Carbene Complexes. Part 9.[1] Electron-rich Olefin-derived Carbene–molybdenum(0) and Amidinium Molybdate(0) Complexes, and the Crystal and Molecular structure of *cis*-Tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)molybdenum(0), *cis*-$[\mathrm{Mo(CO)_4\{CN(Me)CH_2CH_2NMe\}_2}]$ †

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Carbene–Mo^0 complexes are obtained by the thermal reaction of an electron-rich olefin $\ddagger\mathrm{CN(R)CH_2CH_2NR]_2}$, $\mathrm{L^R{}_2}$, with (a) $[\mathrm{Mo(CO)_6}]$ {yielding $[\mathrm{Mo(CO)_5L^R}]$ or *cis*-$[\mathrm{Mo(CO)_4(L^R)_2}]$ (R = Me, Et, or $\mathrm{PhCH_2}$) (the tricarbene complex is unstable)}, and (b) $[\mathrm{Mo(CO)_2(C_5H_5\text{-}\eta)NO}]$ {yielding $[\mathrm{Mo(CO)(C_5H_5\text{-}\eta)(L^R)NO}]$ (R = Me or *p*-tol)}. By contrast, with $[\mathrm{Mo(CO)_3(C_5H_5\text{-}\eta)H}]$ or $[\{\mathrm{Mo(CO)_3(C_5H_5\text{-}\eta)}\}_2]$, the olefin reacts as a reducing agent, yielding the amidinium molybdate(0) complexes $[\mathrm{HL^R}]^+[\mathrm{Mo(CO)_3(C_5H_5\text{-}\eta)}]^-$ or $[\mathrm{L^R{}_2}]^{2+}[\mathrm{Mo(CO)_3(C_5H_5\text{-}\eta)}]^-{}_2$ (R = Me). The six-membered chelate olefin $\ddagger\mathrm{CN(Me)(CH_2)_3NMe]_2}$, $\mathrm{L'^{Me}{}_2}$, behaves qualitatively in a similar fashion, but is less reactive, dicarbene–Mo^0 complexes not being accessible. The *cis*-dicarbene–Mo^0 complexes are isomerised photochemically to the *trans*-complexes, but the former are thermodynamically the more stable. Reaction of $[\mathrm{Mo(CO)_5L^{Et}}]$ with $\mathrm{L^{Me}{}_2}$ yields *cis*-$[\mathrm{Mo(CO)_4(L^{Et})(L^{Me})}]$, whereas $[\mathrm{Mo(CO)_5L^{Me}}]$ with $\mathrm{L^{Et}{}_2}$ affords also *cis*-$[\mathrm{Mo(CO)_4(L^{Me})_2}]$ and *cis*-$[\mathrm{Mo(CO)_4(L^{Et})_2}]$. The redistribution reaction *cis*-$[\mathrm{Mo(CO)_4(L^R)_2}]$ + $[\mathrm{Mo(CO)_6}] \rightleftharpoons 2[\mathrm{Mo(CO)_5L^R}]$ (R = Me or Et) is reversible. Other reactions of monocarbene complexes give *cis*-$[\mathrm{Mo(CO)_4(L^R)Q}]$ [Q = $\mathrm{C_5H_5N}$, $\mathrm{PPh_3}$, or $\mathrm{P(C_6H_{11})_3}$], *fac*-$[\mathrm{Mo(CO)_3(L^R)Q'_2}]$ [$\mathrm{Q'_2} = \{\mathrm{P(OMe)_3}\}_2$ or diphos], or *cis*-$[\mathrm{Mo(CO)_4\{C(OMe)Me\}L^R}]$. $\nu(\mathrm{CN_2})$ is at 1 510—1 480 cm^{-1} for the carbene–Mo^0 complexes, but at 1 700—1 640 cm^{-1} for the amidinium cations, and ν(CO) values are very low; ^{1}H n.m.r. spectra provide information on conformational aspects; $\Delta G^\ddagger$ for Mo–$\mathrm{C_{carb}}$ rotation in *cis*-$[\mathrm{Mo(CO)_4(L^R)_2}]$ is *ca.* 10 kcal mol^{-1}. ^{13}C Chemical shifts for $\mathrm{C_{carb.}}$ and CO are comparable (but are distinguished by ^{1}H decoupling and ^{1}H off-resonance studies). Both are in the range 230—210 p.p.m. upfield from $\mathrm{SiMe_4}$, whereas for $[\mathrm{HL^{Me}}]^+$ or $[\mathrm{L^{Me}{}_2}]^{2+}$ there is a further 50—60 p.p.m. upfield shift for $\delta[\mathrm{C_{carbonium\ ion}}]$. A single-crystal *X*-ray analysis of (4) *cis*-$[\mathrm{Mo(CO)_4(L^{Me})_2}]$ shows octahedral Mo, with Mo–CO mutually-*trans* bond lengths longer by 0.048(2) Å than Mo–CO *trans* to carbene [2.024(3) and 2.032(3) Å]; Mo–$\mathrm{C_{carb}}$ [2.293(3) Å] is appropriate for single bonds. The dihedral angles between the carbene ligand planes and the co-ordination planes in which they are involved are *ca.* 45°, which is sterically the preferred conformation. It is concluded that the carbene ligand is a strong σ-donor but a poor π-acceptor.

EARLIER parts[1] of this series have shown the electron-rich olefins $\ddagger\mathrm{CN(R)CH_2CH_2NR]_2}$, $\mathrm{L^R{}_2}$ (R = alkyl or aryl) to be convenient organic precursors to carbene–transition-metal complexes, especially with the platinum-group metals;[2,3] the *N*-alkyl olefins (R = Me or Et) have been found to be very much more reactive than the aryl (Ph or *p*-tolyl) analogues in this respect.[4] The carbene ligand $\mathrm{\dot{\cdot}CN(R)CH_2CH_2NR}$, ($\mathrm{L^R}$), has been incorporated *via* neutral or anionic ligand displacement or halide-bridge cleavage reactions, and both the synthetic procedures and the general stability of the carbene–metal complexes resemble those of their triphenylphosphine ($\mathrm{PPh_3}$) analogues.[1,3]

Accordingly, we have investigated the reactions of $\mathrm{L^R{}_2}$ with the Group 6 metal hexacarbonyls, known precursors to stable mono-,[5] bis-,[6] and tris-$\mathrm{PPh_3}$-derivatives,[7] and here we describe the ready synthesis and spectroscopic properties of non-labile mono- and bis-carbenemolybdenum(0) complexes, their reactions with neutral ligands, and the accurate crystal structure of *cis*-$[\mathrm{Mo(CO)_4\{\dot{\cdot}CN(Me)CH_2CH_2NMe\}_2}]$, abbreviated as *cis*-$[\mathrm{Mo(CO)_4(L^{Me})_2}]$. The new complexes are included in Table 1.

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† No reprints available.

[1] Part 8, B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, 1974, 1827.

[2] D. J. Cardin, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

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[5] T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Amer. Chem. Soc.*, 1961, **83**, 3200.

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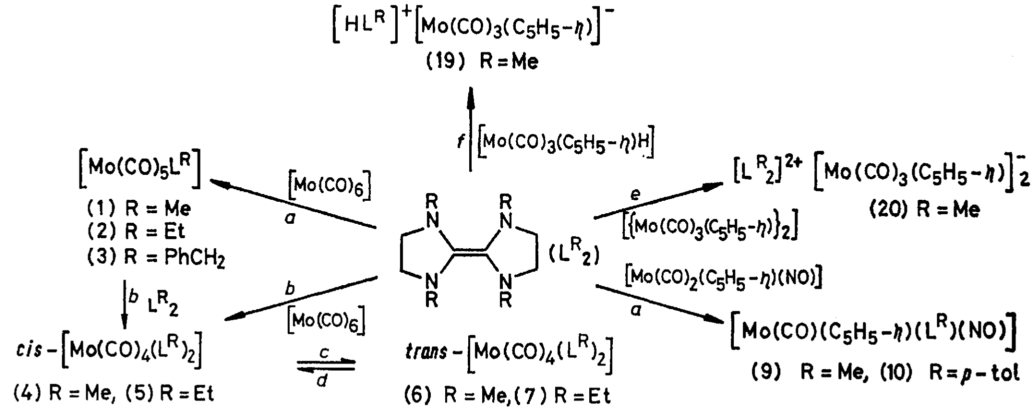

SCHEME 1 Molybdenum(0) complexes derived from $\ddagger[\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}]_2$ (L^R_2) [a] $C_6H_{11}Me$, 100 °C. [b] Decalin, 100—120 °C. [c] $h\nu$, acetone, 25 °C. [d] $CHCl_3$, 25 °C. [e] C_6H_6, 25 °C. [f] C_6H_{14}, 25 °C

TABLE 1

Electron-rich olefin-derived carbenemolybdenum(0) and amidinium molybdate(0) complexes and their characterisation [a]

