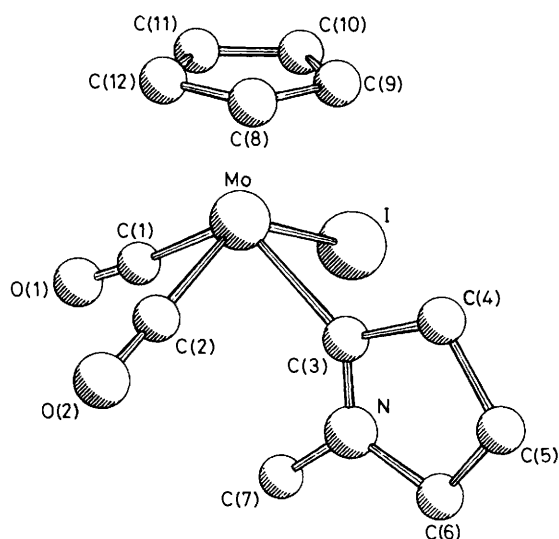


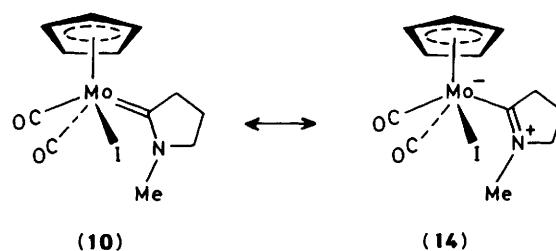
Figure. The molecular structure of *cis*-[MoI(=C(CH₂)₃NMe)(CO)₂(η-C₅H₅)] (10), molecule 1, with atom labelling. The atoms of molecule 2 are similarly labelled but are distinguished by a prime superscript

systems have been discussed elsewhere.¹⁴ The mechanism is probably intramolecular and it is likely (Scheme 5) that a *cis* structure rearranges to a trigonal-bipyramidal system in which the cyclopentadienyl group and one of X or L occupy the axial positions. Isolated examples are known of molecules of this stoichiometry with trigonal-bipyramidal geometries.¹⁵

Reversion back to the four-legged piano stool system leads to either *cis* or *trans* geometries depending between which two ligands the axial X or L migrates. The activation barriers to *cis*-*trans* isomerisation are not particularly dependent upon L (generally a phosphine or phosphite in the systems studied) but are more so upon X (hydride, alkyl, or halide). Significantly, the barriers to interconversion as measured by ¹H n.m.r. spectroscopy are felt to be smaller for hydride as a consequence of its smaller size. The smaller size leads to decreased steric interactions during the isomerisation process.

It might be reasonable to extend this argument to account for the fact that the *trans* complex (7) [or a similar species with the carbene rotated so that the NMe is orientated away from the cyclopentadienyl group as in (10)] is not detected (but see below). Even prolonged heating of (10) in thf or toluene at reflux does not result in the detection or isolation of any *trans* product. Inspection of the Figure indicates that the methyl group occupies a position approaching that where the axial site would be in a trigonal-bipyramidal intermediate of the type shown in Scheme 5. This could prevent the iodide from being able to occupy the axial site, rendering the intermediate inaccessible. Similarly, interactions of the methyl group with the other ligands may prevent the carbene ring moving to the axial site. There are apparently no other kinetically accessible mechanisms available for the *cis*-*trans* isomerisation.

There is also the possibility, that, for whatever reason, the *cis* orientation for this molecule is both the kinetic and the thermodynamic form. There are now strong indications that this is the case. Reaction of the carbene anion [Mo{=C(CH₂)₃NMe}(CO)₂(η-C₅H₅)]⁻¹⁶ with I₂ proceeds as expected by incorporation of 'I⁺' but leads exclusively to *cis*-(10) with no sign of *trans*-(7). Similarly, reaction of *trans*-[WH{=C(CH₂)₃NMe}(CO)₂(η-C₅H₅)]¹⁶ with CHI₃ leads exclusively to *cis*-(13). Such reactions of metal hydrides are generally thought of as radical processes³ and if the tungsten complex (8) is to be accessible this reaction should certainly produce it.

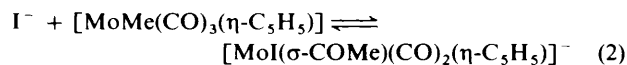
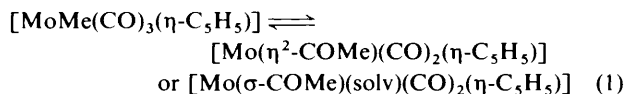


Scheme 4.

There is now the question as to why the *cis* form is more stable for compounds (10) and (13). We do not yet understand the answer to this question in detail. In separate experiments we have synthesised several other complexes of the type [MX{=C(CH₂)₃NMe}(CO)₂(η-C₅H₅)] (M = Mo or W, X = H or SnPh₃).^{16,17} While all the halogeno complexes of the =C(CH₂)₃NMe ligand are *cis*, when X = H or SnPh₃ they are *trans*. On the other hand we have never observed any neutral *cis* complexes of the carbene =C(CH₂)₃O. One *cis* cationic compound of the latter ligand, *cis*-[Mo{=C(CH₂)₃O}(CO)₂(PPh₃)(η-C₅H₅)]⁺, is known,¹⁰ but it isomerizes to the thermodynamically stable *trans* form in solution. The problem is part of the general question concerning the relative stability of *cis* and *trans* forms of [MX(CO)₂L(η-C₅H₅)] which is still unanswered in detail but is a subtle mix of steric and electronic effects.¹⁴

Complexes of six-membered carbene rings are not formed in the reaction of [M(CO)₃(η-C₅H₅)]⁻ with I(CH₂)₄I, instead excess of anion attacks the primary product [M{(CH₂)₄I}(CO)₃(η-C₅H₅)] displacing the second iodide group so forming [(η-C₅H₅)(OC)₃M(CH₂)₄M(CO)₃(η-C₅H₅)] (M = Mo or W).¹ Different results occur in the reaction of anion (9) with I(CH₂)₄I. Addition of I(CH₂)₄I to a solution of (9) at ambient temperature results in rapid darkening to a deep red solution whose i.r. spectrum is qualitatively very similar to that obtained in the I(CH₂)₃I reaction above. The only isolable product is the carbene *cis*-[MoI{=C(CH₂)₄NMe}(CO)₂(η-C₅H₅)] (15) (21%) (Scheme 6) which is fully spectroscopically characterised. The low yield is a consequence of the reluctance of the product to crystallise rather than the formation of side products. The i.r. spectra of compounds (10) and (15) are very similar while both ¹H and ¹³C n.m.r. spectra suggest that (15) is related to (10), differing only in having an extra CH₂ substituent in the carbene ring. We have been unable as yet to isolate products from the analogous reaction of the tungsten anion (12) with I(CH₂)₄I but clearly some reaction does take place.

The important feature of this reaction is that compound (15) is actually formed. One can explain this by comparing the likely mechanisms of formation of (1) (Scheme 1) with that of (10) and (15) (Schemes 3 and 6) and making use of three other observations. First, the i.r. spectrum of a solution in MeOH or thf of [MoMe(CO)₃(η-C₅H₅)] does not change even upon heating. The implication is that an equilibrium such as (1)



involving an η²-acyl, or σ-acyl solvent complex, is likely to lie far to the left (or the activation barrier for the interconversion is high). Secondly, we find that addition of I⁻ to the same solution

Table 3. Atomic positional parameters with estimated standard deviations in parentheses for compound (10)

Atom*	X/a	Y/b	Z/c	Atom*	X/a	Y/b	Z/c
I	0.121 79(15)	-0.056 67(7)	0.167 24(7)	C(8)	0.027 4(20)	0.234 1(10)	0.396 9(12)
I'	0.783 27(11)	0.525 84(7)	0.381 51(6)	C(9)	-0.085 6(18)	0.173 5(15)	0.338 3(11)
Mo	0.200 32(13)	0.114 64(7)	0.312 08(7)	C(10)	-0.052 6(23)	0.079 7(14)	0.361 1(12)
Mo'	0.564 68(13)	0.583 42(7)	0.213 50(7)	C(11)	0.088 2(22)	0.078 7(12)	0.435 8(12)
O(1)	0.551 8(12)	-0.018 6(7)	0.364 3(7)	C(12)	0.135 7(20)	0.175 9(12)	0.458 5(10)
O(2)	0.491 3(12)	0.257 1(6)	0.349 4(7)	C(1')	0.583 7(16)	0.435 2(8)	0.179 0(7)
O(1')	0.589 1(13)	0.347 1(6)	0.157 3(6)	C(2')	0.322 6(15)	0.553 2(8)	0.150 4(8)
O(2')	0.192 9(10)	0.538 0(7)	0.117 2(6)	C(3')	0.408 8(13)	0.645 8(7)	0.320 5(7)
N	0.260 8(16)	0.167 2(8)	0.120 4(7)	C(4')	0.379 2(16)	0.760 6(8)	0.358 0(8)
N'	0.320 3(12)	0.602 4(7)	0.363 2(6)	C(5')	0.242 7(20)	0.775 2(9)	0.419 1(9)
C(1)	0.421 0(16)	0.028 6(8)	0.339 8(9)	C(6')	0.232 2(16)	0.668 7(9)	0.435 6(8)
C(2)	0.381 3(16)	0.204 9(8)	0.334 8(8)	C(7')	0.312 1(17)	0.494 5(8)	0.356 6(9)
C(3)	0.165 5(16)	0.176 4(8)	0.183 4(8)	C(8')	0.541 5(22)	0.723 3(11)	0.140 6(12)
C(4)	0.002 8(22)	0.246 1(12)	0.151 5(10)	C(9')	0.673 4(24)	0.740 5(11)	0.217 1(11)
C(5)	0.029 7(30)	0.279 1(14)	0.060 3(12)	C(10')	0.816 0(18)	0.662 5(12)	0.202 9(9)
C(6)	0.192 7(26)	0.221 4(14)	0.039 3(10)	C(11')	0.763 6(17)	0.600 6(11)	0.119 1(10)
C(7)	0.430 5(22)	0.104 7(13)	0.121 4(11)	C(12')	0.597 1(20)	0.634 2(12)	0.079 4(9)