Compound	No.	Yield (%)	M.p. (θ_c/°C)	Colour	Found (Required) (%)		
					C	H	N
$[Mo(CO)_5L^{Me}]$	(1)	70	108—109	White	35.9 (36.0)	3.3 (3.0)	8.4 (8.4)
$[Mo(CO)_5L^{Et}]$	(2)	75	93	White	39.2 (39.8)	3.9 (3.9)	7.7 (7.7)
$[Mo(CO)_5L^{CH_2Ph}]$	(3)	65	150	White	54.1 (54.3)	3.6 (3.7)	5.8 (5.8)
$cis\text{-}[Mo(CO)_4(L^{Me})_2]$	(4)	100	274 (decomp.)	Pale yellow	41.4 (41.6)	5.2 (5.0)	13.8 (13.8)
$cis\text{-}[Mo(CO)_4(L^{Et})_2]$	(5)	100	186—187	Pale yellow	46.7 (46.9)	6.4 (6.1)	12.2 (12.2)
$cis\text{-}[Mo(CO)_4(L^{CH_2Ph})_2]$		70	224	Pale yellow	64.1 (64.4)	5.3 (5.1)	8.0 (7.9)
$trans\text{-}[Mo(CO)_4(L^{Me})_2]$	(6)	60	b	Orange	41.6 (41.6)	5.2 (5.0)	13.8 (13.8)
$trans\text{-}[Mo(CO)_4(L^{Et})_2]$	(7)	50	b	Orange-red	46.9 (46.9)	6.3 (6.1)	12.0 (12.2)
$[Mo(CO)_5L'^{Me}]$	(8)	15	101	Cream	37.3 (37.9)	3.6 (3.5)	8.1 (8.1)
$cis\text{-}[Mo(CO)_4\{C(OMe)Me\}L^{Me}]$	(13)	50	90—91	Scarlet	39.4 (39.5)	4.8 (4.4)	7.7 (7.7)
$cis\text{-}[Mo(CO)_4(L^{Me})(PPh_3)]$	(14)	70	196	Pale yellow	57.5 (57.2)	4.6 (4.4)	5.1 (4.9)
$cis\text{-}[Mo(CO)_4(L^{Et})\{P(C_6H_{11})_3\}]$	(15)	80	190—195 (decomp.)	Cream	56.5 (56.6)	7.5 (7.7)	4.5 (4.6)
$cis\text{-}[Mo(CO)_4(L^{Me})(C_5H_5N)]$	(16)	60	145 (decomp.)	Bright yellow	43.9 (43.7)	4.0 (3.9)	11.1 (10.9)
$fac\text{-}[Mo(CO)_3(L^{Et})(diphos)]$	(17)	80	238—240	Pale yellow	61.4 (61.3)	5.5 (5.4)	4.0 (4.0)
$fac\text{-}[Mo(CO)_3(L^{Et})\{P(OMe)_3\}_2]$	(18)	90	173	White	35.0 (34.7)	6.1 (5.8)	5.2 (5.1)
$[Mo(CO)(C_5H_5\text{-}\eta)(L^{Me})(NO)]$	(9)	95	163	Crimson-red	41.8 (41.7)	4.9 (4.8)	13.3 (13.2)
$cis\text{-}[Mo(CO)_4(L^{Et})(L^{Me})]$	(12)	60	163	Pale yellow	44.5 (44.5)	5.6 (5.6)	12.9 (12.9)
$[Mo(CO)(C_5H_5\text{-}\eta)(L^{p\text{-tolyl}})(NO)]$	(10)	80	134—140 (decomp.)	Brick-red	58.8 (58.8)	5.1 (4.9)	8.9 (8.9)
$[Mo(CO)(C_5H_5\text{-}\eta)(L'^{Me})(NO)]$	(11)	75	120 (decomp.)	Crimson	43.2 (43.5)	5.2 (5.2)	12.4 (12.7)
$[HL^{Me}]^+[Mo(CO)_3(C_5H_5\text{-}\eta)]^-$	(19)	90	145—146	Yellow	45.3 (45.3)	4.7 (4.7)	8.1 (8.1)
$[L^{Me}_2]^{2+}[Mo(CO)_3(C_5H_5\text{-}\eta)]^-_2$	(20)	65	198—204 (decomp.)	Red-brown	45.2 (45.5)	4.5 (4.4)	8.2 (8.2)
$[HL'^{Me}]^+[Mo(CO)_3(C_5H_5\text{-}\eta)]^-$	(21)	90	112 (decomp.)	Yellow	46.9 (46.9)	5.0 (5.0)	7.8 (7.8)
$[L'^{Me}_2]^{2+}[Mo(CO)_3(C_5H_5\text{-}\eta)]^-_2$	(22)	80	176 (decomp.)	Yellow-orange	46.8 (47.0)	4.7 (4.8)	7.8 (7.8)

[a] $L^R = \colon\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}$ (R = Me, Et, $PhCH_2$, or p-tolyl), $L'^{Me} = \colon\overline{\mathrm{CN(Me)(CH_2)_3N}}\mathrm{Me}$. [b] Isomerises to the *cis*-isomer, 140—160 °C.

Generally $[Mo(CO)_5L]$ complexes, where L = a Fischer-type carbene ligand [*e.g.* C(OMe)Ph or $C(NMe_2)Me$], are labile,[8] whereas $[Mo(CO)_5L^R]$ (R = Me, Et, or $PhCH_2$), (1)—(3) (Table 1), are oxygen- and thermally-stable crystalline solids, being formed in good yield simply by refluxing a small excess of $[Mo(CO)_6]$ with L^R_2 (R = alkyl) in $C_6H_{11}Me$ (Scheme 1). The *cis*-dicarbene complexes (4) and (5) are formed similarly (Scheme 1), but using an excess of the olefin. (The ease of synthesis clearly makes this a much more versatile route than those involving dihydrogen or salt elimination [9,10] with, or without, accompanying thermolysis.[11]) Substitution of CO was found to be a far better route than replacement of norbornadiene (nbdn) or acetonitrile from $[Mo(CO)_4(nbdn)]$ or $cis\text{-}[Mo(CO)_4(MeCN)_2]$ respectively.

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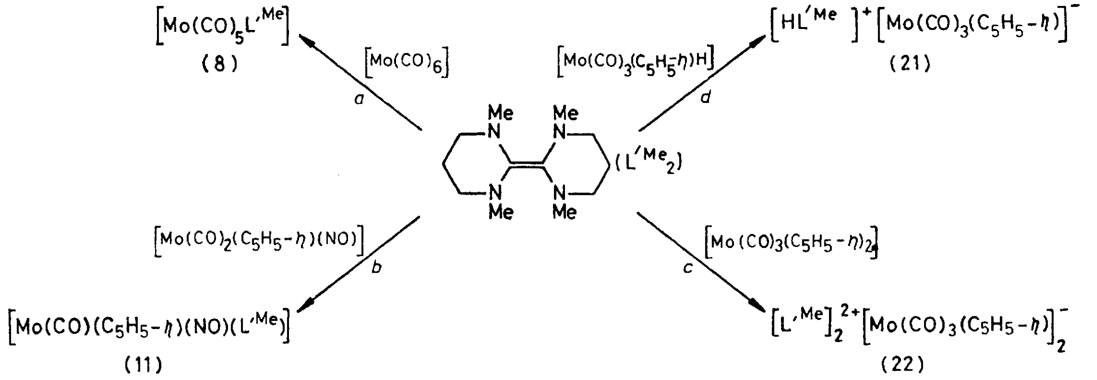
[8] E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445.

[9] K. Öfele and M. Herberhold, *Z. Naturforsch.*, 1973, **28**, 306.

[10] A. J. Hartshorn, M. F. Lappert, and K. Turner, unpublished results.

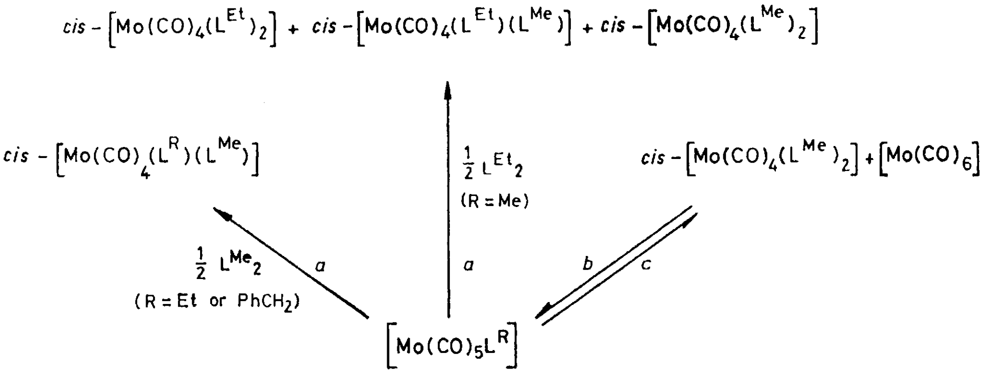
[11] C. G. Kreiter, K. Öfele, and G. W. Wieser, *Chem. Ber.*, 1976, **109**, 1749.

Use of these precursors only afforded relatively low yields of product and the reactions were not clean. Attempts to synthesise a tricarbene complex *via* direct reaction of L^{Me}_2 with $[Mo(CO)_6]$ thermally (t >150 °C), photochemically, or *via* displacement of cycloheptatriene (cht) from $[Mo(CO)_3(cht)]$, were unsuccessful, only (4) being identified. There was i.r. evidence [ν(CO)] for its formation from $[Mo(CO)_3(\text{mesitylene-}\eta)]$ in the absence of solvent at 40 °C, though a pure sample was not isolated. In solution, ready decomposition to (4) occurred; corresponding complexes $[Mo(CO)_3Q_3]$ (Q = PPh_3 [12] or MeCN [13]) are somewhat more stable, but also decompose in solution.



SCHEME 2 Molybdenum(0) complexes derived from $\{\overline{\text{CN(Me)CH}_2\text{CH}_2\text{CH}_2\text{N}}\text{Me}]_2$ (L'^{Me}_2) ^{a} Decalin, 140—160 °C. ^{b} Xylene, 120 °C. ^{c} Acetone, 25 °C. ^{d} Hexane, 25 °C

The *trans*-dicarbene complexes (6) and (7) have been prepared photochemically from the *cis*-isomers (4) and (5) in acetone, but readily and quantitatively reverted to (4) or (5) in solution. (In $CHCl_3$ at 30 °C, 100% conversion was achieved in 1 h, whereas in the solid state, heating to *ca.* 140—160 °C was required.)