* Primed atoms constitute molecule 2.

Table 4. Bond lengths (Å) and angles (°) with estimated standard deviations for the two molecules of (10)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
I-Mo	2.834(1)	2.829(1)	I-Mo-C(1)	82.0(4)	79.6(3)
Mo-C(1)	1.930(13)	1.936(11)	I-Mo-C(2)	131.1(3)	130.5(3)
Mo-C(2)	1.934(12)	1.982(11)	I-Mo-C(3)	77.0(3)	77.1(3)
Mo-C(3)	2.141(12)	2.147(10)	C(1)-Mo-C(2)	74.6(5)	75.2(5)
Mo-C(8)	2.276(16)	2.291(17)	C(1)-Mo-C(3)	113.8(5)	114.3(4)
Mo-C(9)	2.339(17)	2.373(17)	C(2)-Mo-C(3)	74.4(5)	75.7(4)
Mo-C(10)	2.385(18)	2.420(15)	Mo-C(1)-O(1)	174.1(11)	177.8(10)
Mo-C(11)	2.326(17)	2.353(14)	Mo-C(2)-O(2)	178.5(10)	179.3(11)
Mo-C(12)	2.263(16)	2.265(15)	Mo-C(3)-N	133.1(9)	131.4(8)
O(1)-C(1)	1.139(16)	1.153(15)	Mo-C(3)-C(4)	121.0(9)	122.3(7)
O(2)-C(2)	1.150(15)	1.057(15)	N-C(3)-C(4)	105.9(11)	106.2(9)
N-C(3)	1.280(16)	1.288(14)	C(3)-C(4)-C(5)	106.1(13)	106.5(10)
N-C(6)	1.464(21)	1.459(15)	C(4)-C(5)-C(6)	105.8(16)	104.7(10)
N-C(7)	1.453(20)	1.437(15)	C(5)-C(6)-N	104.0(15)	103.2(10)
C(3)-C(4)	1.499(20)	1.524(16)	C(3)-N-C(6)	118.0(12)	116.9(9)
C(4)-C(5)	1.544(26)	1.501(18)	C(3)-N-C(7)	125.1(12)	128.2(10)
C(5)-C(6)	1.444(27)	1.508(18)	C(6)-N-C(7)	116.9(12)	114.5(9)
C(8)-C(9)	1.337(23)	1.353(24)	C(12)-C(8)-C(9)	107.2(15)	108.2(15)
C(9)-C(10)	1.332(25)	1.423(22)	C(8)-C(9)-C(10)	109.7(16)	107.1(14)
C(10)-C(11)	1.369(25)	1.354(20)	C(9)-C(10)-C(11)	108.4(16)	107.3(13)
C(11)-C(12)	1.365(23)	1.350(21)	C(10)-C(11)-C(12)	106.5(15)	109.9(13)
C(12)-C(8)	1.367(22)	1.411(22)	C(11)-C(12)-C(8)	108.3(14)	107.4(14)

does not lead to any change in the i.r. spectrum, no bands assignable to the hypothetical $[\text{MoI}(\sigma\text{-COMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ being present; presumably the equilibrium (2) must also lie to the left. Note, however, that CN^- does react with $[\text{MoMe}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ with formation of the insertion product $[\text{Mo}(\text{CN})(\sigma\text{-COMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$.¹⁸

Thirdly, it is known that the reaction of compound (9) with MeI very quickly results in the formation of the isolable iminoacyl (16) (Scheme 7),⁵ and further, that (16) reacts much more slowly with I^- (produced by elimination from MeI) and subsequently protons (adventitious water or during work-up) to produce the neutral carbene (17). This reaction probably proceeds through the intermediacy of the anion (18). We have repeated this reaction and find essentially similar results but in addition point out that the reaction times leading to the formation of (17) are dramatically reduced by the addition of MeCO_2H and excess of I^- to the reaction mixture. Compound (16) is the product arising from methyl migration in an initially

formed $[\text{MoMe}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (19) to isonitrile. Compound (19) is not detectable and the equilibrium between (19) and (16) therefore lies far in favour of (16). It is the known formation of compound (16) in this reaction that prompts us to suggest the intermediate iminoacyl (11) in Scheme 3.

While the equilibria (1) and (2) lie to the left one does not expect substitution of Me by $(\text{CH}_2)_3\text{I}$ to lead to an appreciable shift in the equilibria. Therefore in the reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ with $\text{I}(\text{CH}_2)_3\text{I}$ (Scheme 1), although the instantaneous concentration of the intermediate acyl $[\text{Mo}\{\sigma\text{-CO}(\text{CH}_2)_3\text{I}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ is very low the ring-closure reaction is fast and results in formation of (1) after a *cis-trans* isomerisation step.¹ All this proceeds before excess of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ can displace the pendant iodide on alkyl (3), which would produce $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}(\text{CH}_2)_3\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$. However, in the corresponding reaction of $\text{I}(\text{CH}_2)_4\text{I}$, the ring-closure reaction of a low-concentration intermediate $[\text{Mo}\{\sigma\text{-CO}(\text{CH}_2)_4\text{I}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ is slower

Table 5. Details of planar fragments of the two molecules. Equations of mean planes are of the form $pX + qY + rZ = d$, where p , q , and r are direction cosines referred to orthogonal crystal axes a , b^* , c^* . Deviations (Å) of atoms from mean planes are given in parentheses

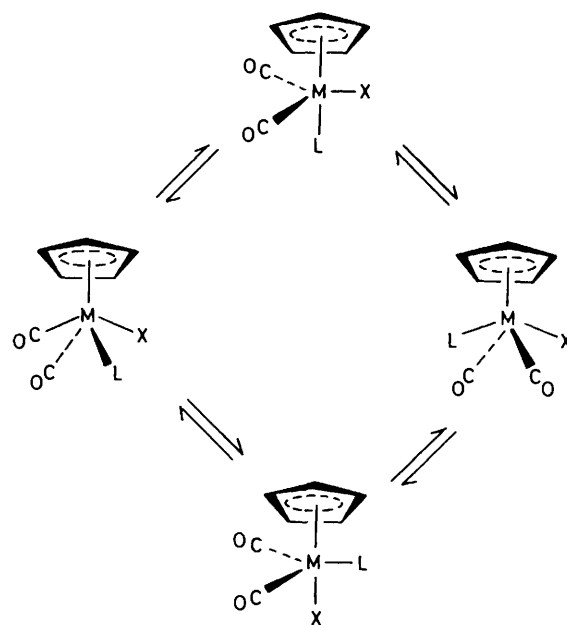
Plane	p	q	r	d	Root mean square deviation
A	C(8)—C(12)				0.006
	0.7551	-0.2611	-0.6014	-4.2947	
	[C(8) 0.001, C(9) 0.004, C(10) -0.007, C(11) 0.008, C(12) -0.006, Mo 2.008]				
B	Mo, N, C(3), C(4), C(6)				0.003
	0.4711	0.7930	0.3863	3.1820	
	[Mo -0.002, N 0.005, C(3) 0.001, C(4) 0.002, C(6) -0.004, C(5) 0.080, C(7) -0.018]				
C	C(4)—C(6)				0.006
	0.5129	0.7352	0.4432	3.0919	
	[Mo 0.273, N 0.129, C(3) 0.129, C(7) 0.212]				
A'	C(8')—C(12')				0.006
	-0.5736	-0.5715	0.5868	-8.1870	
	[C(8') -0.008, C(9') 0.006, C(10') -0.002, C(11') -0.003, C(12') 0.007, Mo' 2.020]				
B'	Mo', N', C(3'), C(4'), C(6')				0.017
	-0.6635	0.0980	-0.7417	-3.8203	
	[Mo' -0.009, N' 0.028, C(3') -0.006, C(4') 0.010, C(6') -0.023, C(5') 0.226, C(7') -0.042]				
C'	C(4')—C(6')				0.017
	-0.5702	-0.1294	-0.8112	-5.9760	
	[Mo' 0.764, N' 0.381, C(3') 0.354, C(7') 0.595]				
Inter-planar angles (°)		Molecule 1	Molecule 2		
A—B		94.8	96.4		
A—C		94.1	94.3		
B—C		5.2	14.7		

for entropic reasons¹⁰ and nucleophilic replacement of I^- in $[Mo\{(CH_2)_4I\}(CO)_3(\eta-C_5H_5)]^-$ by $[Mo(CO)_3(\eta-C_5H_5)]^-$ is the favoured path.