SCHEME 3 Some reactions of $[Mo(CO)_5L^R]$ (R = Me, Et, or $PhCH_2$) with and without the electron-rich olefins L^R_2 (R = Me or Et) ^{a} $C_6H_{11}Me$, 85—90 °C. ^{b} $C_6H_{11}Me$, 100 °C. ^{c} Decalin, 160—180 °C.

It is interesting to note the remarkable difference in reactivity of the electron-rich olefin by changing (i) its *N*-substituents from alkyl to aryl, or (ii) its conformation. Thus, (i), L^R_2 when R = aryl has proved totally unreactive towards both $[Mo(CO)_6]$ and $[Mo(CO)_4(nbdn)]$; and (ii) the related olefins $\{\overline{\text{CN(Me)CH}_2\text{CH}_2\text{CH}_2\text{N}}\text{Me}]_2$ L'^{Me}_2 and $\{C(NMe_2)_2]_2$ (tdae) are far less reactive: L'^{Me}_2 affords the monocarbene complex (8) (Scheme 2) only under forcing conditions, but no carbene metal complexes derived from tdae have been observed.[4] Nevertheless L^{Me}_2, L'^{Me}_2, and tdae (but not L^{aryl}_2) all form Mo^0 heteroatom donor complexes.[14] The complex $[Mo(CO)_2(C_5H_5\text{-}\eta)(NO)]$ proved reactive to L^R_2 (both for R = Me and most surprisingly R = *p*-tolyl) and L'^{Me}_2 (Scheme 1) affording moderately stable crystalline monocarbene compounds (9)—(11). However, even with L^{Me}_2 only one carbonyl ligand could be displaced thermally, a further similarity to PPh_3 chemistry.[15] A Fischer-type carbene analogue has been mentioned [16] and has been used as a ' carbene transfer ' reagent.[17,18] We have not investigated this type of reaction with our complexes since L^R_2 (R = alkyl) has proved [4] a satisfactory precursor to carbene complexes

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[12] J. Lewis and R. Whyman, *J. Chem. Soc.* (*A*), 1967, 77.

[13] J. M. Graham and M. Kilner, *J. Organometallic Chem.*, 1974, **77**, 247.

[14] B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Chem. Comm.*, 1975, 683.

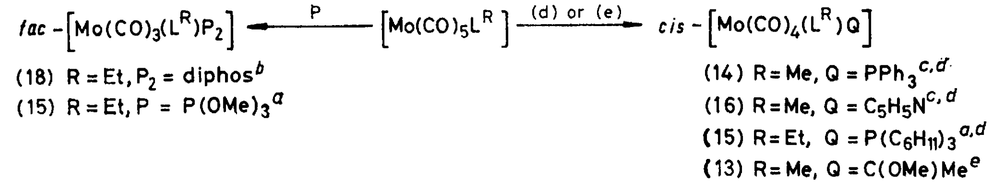
[15] H. Brunner, *J. Organometallic Chem.*, 1969, **16**, 119.

[16] H. J. Beck, Dissertation, Technische Hochschule, München, 1970.

[17] E. O. Fischer and H. J. Beck, *Angew. Chem. Internat. Edn.*, 1970, **9**, 72.

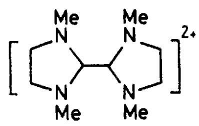
[18] E. O. Fischer, *Rev. Pure Appl. Chem.*, 1970, **24**, 407

of metals not directly available *via* the original Fischer technique[19] (*e.g.* Fe^0 or Ni^0). Reaction of $[Mo(CO)_5L^{Et}]$, (2), with L^{Me}_2 at 80 °C in $C_6H_{11}Me$ afforded mainly the mixed dicarbene complex (**12**), but under more vigorous conditions scrambling was found to occur. Likewise, the related equilibrium between $[Mo(CO)_6]$ and *cis*-$[Mo(CO)_4(L^{Me})_2]$, (4), gave a low yield of $[Mo(CO)_5L^{Me}]$, (1), although at a lower temperature the equilibrium was almost entirely in favour of the reactants, probably because of the almost total insolubility of (4) under these conditions (Scheme 3). {Similar disproportionation, or *cis–trans* isomerisation reactions, have been reported by Öfele, Herberhold, Kreiter, and Wieser[9,11,20] on some closely related carbene-Group 6 metal complexes, $[Mo(CO)_5L] \longrightarrow$ *cis*-$[Mo(CO)_4L_2] \rightleftharpoons$ *trans*-$[Mo(CO)_4L_2]$; L = $\dot{\overline{\text{C}N(Me)CH{=}CHN}}$Me.} The involvement of a free carbene or its dimer, the electron-rich olefin, in these reactions has not yet been established, but investigation of the presently unknown $[Mo(CO)_5\{C(NMe_2)_2\}]$ may resolve the problem. The Cr analogue is known[10] and its properties are almost identical to those of $[Cr(CO)_5\{\overline{\text{CN(Me)CH}_2\text{CH}_2\text{N}}\text{Me}\}]$, but the corresponding olefin $\nleq C(NMe_2)_2]_2$, tdae, is not a carbene-metal complex precursor; thus if the thermolysis experiment should afford the dicarbene species, tdae itself is most unlikely to have been involved.

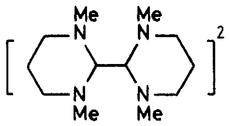


SCHEME 4 Some reactions of $[Mo(CO)_5L^R]$ [R = Me or Et]

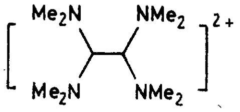
[a] *hν*, hexane, 25 °C. [b] *hν*, toluene, 25 °C. [c] $C_6H_{11}Me$, 100 °C. [d] Addition of Q. [e] (i) LiMe in Et_2O, 0 °C; (ii) $MeOSO_2F$ in Et_2O–H_2O, 0—10 °C.



(23) $[L^{Me}_2]^{2+}$



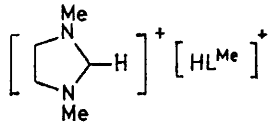
(24) $[L'^{Me}_2]^{2+}$



(25) $[tdae]^{2+}$

The strength of the Mo–$C_{carb.}$ bond, or the resistance to displacement of L^R, is reflected in the range of reactions of $[Mo(CO)_5L^R]$, (1) or (2) (Scheme 4); thus the stable mixed *cis*-dicarbene complex (**13**) containing the [:C(OMe)Me] ligand may be prepared *via* the basic Fischer synthesis upon (1) (but utilising $MeOSO_2F$ as the alkylating reagent[21]), whereas the reverse procedure, $[Mo(CO)_5\{C(OMe)Me\}] + L^{Me}_2$, causes displacement of the ethylidene moiety. Pyridine, tertiary phosphites, or mono- or bi-dentate tertiary phosphine ligands may also be introduced thermally or photochemically without displacement of L^R from the co-ordination sphere. With PPh_3 or $P(C_6H_{11})_3$, only one CO ligand is displaced, but with the stronger π-acceptor $P(OMe)_3$, ready elimination of two CO groups occurs, as is also observed with the chelating diphos ligand.

Pyridine, which readily displaces [:C(OMe)Me] from $[Cr(CO)_5\{C(OMe)Me\}]$,[22] effects CO displacement from $[Mo(CO)_5L^{Me}]$, (1). The reactions of the monocarbene-molybdenum complexes (1) and (2) therefore resemble their tertiary phosphine, rather than their Fischer-carbene analogues, although the latter can also afford mixed carbene–phosphine complexes under mild conditions.[23]



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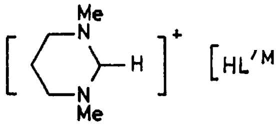

(27)

Although their availability as carbenemetal complex precursors is very different, L^{Me}_2, L'^{Me}_2, and tdae behave similarly in their reducing capacity,[24] showing the highest occupied molecular orbital at the remarkably low, first vertical-ionisation potential of *ca.* 6 eV,[25] and readily form the stable dications (23)—(25). Some reactions of tdae have been described by King,[26] but that involving $[\{Mo(CO)_3(C_5H_5\text{-}\eta)\}_2]$ {forming the anion $[Mo(CO)_3(C_5H_5\text{-}\eta)]^-$} did not yield an analytically pure product. Similar redox reactions occur with L^{Me}_2 and L'^{Me}_2, and analytically pure materials were isolated. The hydride $[Mo(CO)_3(C_5H_5\text{-}\eta)H]$ is also reduced, the counter cation being (25) or (27) [see complexes (19) and

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[19] E. O. Fischer and A. Maasböl, *Angew. Chem. Internat. Edn.*, 1964, **3**, 580.

[20] K. Öfele and M. Herberhold, *Angew. Chem. Internat. Edn.*, 1970, **9**, 739.

[21] N. Farrell, D.Phil. Thesis, University of Sussex, 1974.

[22] E. O. Fischer, B. Heckl, and H. Werner, *J. Organometallic Chem.*, 1971, **28**, 359.

[23] H. Werner and H. Rascher, *Helv. Chim. Acta*, 1968, **51**, 1765.

[24] *Cf.* N. Wiberg, *Angew. Chem. Internat. Edn.*, 1968, **7**, 766.

[25] B. Çetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Chem. Comm.*, 1971, 1370.

[26] R. B. King, *Inorg. Chem.*, 1965, **4**, 1518.

(21)]; whereas treatment of the hydride with a tertiary phosphine leads to CO substitution.[27]

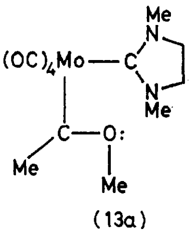
Spectroscopic Properties.—The values of ν(CO) (Table 2) are amongst the lowest observed for each class of compound.[28] This coupled with (i) the long Mo–C$_{carb.}$ bond length {*vide infra* for *cis*-[Mo(CO)$_4$(L^{Me})$_2$]} appropriate for a metal–carbon single rather than double bond, (ii) the difficulty of displacement of the carbene ligand from the co-ordination sphere of the metal, and (iii) the low stability of electron-rich oligocarbenemetal complexes, *cf.* [Mo(CO)$_3$(L^R)$_3$], is consistent with the proposition that the carbene ligand is a good σ-donor but poor π-acceptor.