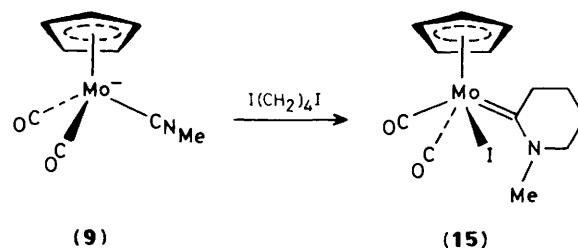
The situation is different in the corresponding isonitrile reactions. The reaction of compound (9) with $I(CH_2)_3I$ gives, as the primary product, $[Mo\{(CH_2)_3I\}(CNMe)(CO)_2(\eta-C_5H_5)]$ (5) (Scheme 3), which rearranges rapidly to the intermediate (11); its reaction with I^- and subsequent ring closure producing (10) is facile. With an extra CH_2 group, the primary product in the reaction of (9) with $I(CH_2)_4I$ will be $[Mo\{(CH_2)_4I\}(CNMe)(CO)_2(\eta-C_5H_5)]$, although it is not detected. Insertion to give its isomeric iminoacyl proceeds easily and subsequent reaction with I^- and ring closure proceeds to form the six-membered ring carbene (15). These steps take place *before* excess of (9) is able to displace iodide from the pendant $(CH_2)_4I$ group in a competing reaction. Therefore formation of compound (15) depends on the facile formation of an iminoacyl intermediate by an alkyl to isonitrile insertion step.

The accelerated formation of compound (17) through addition of acid and excess of I^- mentioned above indicates that the unreported tungsten analogue (21) might be available by a similar route. This is the case. Treatment of a solution of $[W(CNMe)(CO)_2(\eta-C_5H_5)]^-$ (12) in thf with MeI at ambient temperature results in a rapid darkening of the solution. The i.r. spectrum of this solution in the carbonyl region consists predominantly of two new bands [$\nu(CO)(thf)$ 1913s and 1809s cm^{-1}] assigned to the iminoacyl $[W(CO)_2(MeNCMe)(\eta-C_5H_5)]$ (20) on the basis of comparison of its i.r. spectrum with that of the molybdenum analogue (16).⁵

Addition of excess of I^- and $MeCO_2H$ to the reaction



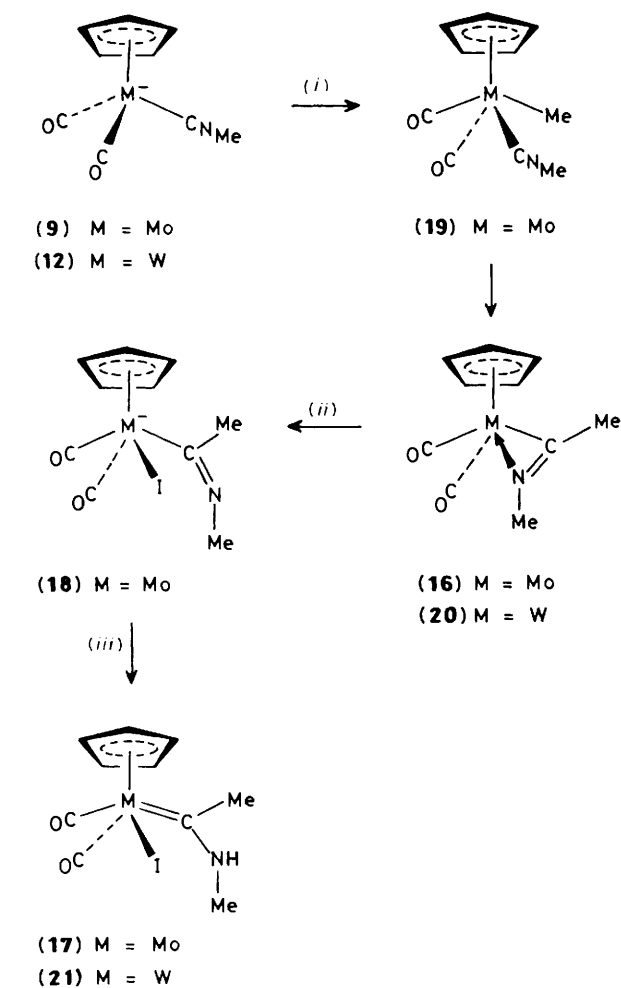
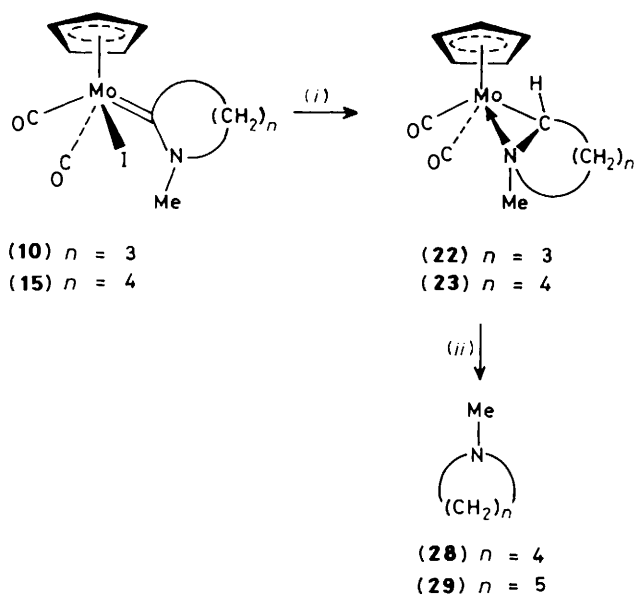
Scheme 5.



Scheme 6.

mixture followed by stirring for 3 h at ambient temperature gives rise to the acyclic carbene (21) whose spectroscopic properties are qualitatively similar to those of (17). The ^{13}C n.m.r. spectrum is qualitatively very similar to that of the cyclic complex (13) in the carbene and carbonyl region although the signal/noise ratio is not sufficient to measure the $J(^{13}C^{183}W)$ coupling constants.

Interesting structures arise from the reaction of the carbene complexes (10) and (15) with the hydride source $Li(BEt_3H)$ (Scheme 8). Addition of $Li(BEt_3H)$ to a solution of (10) in thf results in a rapid reaction during which the two i.r. bands of (10) are replaced predominantly by two new bands [$\nu(CO)$ 1913s and 1817s cm^{-1}] which correspond to complex (22). In analogous fashion the carbene (15) reacts with $Li(BEt_3H)$ affording (23) as the only identified product. These reactions are related to those of (1) and its methylcyclopentadienyl analogue (24) which react with $Li(BEt_3H)$ with formation of (25) and (26) (Scheme 1) respectively.¹⁹ Careful comparison of coupling constants for the C_4H_7NMe ring protons of compound (22) in the 1H n.m.r. spectrum at 400 MHz (Table 1) with those of (26) (which has been crystallographically characterised) and (25) suggests the geometries of all three complexes are virtually identical. The 1H and ^{13}C n.m.r. data for (22) and (23) suggest their structures differ only in that (23) has an extra CH_2 group. All other spectroscopic data are consistent with structures (22) and (23). We regard the Mo—N interaction as a dative type from the nitrogen to molybdenum.

Scheme 7. (i) MeI, $-I^-$; (ii) I^- ; (iii) H^+ Scheme 8. (i) $Li(BEt_3H)$; (ii) H^+

We have previously suggested¹⁹ that the formation of compounds (25) and (26) proceeds by direct donation of hydride at the carbene atoms of (1) and (24) respectively followed by displacement of I^- ; it seems reasonable that a similar process occurs here for (22) and (23) except that a nitrogen atom rather than oxygen enters into the co-ordination sphere of molybdenum.¹⁹

From a reactivity point of view the $O \rightarrow Mo^{II}$ bond in complex (25) is labile¹⁹ and readily cleaved by PPh_3 to give $trans-[Mo(\sigma-C_4H_7O)(CO)_2(PPh_3)(\eta-C_5H_5)]$ (27). Although one might expect similar lability for the $N \rightarrow Mo^{II}$ bond in (22) and (23), neither complex reacts with PPh_3 in thf even after prolonged heating at reflux and they are recovered unchanged. However (22) is reactive towards acid, treatment with H_2SO_4 resulting in rapid decomplexation of the C_4H_7NMe ring and providing unidentified metal species together with a reasonable yield (43%) of *N*-methylpyrrolidine, $\overline{CH_2(CH_2)_3NMe}$ (28), characterised and quantified by g.l.c. and g.c.-mass spectrometry. In a similar fashion, acidification of compound (23) provides a respectable yield (54%) of *N*-methylpiperidine (29).