TABLE 2

Selected i.r. data on electron-rich olefin derived carbene-molybdenum(0) and amidinium molybdate(0) complexes

Compound	ν(CO) (cm^{-1})	ν(CN$_2$) [a] (cm^{-1})
(1)	2 064m, 1 931vs [b]	1 496m
(2)	2 060m, 1 928vs [b]	1 485m
(3)	2 065m, 1 933vs [b]	1 482m
(4)	1 994m, 1 868s, 1 863s, 1 838s [c]	1 498m
(5)	1 993m, 1 870s, 1 862s, 1 839s [c]	1 485m
(6)	1 847 [d]	1 495m
(7)	1 844 [d]	1 480m
(8)	2 059m, 1 921vs [b]	1 508m
(13)	2 014m, 1 919s, 1 900s, 1 894s [b]	1 506m
(14)	2 008s, 1 889s, 1 885s, 1 854s [e]	1 505m
(15)	2 003s, 1 883s, 1 875s, 1 835s [e]	1 490m
(16)	1 996s, 1 899s, 1 861s, 1 818s [a]	1 505m
(17)	1 920s, 1 828s, 1 805s [a]	1 492m
(18)	1 951s, 1 862s, 1 850s [f]	1 490m
(9)	1 876,[e] 1 581 [e,g]	1 517m
(12)	1 993m, 1 873s, 1 864s, 1 839s [c]	1 497m, 1 483m
(10)	1 880 [e] 1 590 [e,g]	1 519m
(11)	1 861 [e] 1 580 [e,g]	1 527m
(19)	1 890s, 1 760s, 1 740s [a]	1 665s,[h] 1 538w [i]
(20)	1 888s, 1 765s, 1 740s [a]	1 655s,[h] 1 540w [i]
(21)	1 892s, 1 762s, 1 743s [a]	1 702s,[h] 1 520w [i]
(22)	1 890s, 1 758s, 1 742s [a]	1 675s,[h] 1 515w [i]

[a] Dilute Nujol mull. [b] Hexane solution. [c] thf solution. [d] Toluene solution. [e] CH$_2$Cl$_2$ solution. [f] C$_6$H$_{11}$Me solution. [g] ν(NO) cm^{-1}. [h] ν(CN$_2$)$_{asym}$. [i] ν(CN$_2$)$_{sym}$.



(13a)

ν(CN$_2$) has diagnostic value; in compounds containing carbene ligands a medium band at *ca.* 1 510—1 480 cm^{-1} is observed, whereas the electron-rich cations show a strong absorption in the region 1 700—1 640 cm^{-1}.

^{1}H N.m.r. spectroscopy shows (Table 3) the expected simple spectra at ambient temperatures except in the complexes [Mo(CO)(C$_5$H$_5$-η)(L^R)(NO)], (9)—(11), in which the ring methylene signals are complex, due to the chiral Mo centre.

TABLE 3

Selected ^{1}H n.m.r. spectroscopic data [a] on electron-rich olefin-derived carbenemolybdenum(0) and amidinium molybdate(0) complexes [a]

Compound	Solvent	Ring CH$_2$	N–CH$_3$	N–CH$_2$	N–CH$_2$–C*H*$_3$	Others
(1)	CDCl$_3$	6.40	6.65			
(2)	CDCl$_3$	6.45		6.15q	8.75t	
(3)	CDCl$_3$	6.67		4.92		
(4)	CDCl$_3$	6.52	6.75			
(5)	CDCl$_3$	6.50		6.18q	8.85t	
(6)	CDCl$_3$	6.47	6.60			
(7)	CDCl$_3$	6.40		5.85q	8.75t	
(8)	CDCl$_3$		6.40	6.8t		
(13)	C$_6$H$_6$	7.48	7.10			
(14)	CDCl$_3$	6.75	7.00			
(15)	C$_6$H$_6$	7.20		6.20q	8.90t	
(16)	CH$_2$Cl$_2$	6.60	6.87			
(17)	CDCl$_3$	6.40		6.2—6.6m	8.85t	
(18)	C$_6$H$_6$	7.15		6.05q	8.90t	
(9)	CDCl$_3$	6.4m	6.87			4.65 [b]
(12)	CDCl$_3$	6.52	6.78	6.20q	8.85t	
(10)	CDCl$_3$	5.90m			7.60	5.08 [b]
(11)	CDCl$_3$		6.70	6.8m		4.63 [b]
(19)	(CD$_3$)$_2$SO	6.26	7.03			1.6,[c] 5.10 [b]
(20)	(CD$_3$)$_2$SO	5.94	6.91			5.10 [b]
(21)	(CD$_3$)$_2$SO		6.53	6.35t		1.77,[c] 5.10 [b]
(22)	(CD$_3$)$_2$SO		6.67	6.25t		5.10 [b]

[a] All values quoted in τ, relative to SiMe$_4$ = 10; all resonances singlets unless otherwise stated in parentheses. [b] C$_5$*H*$_5$-η. [c] $>$C–*H*.

A variable-temperature study of (13) shows that at least over the range −90 to +30 °C in [^{2}H$_6$]acetone, there is a preferred conformer, most likely of the *syn* structure (13a), because there are only three distinct Me signals (*C*-, *O*-, and *N*-Me). Similar complexes, such as *cis*-[Cr(CO)$_4${C(OMe)Me}PR$_3$] (R = cyclohexyl or Ph) exist preferentially in this form,[29] presumably for steric reasons, though the *anti*-conformation is adopted in the parent carbenepentacarbonyl complex.[30] The *cis*-dicarbene complexes (4) or (5) exhibit temperature-dependent spectra (Table 4) similar to those reported by

TABLE 4

Variable-temperature ^{1}H n.m.r. spectroscopic data [a] on *cis*-dicarbene-Mo^0 complexes

Compound	^{1}H observed signal	θ$_c$/°C [b]	Δ*G*‡ [c,d]/ kcal mol^{-1}
cis-[Mo(CO)$_4$(L^{Me})$_2$]	N–C*H*$_3$	−70	10.1
cis-[Mo(CO)$_4$(L^{Et})$_2$]	N–C*H*$_2$CH$_3$	−76	9.5
cis-[Mo(CO)$_4$(L^{CH_2Ph})$_2$]	N–C*H*$_2$Ph	−72	9.6

[a] All samples run as saturated solutions in [^{2}H$_6$]acetone at 100 MHz, internal SiMe$_4$ lock signal. [b] Temperature calibrated *via* ethylene glycol. [c] ±0.5 kcal mol^{-1}. [d] *cf.* Procedure of R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1971, **5**, 528; J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776.

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Kreiter, Öfele, and Wieser[11] on some related Group 6 metal zerovalent carbene complexes. Our results show slightly larger values of $\Delta G^{\ddagger}$ than found for *cis*-$[\mathrm{Mo(CO)_4}\{\overline{\mathrm{CN(Me)CH{:}CHN}}\mathrm{Me}\}_2]$. This may be a consequence of the change in hybridisation of the ring carbons from sp^2 to sp^3, affording a sterically more demanding ligand (our values for the Cr and W analogues are also consistently higher[4]). We agree with the explanation of the high barrier to rotation of the cyclic carbene ligands around the Mo–$\mathrm{C_{carb.}}$ bonds as due to steric interactions between the *N*-alkyl groups when in a mutually *cis*-configuration. Furthermore, neither $[\mathrm{Mo(CO)_5L^{Me}}]$, (1), nor *trans*-$[\mathrm{Mo(CO)_4(L^{Et})_2}]$, (7), show a similar temperature dependence down to at least −85 °C. The absence of different N–CH_3 resonances for the $\mathrm{L^{Me}}$ fragment in *cis*-$[\mathrm{Mo(CO)_4\{C(OMe)Me\}L^{Me}}]$, (13), also suggests only one form; the barrier to Mo–C rotation of Mo–$\mathrm{L^{Me}}$ is expected to be lower when the *cis*-ligand, [C(OMe)Me], is in the *syn*-configuration.

TABLE 5

Selected ^{13}C n.m.r. spectroscopic data on electron-rich olefin-derived carbenemolybdenum(0) and amidinium molybdate(0) complexes[a]

Compound	Solvent	$\mathrm{C_{carb.}}$	Mutually *cis*-CO	Mutually *trans*-CO	Ring CH_2	N–CH_2–	N–CH_3
(1)	C_6D_6	215.1	212.5	207.4	51.2		38.8
(2)	C_6D_6	213.3	212.5	207.1	47.1	46.5	
(3)	C_6D_6	216.6	211.8	206.8	47.9	56.2	
(4)	$CDCl_3$	222.9	219.4	211.4	51.7		38.8
(5)	CD_2Cl_2	220.2	219.7	211.3	47.8	46.3	
(6)	CD_2Cl_2	225.3	217.5[b]		52.0		39.7
(7)	CD_2Cl_2	223.7	218.1[b]		48.0	46.8	
(8)	C_6D_6	213.1	213.7	207.5		49.9	46.6
(13)	C_6D_6	219.5 (350.5[c])	(222.7, 218.5)	211.7	51.2		38.6
(14)	CD_2Cl_2	221.4[d]	(218.3,[e] 217.5[f])	211.8[g]	51.9		39.6
(18)	$CDCl_3$	221.1[h]	(219.4,[i] 218.2[j])		47.6	46.8	
(9)[k]	$CDCl_3$	223.0	250.9		51.7		38.4
(10)[l]	$CDCl_3$	229.1	248.5		54.6		21.1[m]
(19)	$(CD_3)_2SO$	185.4[n]	235.3[o]		50.4		34.3
(20)	$(CD_3)_2SO$	148.8[n]	235.4[o]		52.2		34.4

[a] Values quoted in p.p.m. relative to $\mathrm{SiMe_4} = 0$. [b] Four equivalent CO's. [c] δ-*C*(OMe)Me. [d] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 9.1$ Hz. [e] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) < 1.5$ Hz. [f] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 16.8$ Hz. [g] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 7.6$ Hz. [h] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 13.0$ Hz. [i] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 12.2$ Hz. [j] $^2J(^{13}\mathrm{C}-^{31}\mathrm{P}) = 17.5$ Hz. [k] δ-C(C_5H_5) = 92.8. [l] δ-C(C_5H_5) = 93.4. [m] Aryl-CH_3. [n] δ-*C*(carbonium ion). [o] Three equivalent CO's.