Experimental

Infrared spectra were measured using a Perkin-Elmer 257 instrument and calibrated using the absorption of polystyrene film at 1601.4 cm^{-1} or on a Perkin-Elmer 1710 Fourier-transform instrument linked to a Perkin-Elmer 4600 data station. Proton n.m.r. spectra were recorded using a Bruker WP-80SY (80 MHz), Perkin-Elmer R34 (220 MHz), Bruker AM-250 (250 MHz), or Bruker WH-400 (400 MHz) spectrometer. Carbon-13 spectra were obtained using a JEOL PFT-100 (25.15 MHz) or a Bruker AM-250 (62.9 MHz) instrument. Mass spectra were recorded with a Kratos MS25 spectrometer operating at low resolution using the electron-impact or chemical ionisation (NH_3) modes.

All reactions were performed under nitrogen or argon atmospheres using deoxygenated solvents dried with an appropriate agent, thf from sodium-benzophenone and light petroleum (b.p. $40-60^\circ\text{C}$ throughout) from $LiAlH_4$. Alumina was Brockmann Activity I and deactivated with water (5% w/w throughout). The compounds $MeNC$,²⁰ $[MCl(CNMe)(CO)_2(\eta-C_5H_5)]^-$ (M = Mo or W),^{5,7} and $[M(CNMe)(CO)_2(\eta-C_5H_5)]^-$ (M = Mo or W)⁵ are available through literature procedures but we typically prepared the anions by sodium dihydronaphthylide reduction of the chlorides.¹⁶

Preparations.—*cis*- $[MoI\{=C(CH_2)_3NMe\}(CO)_2(\eta-C_5H_5)]$ (10). A mixture of $I(CH_2)_3I$ (2.66 g, 9.0 mmol) and the anion $[Mo(CNMe)(CO)_2(\eta-C_5H_5)]^-$ (9) (6.0 mmol) in thf (100 cm³) was stirred for 1 h. Removal of solvent and chromatography on alumina [$8 \times 2\text{ cm}$, elution with dichloromethane-light petroleum (1:3)] gave naphthalene mixed with small quantities of an unidentified yellow material followed by maroon *cis*- $[MoI\{=C(CH_2)_3NMe\}(CO)_2(\eta-C_5H_5)]$ (10) (1.59 g, 62%) which was crystallised from toluene.

cis- $[W\{=C(CH_2)_3NMe\}(CO)_2(\eta-C_5H_5)]$ (13). In a similar manner to the preparation of (10) above, complex (13) was synthesised in 69% yield from the anion $[W(CNMe)(CO)_2(\eta-C_5H_5)]^-$ (12) (6.0 mmol) and $I(CH_2)_3I$ (2.66 g, 9.0 mmol) (reaction time 3 h) and crystallised from toluene.

cis- $[MoI\{=C(CH_2)_4NMe\}(CO)_2(\eta-C_5H_5)]$ (15). In a similar manner to the preparation of (10) above, complex (15) was synthesised in 21% yield through treatment of a solution of the anion $[Mo(CNMe)(CO)_2(\eta-C_5H_5)]^-$ (9) (6.0 mmol) with $I(CH_2)_4I$ (2.79 g, 9.0 mmol). It was recrystallised from diethyl ether.

cis- $[MoI(=CMeNHMe)(CO)_2(\eta-C_5H_5)]$ (17). A solution of

the anion $[\text{Mo}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ (**9**) (6.0 mmol) in thf (100 cm³) was treated with MeI (1.70 g, 12.0 mmol) and the resulting solution stirred at room temperature (15 min) during which it turned deep red. The reaction mixture was treated with $\text{LiI}\cdot 3\text{H}_2\text{O}$ (2.41 g, 18.0 mmol) and glacial acetic acid (1.44 g, 24.0 mmol), and stirring was continued for a further 2 h. Removal of solvent and chromatography on alumina (8 × 2 cm) eluting with an increasing proportion of CH_2Cl_2 mixed with light petroleum provided small quantities of an unidentified yellow dicarbonyl mixed with naphthalene. Further elution with CH_2Cl_2 afforded *cis*- $[\text{Mo}(\text{CMeNHMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**17**) (1.32 g, 55%).

cis- $[\text{Wl}(\text{CMeNHMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**21**). A solution of the anion $[\text{W}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ (**12**) (6.0 mmol) was treated with MeI (1.70 g, 12.0 mmol) and the resulting solution stirred at room temperature (3 h) during which time the solution turned deep red as the primary product $[\text{WMe}(\text{CNMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [$\nu(\text{CO})(\text{thf})$ 1945s, 1933s, 1869s, $\nu(\text{CN})(\text{thf})$ 2145s cm⁻¹] rearranged to the iminoacyl $[\text{W}(\text{CMeNHMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [$\nu(\text{CO})(\text{thf})$ 1913s and 1809s cm⁻¹]. The reaction mixture was treated with $\text{LiI}\cdot 3\text{H}_2\text{O}$ (2.41 g, 18.0 mmol) and glacial acetic acid (1.44 g, 24.0 mmol), stirring was then continued for a further 3 h. Removal of solvent and chromatography on alumina (8 × 2 cm) eluting with an increasing proportion of CH_2Cl_2 mixed with light petroleum provided an unidentified yellow dicarbonyl mixed with naphthalene. Further elution with CH_2Cl_2 afforded *cis*- $[\text{Wl}(\text{CMeNHMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**21**) (1.76 g, 60%) isolated as dark red-orange crystals.

$[\text{Mo}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**22**) A solution of $\text{Li}(\text{BEt}_3\text{H})$ (6 cm³, 1.0 mol dm⁻³ in thf, 6.0 mmol) was added to a thf (30 cm³) solution of *cis*- $[\text{Mo}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**10**) (0.85 g, 2 mmol) at ambient temperature and the resulting solution stirred for 2 h. Removal of solvent, extraction into light petroleum, filtration through alumina, and crystallisation from light petroleum provided yellow crystalline $[\text{Mo}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**22**) (0.22 g, 36%).

$[\text{Mo}\{\overline{\text{C}}(\text{CH}_2)_4\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**23**). In a similar fashion to the preparation of (**22**) above, complex (**23**) was isolated in 27% yield starting from the carbene (**15**) (0.88 g, 2.0 mmol).

Reaction of $[\text{WH}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with CHI_3 .—A solution of the hydride $[\text{WH}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^{16}$ (0.6 mmol) in thf (50 cm³) was treated with CHI_3 (0.236 g, 0.6 mmol) at -78 °C and the resulting solution allowed to warm towards ambient temperature. During this time the solution became dark orange. Removal of solvent and chromatography on alumina (8 × 2 cm, elution with light petroleum) provided naphthalene (from the synthesis of the hydride¹⁶) and upon elution with CH_2Cl_2 , *cis*- $[\text{Wl}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**13**) (0.29 g, 93%), crystallised from toluene.

Acidification of $[[\text{Mo}\{\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**22**).—A solution of compound (**22**) (0.03 g, 0.1 mmol) in diethyl ether was treated with H_2SO_4 (0.02 g, ca. 0.2 mmol) and stirred (5 min) at ambient temperature during which time the solution turned black and deposited a black tar. The $[\text{C}_4\text{H}_8\text{NMe}]^+$ salt was extracted with water (2 × 10 cm³) and the aqueous solution rendered alkaline with NaOH solution. The alkaline aqueous layer was extracted by diethyl ether (3 × 10 cm³) providing a solution of *N*-methylpyrrolidine (**28**) in diethyl ether. Analysis by g.l.c. and g.c.-mass spectrometry gave a mass spectrum identical to that of authentic material and integration

of the g.l.c. traces against standards indicated a 43% isolated yield.

Acidification of $[\text{Mo}\{\overline{\text{C}}(\text{CH}_2)_4\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (**23**).—In a similar fashion to the above experiment, a 54% yield of *N*-methylpiperidine (**29**) was obtained by the acidification of compound (**23**) (0.032 g, 0.1 mmol). Again the mass spectrum matched that of an authentic sample.

Crystallography.—*Crystal data.* $\text{C}_{12}\text{H}_{14}\text{IMoNO}_2$, (**10**), $M = 427.05$, recrystallises from light petroleum as red needles, crystal dimensions 0.50 × 0.09 × 0.09 mm, triclinic, $a = 7.824(3)$, $b = 13.363(6)$, $c = 14.559(6)$ Å, $\alpha = 78.62(4)$, $\beta = 77.37(3)$, $\gamma = 80.99(4)^\circ$, $U = 1445.8(11)$ Å³, $D_c = 1.962$ g cm⁻³, $Z = 4$, space group $P\bar{1}$ (C_i , no. 2, confirmed by the analysis), Mo- K_α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 29.90$ cm⁻¹, $F(000) = 816$.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < \theta < 50^\circ$ on a Nicolet R3m diffractometer by the omega scan method. The 2378 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 (C-H 0.97 Å); their contributions were included in structure-factor calculations ($B = 7.0$ Å²) but no refinement of positional parameters was permitted. Refinement converged to R 0.0385 with allowance for thermal anisotropy of all non-hydrogen atoms and for the anomalous scattering of iodine and molybdenum. Scattering factors were taken from ref. 21; unit weights were used throughout the refinement. Computer programs were SHELXTL as implemented on the Nova 3 computer and those of the Sheffield X-ray system.

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