^{13}C N.m.r. spectral data for several of the new complexes are given in Table 5. Although the chemical shift of $\mathrm{C_{carb.}}$ in these compounds was comparable to that of the carbonyl carbon atoms, positive identification of the $\mathrm{C_{carb.}}$ signal proved possible by two observations: (i) the signal intensity in the ^{1}H decoupled mode was enhanced to that of a comparable non-protonated carbon (CO *trans* to $\mathrm{C_{carb.}}$), and (ii) ^{1}H off-resonance studies caused some broadening and reduction in peak height relative to CO *trans* to $\mathrm{C_{carb.}}$. A third, possibly related, observation was that concerning the intensity of the CO *cis* to $\mathrm{C_{carb.}}$ signal, which decreased (without broadening) during the ^{1}H off-resonance studies. Therefore there may be a small degree of relaxation of $\mathrm{C_{carb.}}$ by a through-bond interaction with both *N*-alkyl and ring $\mathrm{CH_2}$ protons even though the distance dependence of $^{13}\mathrm{C}-^{1}\mathrm{H}$ dipole–dipole relaxation is *ca.* $1/r^6$ (r = internuclear distance)[31] and has been discounted in T_1 measurements of Fischer-type carbenechromium(0) complexes.[32]

It has been argued that the H atoms of the carbene *N*-alkyl substituent may interact within the van der Waals radius of the CO groups *cis* to the carbene ligand (as demonstrated when the *cis*-ligand is another carbene by ^{1}H n.m.r. spectroscopy[11]) and it seems possible that it is this same interaction which may affect the relaxation time and increase the intensity of the *cis*-CO ligands. The actual values of chemical shift, for carbene carbons, are considerably upfield and in the range 230—210 p.p.m., but at lower field than that found for $\mathrm{Pt^{II}}$ (ref. 33) or $\mathrm{Rh^{I}}$ (ref. 4) electron-rich olefin-derived carbene-metal complexes (in the region 215—175 p.p.m.). The high field shift relative to Fischer-type carbene carbons[34] is due mainly to the presence of two *N*-heteroatoms directly bonded to $\mathrm{C_{carb.}}$, thereby increasing the local electron density and causing, at least to a significant extent, the observed upfield shifts.[33,35,36] However, the ^{13}C n.m.r. spectra of the related compound *cis*-$[\mathrm{Mo(CO)_4}\{\overline{\mathrm{CN(Me)CH{:}CHN}}\mathrm{Me}\}_2]$ shows[11] $\mathrm{C_{carb.}}$ to be at 196 p.p.m., *ca.* 30 p.p.m. to high field of (4), and this relatively large shift in δ($\mathrm{C_{carb.}}$) for such apparently similar ligands provides a measure of the extra stabilisation afforded by the aromatic nature of the ring.

Two general trends are noticeable in the values of $\mathrm{C_{carb.}}$: (i) $\mathrm{L^{Et}} < \mathrm{L^{Me}}$, and (ii) mono- < di-carbene complexes. The latter may be explained by the greater −*I* effect of the $[\mathrm{Mo(CO)_5}]$ compared to a $[\mathrm{Mo(CO)_4L^R}]$

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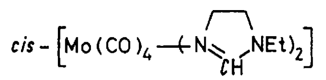
fragment, but that for (i) is not clear, unless L^{Et} is a slightly weaker donor than L^{Me}, in which case a higher electron density at $C_{carb.}(L^{Et})$ (and a shift to high field of $C_{carb.}$) *would* be expected. This is consistent with i.r. spectral data: $\nu(CN_2)$ in L^{Et} complexes is consistently *ca.* 20 cm^{-1} lower, indicating a slightly smaller interaction of the nitrogen lone pair with the vacant p_z orbital of the carbene carbon. This in turn may be a result of a lowering of the planarity of the ring (and hence the overlap integral) and could be due to a greater steric requirement of an Et compared to a Me group.

The values of $\delta(CO)$ in $[Mo(CO)_5L^R]$, (1)—(3), are similar to those reported for $[Mo(CO)_5PPh_3]$ [37] and in *cis*-$[Mo(CO)_4(L^R)_2]$, (4) and (5), to those for $[Mo(CO)_4(diphos)]$; [37] in both mono- and di-carbene complexes the small low field shifts observed (*ca.* 1 p.p.m.) are consistent with the greater σ-donor-π-acceptor ratio of the carbene ligand(s). Similarly $\delta(CO)$ in *trans*-$[Mo(CO)_4(L^R)_2]$, (6) and (7), are 7—8 p.p.m. downfield of the complex *trans*-$[Mo(CO)_4\{P(OMe)_3\}_2]$ [37] which contains the relatively good π-acceptor phosphite ligand. Additionally it is noticeable that in (18), which contains only three CO ligands, the values of $\delta(C_{carb.})$ and $\delta(CO)$ are little different from those in the dicarbenetetracarbonyl complexes (4) and (5).

In the compounds containing P-ligands there seems nothing unusual in the values of $^2J(^{13}C-^{31}P)$, although *trans*-couplings are greater than *cis* (see also refs. 34 and 38).

The ^{13}C n.m.r. spectrum of *cis*-$[Mo(CO)_4\{C(OMe)Me\}L^{Me}]$, (13), is the first reported of a Mo^0 complex containing a Fischer-type carbene ligand. Direct comparison with $C_{carb.}$ of L^{Me} shows a downfield shift of *ca.* 130 p.p.m. and the chemical shift value of 350.5 p.p.m. is probably very close (± 2 p.p.m.) to that which would be observed in the parent compound $[Mo(CO)_5\{C(OMe)Me\}]$. {In the Cr and W analogues of (13) there is very little difference in the values of $\delta[C(OMe)Me]$ from the pentacarbonyl complexes.} [4]


(28)

In the electron-rich cations such as $[HL^{Me}]^+$, (26), or $[L^{Me}{}_2]^{2+}$, (23), there is a large (50—60 p.p.m.) upfield shift in the value of $C_{carbonium\ ion}$, compared to $C_{carb.}$, consistent with the noted increase in the value of $\nu(CN_2)$ (*ca.* 150 cm^{-1}), indicating more substantial CN double-bond character and a corresponding increase in electron density at $C_{carbonium\ ion}$; and additionally supports the suggestion that the large low-field shift of $C_{carb.}$ arises from a second-order paramagnetic term on the metal atom.[34] It is interesting to note that *C* in the 2-imidazoline complex (28) [4] is at lower field than $C_{carbonium\ ion}$ in $[L^{Me}{}_2]^{2+}$, but similar to that in $[HL^{Me}]^+$, suggestive of the positive charge being extensively localised on the *N*-atoms of these carbonium ions which may more correctly be considered as amidinium cations.

Crystal and Molecular Structure of cis-$[Mo(CO)_4(L^{Me})_2]$, (4).—The bonding environment in monocarbene–transition-metal complexes is now well established,[3] although this is the first study either of a carbene complex of Mo^0 or of a dicarbenemetal species. {Furthermore, the only previous *X*-ray report of an oligocarbene–metal complex was in a recent preliminary account of *trans*-$[RuCl_2(L^{Et})_4]$.[39]} The relative disposition of the two carbene ligands in (4) is of particular interest. It has been suggested that in a *trans*-dicarbenemetal complex the $C_{carb.}-M-C_{carb.}$ moiety may be regarded as pseudo-allenic with an expected preference therefore for a mutually perpendicular arrangement of the two carbene ligands; [40] this analysis clearly ignored steric factors which, however, might well favour the same structure.

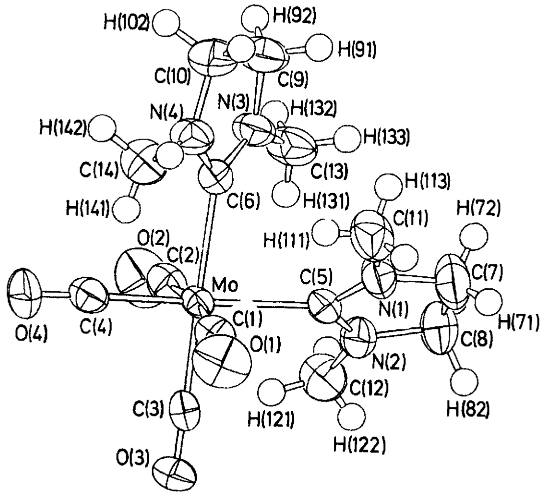


Diagram of the molecule *cis*-$[Mo(CO)_4(L^{Me})_2]$ showing the atom numbering system used, and anisotropic thermal motion (ellipsoids are scaled to enclose 50% probability)

The excellent agreement of chemically equivalent bond lengths in this present study of a *cis*-dicarbene complex allows precise comparison to be made of the two independent carbene ligands and shows that the Mo–CO (mutually *trans*) bond lengths are significantly longer by 0.048(2) Å than the Mo–CO (*trans* to carbene) distances. Important bond lengths and angles are in Table 6 and the structure is illustrated in the Figure.

The mutually-*trans* Mo–CO values [2.024(3) and 2.032(3) Å] are within the range [1.95(4)—2.05(2) Å] already reported,[41] as are the Mo–CO (*trans* to carbene) values [1.979(3) and 1.981(3) Å], but here the two types differ significantly, as indeed they do in *cis*-bis(phosphine)

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TABLE 6

Molecular geometry

(*a*) Bond lengths (Å)

		Means		
Mo–C(1)	2.032(3)	2.028(2)	Mo–C(2)	2.024(3)
Mo–C(3)	1.979(3)	1.980(2)	Mo–C(4)	1.981(3)
Mo–C(5)	2.293(3)	2.293(3)	Mo–C(6)	2.293(3)
C(1)–O(1)	1.144(4)	1.145(3)	C(2)–O(2)	1.146(4)
C(3)–O(3)	1.156(3)	1.157(2)	C(4)–O(4)	1.157(3)
C(5)–N(1)	1.341(3)	1.341(2)	C(6)–N(3)	1.336(3)
C(5)–N(2)	1.342(3)		C(6)–N(4)	1.344(3)
N(1)–C(7)	1.455(4)	1.459(2)	N(3)–C(9)	1.466(4)
N(2)–C(8)	1.457(4)		N(4)–C(10)	1.459(4)
N(1)–C(11)	1.437(5)	1.440(3)	N(3)–C(13)	1.442(5)
N(2)–C(12)	1.438(4)		N(4)–C(14)	1.442(4)
C(7)–C(8)	1.490(6)	1.490(4)	C(9)–C(10)	1.490(5)
C(7)–H(71)	1.02(5)	0.99(2)	C(9)–H(91)	1.05(4)
C(7)–H(72)	0.90(4)		C(9)–H(92)	0.91(4)
C(8)–H(81)	0.96(4)		C(10)–H(101)	0.96(4)
C(8)–H(82)	1.06(5)		C(10)–H(102)	1.04(5)
C(11)–H(111)	0.89(4)	0.94(2)	C(13)–H(131)	0.91(3)
C(11)–H(112)	0.94(5)		C(13)–H(132)	0.91(5)
C(11)–H(113)	0.93(4)		C(13)–H(133)	1.02(4)
C(12)–H(121)	0.98(4)		C(14)–H(141)	0.91(4)
C(12)–H(122)	0.90(5)		C(14)–H(142)	0.96(5)
C(12)–H(123)	0.97(5)		C(14)–H(143)	0.91(5)

(*b*) Bond angles (°)

C(1)–Mo–C(2)	169.82(11)	169.82(11)		
C(1)–Mo–C(3)	82.98(11)	83.20(8)	C(2)–Mo–C(4)	83.41(13)
C(1)–Mo–C(4)	90.34(12)	89.56(8)	C(2)–Mo–C(3)	88.77(12)
C(1)–Mo–C(5)	90.31(11)	91.05(8)	C(2)–Mo–C(6)	91.78(11)
C(1)–Mo–C(6)	96.56(11)	96.35(8)	C(2)–Mo–C(5)	96.14(11)
C(3)–Mo–C(6)	178.98(10)	178.74(7)	C(4)–Mo–C(5)	178.50(10)
C(3)–Mo–C(5)	93.44(10)	93.19(7)	C(4)–Mo–C(6)	92.94(10)
C(3)–Mo–C(4)	87.99(11)	87.99(11)		
C(5)–Mo–C(6)	85.64(10)	85.64(10)		
Mo–C(1)–O(1)	172.14(28)	172.07(20)	Mo–C(2)–O(2)	172.00(27)
Mo–C(3)–O(3)	176.50(23)	176.14(18)	Mo–C(4)–O(4)	175.77(26)
Mo–C(5)–N(1)	127.11(20)	126.77(10)	Mo–C(6)–N(3)	126.39(19)
Mo–C(5)–N(2)	126.42(19)		Mo–C(6)–N(4)	127.05(18)
C(5)–N(1)–C(7)	113.57(29)	113.58(14)	C(6)–N(3)–C(9)	113.57(26)
C(5)–N(2)–C(8)	113.61(26)		C(6)–N(4)–C(10)	113.55(25)
C(5)–N(1)–C(11)	128.25(28)	127.61(13)	C(6)–N(3)–C(13)	127.89(26)
C(5)–N(2)–C(12)	127.27(25)		C(6)–N(4)–C(14)	127.03(25)
C(7)–N(1)–C(11)	117.97(31)	118.64(15)	C(9)–N(3)–C(13)	118.31(27)
C(8)–N(2)–C(12)	119.12(29)		C(10)–N(4)–C(14)	119.17(28)
N(1)–C(7)–C(8)	103.06(29)	102.91(15)	N(3)–C(9)–C(10)	102.59(28)
N(2)–C(8)–C(7)	102.99(30)		N(4)–C(10)–C(9)	103.00(28)
N(1)–C(5)–N(2)	106.45(23)	106.49(16)	N(3)–C(6)–N(4)	106.52(22)
N(1)–C(7)–H(71)	109(3)	109 (1)	N(3)–C(9)–H(91)	108(2)
N(1)–C(7)–H(72)	112(3)		N(3)–C(9)–H(92)	111(3)
N(2)–C(8)–H(81)	109(2)		N(4)–C(10)–H(101)	105(2)
N(2)–C(8)–H(82)	108(2)		N(4)–C(10)–H(102)	112(2)
C(8)–C(7)–H(71)	117(3)	114 (1)	C(10)–C(9)–H(91)	112(2)
C(8)–C(7)–H(72)	116(3)		(C10)–C(9)–H(91)	120(3)
C(7)–C(8)–H(81)	110(2)		C(9)–C(10)–H(101)	111(2)
C(7)–C(8)–H(82)	115(3)		C(9)–C(10)–H(102)	112(2)
N(1)–C(11)–H(111)	116(2)	111 (1)	N(3)–C(13)–H(131)	115(2)
N(1)–C(11)–H(112)	108(3)		N(3)–C(13)–H(132)	109(3)
N(1)–C(11)–H(113)	109(2)		N(3)–C(13)–H(133)	107(2)
N(2)–C(12)–H(121)	116(2)		N(4)–C(14)–H(141)	115(3)
N(2)–C(12)–H(122)	110(3)		N(4)–C(14)–H(142)	109(3)
N(2)–C(12)–H(123)	112(2)		N(4)–C(14)–H(143)	108(3)
H(71)–C(7)–H(72)	99(4)	107 (1)	H(91)–C(9)–H(92)	103(3)
H(81)–C(8)–H(82)	111(3)		H(101)–C(10)–H(102)	113(3)
H(111)–C(11)–H(112)	111(4)	108 (1)	H(131)–C(13)–H(132)	108(3)
H(111)–C(11)–H(113)	106(3)		H(131)–C(13)–H(133)	107(3)
H(112)–C(11)–H(113)	107(4)		H(132)–C(13)–H(133)	111(3)
H(121)–C(12)–H(122)	111(3)		H(141)–C(14)–H(142)	108(4)
H(121)–C(12)–H(123)	109(4)		H(141)–C(14)–H(143)	112(4)
H(122)–C(12)–H(123)	97(4)		H(142)–C(14)–H(143)	104(4)

TABLE 6 (*Continued*)

(*c*) Intermolecular contacts (Å) within the sum of the contact radii: 2.4 for Mo. 1.7 for O, N, and C, and 1.2 Å for H

$O(1) \cdots O(4^{I})$	3.382(4)	$O(3) \cdots H(92^{II})$	2.67(4)
$O(3) \cdots C(9^{II})$	3.300(5)	$O(3) \cdots H(92^{V})$	2.88(4)
$O(4) \cdots C(14^{I})$	3.314(5)	$O(3) \cdots H(112^{IV})$	2.81(5)
$O(1) \cdots H(81^{III})$	2.80(4)	$O(3) \cdots H(132^{V})$	2.72(5)
$O(1) \cdots H(123^{III})$	2.88(5)	$O(4) \cdots H(71^{VI})$	2.64(5)
$O(2) \cdots H(91^{V})$	2.84(4)	$O(4) \cdots H(141^{I})$	2.59(4)

Roman numeral superscripts refer to the following co-ordinate transformations relative to the reference molecule at x, y, z

I $-x, -y, -z$	II $x, \frac{1}{2} - y, \frac{1}{2} + z$	III $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$
IV $-x, y - \frac{1}{2}, \frac{1}{2} - z$	V $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	VI $x, \frac{1}{2} - y, z - \frac{1}{2}$

complexes; for both classes this is associated with the poor π-acceptor character of the carbene or phosphine ligands, in contrast to CO.

The Mo–$C_{carb.}$ lengths are identical [2.293(3) Å] and are comparable with the Mo–CH_3 values [2.27(1)—2.31(1) Å] in $Li_4Mo_2(CH_3)_8\cdot4$ thf [42] and with the Mo–C_6F_5 distance [2.44(9) Å] in $[Mo(CO)_2(C_6F_5)(C_7H_7\text{-}\eta)]$; [43] they are appreciably longer than the distance [2.03(3) Å] in the Mo^{II} carbene chelate $[Mo(CO)_2(C_5H_5\text{-}\eta)\{NN(Me)C(CO_2Et)C(OH)\}]^+$, [44,45] but this may largely be attributed to the difference in Mo^0 and Mo^{II} radii. There is thus little evidence for Mo–$C_{carb.}$ double-bond character.

The geometry of the carbene ligand is similar to that already determined in both *cis*-(23) and *trans*-$[PtCl_2(L^{Ph})PEt_3]$ (24) [46] and in *trans*-$[Rh\{NC(CF_3)_2\}L^{Me}(PPh_3)_2]$ (25) [47] (see Table 7). These d^8 compounds are square planar and the plane of the carbene ligand is approximately perpendicular to the co-ordination plane of the metal. In (4), where the metal is octahedrally co-ordinated, the dihedral angles between the carbene ligand planes and the co-ordination planes in which they are involved are *ca.* 45°, *i.e.* in all examples the sterically preferred conformer is found.

TABLE 7

Mean bond lengths (Å) in the carbene ligand

$\dot{:}CN(R)\cdot[CH_2]_2\cdot NR$ (L^R) (R = Me or Ph)

	a (4)	*b* (25)	*c* (23)	*d* (24)
$C_{carb.}$–N	1.341 (2)	1.355 (18)	1.327 (11)	1.348 (18)
N–CH_2	1.459 (2)	1.494 (25)	1.482 (14)	1.49(2)
CH_2–CH_2	1.490 (4)	1.498 (35)	1.47	1.49
N–R	1.440 (3) (sp^3)	1.435 (20) (sp^3)	1.395 (13) (sp^2)	1.403 (83) (sp^2)

[a] This work, *cis*-$[Mo(CO)_4(L^{Me})_2]$. [b] From ref. 47, *trans*-$[Rh\{N\dot{:}C(CF_3)_2\}L^{Me}(PPh_3)_2]$. [c] From ref. 47, *cis*-$[PtCl_2L^{Ph}(PEt_3)]$. [d] Ref. 46, *trans*-$[PtCl_2L^{Ph}(PEt_3)]$.

EXPERIMENTAL

General Procedures.—All reactions were carried out under an atmosphere of dry nitrogen or argon. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use and chlorinated solvents were distilled from phosphorus pentaoxide. Analyses were carried out in our microanalytical laboratory by Mr. and Mrs. A. G. Olney and ^{13}C n.m.r. spectra were obtained by Mr. T. M. Siverns on a JEOL PFT-100 Fourier-transform spectrometer. I.r. spectra (4 000—250 cm^{-1}) were examined as Nujol mulls using a Perkin-Elmer 457 grating spectrophotometer and ^1H n.m.r. spectra were recorded on Varian Associates HA100, A60, or T60 spectrometers. M.p.s were determined in evacuated sealed tubes and are uncorrected. The electron-rich olefins were prepared by literature methods [48] from the relevant diamine. Other starting materials were prepared by standard literature procedures [49] and $[Mo(CO)_6]$ was used as purchased from B.D.H. Ltd. Only typical experiments are described; further data are in refs. 4 and 50.

$[Mo(CO)_5L^R]$ (R = Me, Et, *or* $PhCH_2$).—Hexacarbonylmolybdenum(0) (2.64 g, 10 mmol) and bi(1,3-dimethylimidazolidin-2-ylidene) (0.98 g, 5 mmol) in methylcyclohexane (MeC_6H_{11}) (25 cm^3) were heated under reflux for 2 h. Carbon monoxide was evolved and a small quantity of yellow precipitate formed. The solution was filtered whilst hot and the solvent removed under reduced pressure at 20 °C. The residue was extracted with cold ether (30 cm^3) and filtered. The volume was reduced to 5—10 cm^3. Addition of hexane (20 cm^3) and cooling (−30 °C, 48 h) afforded white crystals of *pentacarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*molybdenum*(0) (2.34 g, 70%).

$[Mo(CO)_5L'^{Me}]$.—Hexacarbonylmolybdenum(0) (0.53 g, 2.0 mmol) and bi(1,3-dimethylperhydropyrimidin-2-ylidene) (0.45 g, 2.0 mmol) in decalin (10 cm^3) were heated to 150 °C (20 min). Carbon monoxide was evolved and the solution became yellow and oily. The solvent was removed by distillation under reduced pressure and the residue extracted with ether (2 × 5 cm^3); the extract was cooled to −20 °C and filtered. The volume was reduced to *ca.* 5 cm^3, hexane (10 cm^3) was added, and cooling (−25 °C, 24 h) afforded a pale yellow solid which was twice recrystallised (Et_2O–n-C_6H_{14} at −20 °C) to give cream crystals of *pentacarbonyl*(1,3-*dimethylperhydropyrimidin*-2-*ylidene*)*molybdenum*(0) (0.10 g, 15%).

cis-$[Mo(CO)_4(L^R)_2]$ (R = Me *or* Et).—Hexacarbonylmolybdenum(0) (2.64 g, 10.0 mmol) and a small excess of bi(1,3-dimethylimidazolidin-2-ylidene) (2.94 g, 15.0 mmol) in $C_6H_{11}Me$ (30 cm^3) were heated at reflux for 5 h. Ana-

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lytically pure yellow microcrystals of cis-*tetracarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*molybdenum*(0) (4.04 g, 100%) were precipitated and these were filtered off, washed with ether (3 × 10 cm^3), and dried *in vacuo*. [When decalin was used as solvent the reaction could be carried out at a higher temperature (120—140 °C); this resulted in a quicker (*ca*. 30 min) reaction time, but it proved difficult to remove all traces of decalin from the product. The reaction can be carried out at 160—200 °C in the absence of solvent, using a small excess of the olefin.]

trans-$[Mo(CO)_4(L^R)_2]$ (R = Me *or* Et).—*cis*-Tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)molybdenum(0) (0.404 g, 1.0 mmol) was dissolved at 40 °C in the minimum quantity of acetone (*ca*. 5 cm^3) and this solution (in Pyrex) was irradiated at 25 °C using a Hanovia lamp. trans-*Tetracarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*molybdenum*(0) (0.24 g, 60%) slowly precipitated as deep orange microcystals; these were periodically filtered off, the solution concentrated, and the irradiation continued until precipitation ceased.

TABLE 8

Atomic positional (fractional) and thermal parameters *

	x	y	z	β/Å^2
Mo	0.267 84(3)	0.149 03(1)	0.216 37(1)	
O(1)	−0.109 6(3)	0.128 0(2)	0.153 6(2)	
O(2)	0.645 3(3)	0.111 6(2)	0.287 7(2)	
O(3)	0.309 2(3)	−0.009 5(1)	0.367 4(2)	
O(4)	0.214 3(3)	−0.010 6(1)	0.063 3(2)	
N(1)	0.221 3(3)	0.343 0(1)	0.309 3(2)	
N(2)	0.445 5(3)	0.273 2(2)	0.428 2(2)	
N(3)	0.332 7(3)	0.337 9(1)	0.126 0(2)	
N(4)	0.101 8(3)	0.275 0(2)	0.005 4(2)	
C(1)	0.023 0(4)	0.141 5(2)	0.172 1(2)	
C(2)	0.512 0(4)	0.131 9(2)	0.264 0(2)	
C(3)	0.298 1(3)	0.050 5(2)	0.314 4(2)	
C(4)	0.228 2(4)	0.049 8(2)	0.116 7(2)	
C(5)	0.315 1(3)	0.266 5(2)	0.329 3(2)	
C(6)	0.231 4(3)	0.265 0(2)	0.104 2(2)	
C(7)	0.295 3(7)	0.409 1(3)	0.394 4(4)	
C(8)	0.445 3(6)	0.358 5(3)	0.478 8(3)	
C(9)	0.265 9(6)	0.405 7(3)	0.041 6(3)	
C(10)	0.115 4(5)	0.357 1(3)	−0.044 8(3)	
C(11)	0.069 0(6)	0.369 3(3)	0.214 1(4)	
C(12)	0.579 8(5)	0.207 4(3)	0.485 6(3)	
C(13)	0.487 2(6)	0.359 9(3)	0.222 8(3)	
C(14)	−0.034 4(5)	0.210 5(3)	−0.055 0(3)	
H(71)	0.206 (6)	0.428 (3)	0.408 (4)	9.5(14)
H(72)	0.316 (6)	0.465 (3)	0.377 (3)	8.6(13)
H(81)	0.546 (5)	0.393 (3)	0.501 (3)	7.5(11)
H(82)	0.439 (6)	0.340 (3)	0.543 (4)	10.3(15)
H(91)	0.234 (5)	0.466 (3)	0.065 (3)	7.8(11)
H(92)	0.348 (6)	0.426 (3)	0.033 (3)	7.9(12)
H(101)	0.014 (4)	0.392 (2)	−0.068 (3)	5.6(8)
H(102)	0.131 (5)	0.339 (2)	−0.104 (3)	7.4(11)
H(111)	0.029 (5)	0.328 (3)	0.163 (3)	5.7(9)
H(112)	−0.013 (6)	0.384 (3)	0.228 (4)	10.1(15)
H(113)	0.089 (5)	0.423 (3)	0.189 (3)	6.8(11)
H(121)	0.562 (5)	0.146 (2)	0.454 (3)	6.5(10)
H(122)	0.605 (6)	0.203 (3)	0.551 (4)	8.2(12)
H(123)	0.688 (6)	0.231 (3)	0.502 (4)	9.5(13)
H(131)	0.521 (4)	0.316 (2)	0.273 (2)	4.4(7)
H(132)	0.571 (6)	0.368 (3)	0.211 (4)	8.2(13)
H(133)	0.466 (4)	0.419 (3)	0.249 (3)	6.3(9)
H(141)	−0.027 (5)	0.156 (3)	−0.023 (3)	7.3(11)
H(142)	−0.041 (6)	0.197 (3)	−0.118 (4)	8.9(13)
H(143)	−0.133 (6)	0.241 (3)	−0.077 (4)	9.3(13)

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

cis-$[Mo(CO)_4(L^{Me})(PPh_3)]$.—Pentacarbonyl-1,3-dimethylimidazolidin-2-ylidenemolybdenum(0) (0.33 g, 1.0 mmol) and triphenylphosphine (0.26 g, 1.0 mmol) in MeC_6H_{11} (10 cm^3) were refluxed (1 h) after which time pale yellow microcrystals of cis-*tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*triphenylphosphinemolybdenum*(0) (0.39 g, 70%) precipitated; these were filtered off, washed with warm hexane (2 × 10 cm^3), and dried *in vacuo*.

cis-$[Mo(CO)_4(L^{Me})(C_5H_5N)]$.— Pentacarbonyl(1,3-dimethylimidazolidin-2-ylidene)molybdenum(0) (0.33 g, 1.0 mmol) and pyridine (0.40 g, 5 mmol) were refluxed together in $C_6H_{11}Me$ (10 cm^3) to afford a deep yellow microcrystalline precipitate of cis-*tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*pyridinemolybdenum*(0) (0.23 g, 60%) which was filtered off, washed with cold ether (4 × 5 cm^3), and dried *in vacuo*. The compound slowly turned green upon exposure to air.

cis-$[Mo(CO)_4(L^{Et})\{P(C_6H_{11})_3\}]$.— Pentacarbonyl(1,3-diethylimidazolidin-2-ylidene)molybdenum(0) (0.72 g, 2.0 mmol) and tricyclohexylphosphine (0.84 g, 3.0 mmol) in hexane (20 cm^3) were irradiated (8 h) using a Hanovia lamp. The cream solid was recrystallised (CH_2Cl_2–n-C_6H_{14}) to afford cream crystals of cis-*tetracarbonyl*(*tricyclohexylphosphine*)(1,3-*diethylimidazolidin*-2-*ylidene*)*molybdenum*(0) (1.0 g, 80%).

cis-$[Mo(CO)_4\{C(OMe)Me\}L^{Me}]$.—To pentacarbonyl(1,3-dimethylimidazolidin-2-ylidene)molybdenum (0.66 g, 2.0 mmol) in ether (10 cm^3), LiMe (3.2 cm^3, 0.7 mol dm^{-3}) in ether was added dropwise to form a yellow-orange precipitate. Methyl fluorosulphonate (0.24 g, 2.1 mmol) was added and the mixture stirred (15 °C, 4 h). Degassed H_2O (10 cm^3) was added and the stirring was continued (3 h). The ether layer was separated, dried ($MgSO_4$), and filtered. Ether was removed under reduced pressure; the residue was dissolved in n-C_6H_{14}–Et_2O (1 : 1, 10 cm^3) and filtered. Cooling (−25 °C, 7 days) afforded scarlet crystals of cis-*tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(1′-*methoxyethylidene*)*molybdenum*(0) (0.36 g, 50%).

cis-$[Mo(CO)_4(L^{Et})(L^{Me})]$.—To pentacarbonyl(1,3-diethylimidazolidin-2-ylidene)molybdenum(0) (0.14 g, 0.39 mmol) in $C_6H_{11}Me$ (10 cm^3) bi(1,3-dimethylimidazolidin-2-ylidene) (0.04 g, 0.20 mmol) was added and the mixture was heated (80 °C, 1 h). A yellow precipitate formed which was filtered off, washed with ether (3 × 5 cm^3), and recrystallised (PhMe–n-C_6H_{14} at −25 °C) to afford pale yellow crystals of cis-*tetracarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)-1,3-*dimethylimidazolidin*-2-*ylidenemolybdenum*(0) (0.12 g, 70%).

fac-$[Mo(CO)_3(L^{Et})\{P(OMe)_3\}_2]$.— Pentacarbonyl(1,3-diethylimidazolidin-2-ylidene)molybdenum(0) (0.72 g, 2.0 mmol) and trimethyl phosphite (1.24 g, 10 mmol) were irradiated using a Hanovia lamp in hexane solution (10 cm^3) for 8 h. The cream microcrystalline solid which formed was recrystallised (PhMe–n-C_6H_{14}) to afford white crystals of fac-*tricarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)-*bis*(*trimethyl phosphite*)*molybdenum*(0) (1.0 g, 90%).

$[Mo(CO)(C_5H_5\text{-}\eta)(L^R)(NO)]$.—(i) (R = Me). To dicarbonyl(η-cyclopentadienyl)nitrosylmolybdenum(0) (0.25 g, 1.0 mmol) in toluene (10 cm^3) bi(1,3-dimethylimidazolidin-2-ylidene) (0.14 g, 0.7 mmol) was added, and the mixture was heated (100 °C, 30 min); the initially pale orange solution became deep red. This solution was cooled (−25 °C, 24 h) to deposit dark red crystals of *carbonyl*(η-*cyclopentadienyl*)(1,3-*dimethylimidazolidin*-2-*ylidene*)*nitrosylmolybdenum*(0) (0.29 g, 90%).

(ii) (R = *p*-tolyl). To dicarbonyl(η-cyclopentadienyl)nitrosylmolybdenum(0) (0.25 g, 1.0 mmol) in xylene (15 cm^3) bi(1,3-di-*p*-tolylimidazolidin-2-ylidene) (0.25 g, 0.5 mmol) was added and the mixture was refluxed (4—6 h). The solution was cooled to 30 °C and filtered. Addition of ether (10 cm^3) and cooling (−25 °C, 48 h) afforded small red crystals of *carbonyl(η-cyclopentadienyl)(1,3-di-*p*-tolylimidazolidin-2-ylidene)nitrosylmolybdenum*(0) (0.37 g, 80%).

[Mo(CO)(C$_5$H$_5$-η)(L$'^{Me}$)(NO)].—To dicarbonyl(η-cyclopentadienyl)nitrosylmolybdenum(0) (0.25 g, 1.0 mmol) in xylene (10 cm^3) bi(1,3-dimethylperhydropyrimidin-2-ylidene) (0.22 g, 1.0 mmol) was added and the mixture was heated (120 °C, 3 h). The solution was allowed to cool to 0 °C and then filtered. Addition of hexane (10 cm^3) and cooling (−25 °C, 72 h) afforded crimson-brown microcrystals of *carbonyl(η-cyclopentadienyl)(nitrosyl)-1,3-dimethylperhydropyrimidin-2-ylidenemolybdenum*(0) (0.15 g, 45%).

[L$^{Me}{}_2$]$^{2+}$ *or* [L$'^{Me}{}_2$]$^{2+}$ [Mo(CO)$_3$(C$_5$H$_5$-η)]$^-{}_2$.—Bis[tricarbonyl(η-cyclopentadienyl)molybdenum(I)] (0.22 g, 0.45 mmol) was suspended in benzene (10 cm^3) and a solution of bi(1,3-dimethylimidazolidin-2-ylidene) (0.09 g, 0.45 mmol) in hexane (5 cm^3) was added to form an orange-brown precipitate. This was filtered off. To the residue, toluene (5 cm^3) and dimethylformamide (*ca.* 5 cm^3) were added dropwise until the solid just dissolved. After filtration, ether was carefully layered onto the solution which was left undisturbed (20 °C, 5 days) to deposit long red-brown needles of *bi(1,3-dimethylimidazolidin-2-ylidinium) bis[tricarbonyl(η-cyclopentadienyl)molybdate*(0)] (0.20 g, 65%).

[HL^{Me}]$^+$ *or* [HL$^{Me'}$]$^+$ [Mo(CO)$_3$(C$_5$H$_5$-η)]$^-$.—To a solution of tricarbonyl(η-cyclopentadienyl)hydridomolybdenum(II) (0.24 g, 1.0 mmol) in hexane (10 cm^3) bi(1,3-dimethylperhydropyrimidin-2-ylidene) (0.12 g, 0.55 mmol) was added. The pale yellow precipitate was filtered off and recrystallised (Me$_2$CO–Et$_2$O at −20 °C, 72 h) to afford needles of *1,3-dimethylperhydropyrimidin-2-ylidinium tricarbonyl(η-cyclopentadienyl)molybdate*(0) (0.32 g, 90%).

Crystal Structure Analysis of (4), cis-[Mo(CO)$_4$(L^{Me})$_2$]

Data are in Tables 6—8 and the Figure.

Crystal Data.—C$_{14}$H$_{20}$MoN$_4$O$_4$, M = 404.28, Monoclinic, a = 9.490(1), b = 14.404(1), c = 15.470(2) Å, β = 123.33(1)°, U = 1 766.8 Å^3, D_m = 1.51 g cm^{-3}, Z = 4, D_c = 1.520 g cm^{-3}, $F(000)$ = 824. Space group $P2_1/c$ (C^5_{2h}). Cu-K_α radiation, λ = 1.5418 Å; μ(Cu-K_α) = 65.92 cm^{-1}.

Cell dimensions were obtained by least-squares refinement of the setting angles of twelve carefully centred reflections having 2θ values between 90 and 120° on a Picker FACS 1 automatic four-circle diffractometer with graphite-monochromated Cu-$K_{\alpha1}$ radiation (λ = 1.540 51 Å). The crystal used was a small, well-formed, yellow parallelepiped with {110} and {001} faces and dimensions 0.070($\|$ a) × 0.072($\|$ b) × 0.220($\|$ c) mm and was mounted with its c axis approximately coincident with the instrumental ϕ axis.

Intensity data were collected by the θ—2θ continuous scan technique using a scan speed of 2° min^{-1} and scan range from (2θ −0.9)° to (2θ +0.9 + Δ)° where Δ is the 2θ separation (°) of the Cu-$K_{\alpha1}$ and $K_{\alpha2}$ peaks for the reflection concerned. Stationary background counts of 10 s duration were made at each extreme of the scan range. The intensities of three standard reflections monitored during data collection did not vary significantly. Intensities were collected for reflections where 3° < 2θ(Cu-K_α) < 127°. Of the 3 602 reflections measured, 2 954 (82%) for which $I > 3\sigma(I)$ were accepted as being significantly above background and after sorting and averaging only the unique 2 439 were used in subsequent calculations.

A value of 0.03 was used for the experimental uncertainty factor ρ.[51] Intensities were corrected for Lorentz and polarisation effects and later for absorption. Transmission factors for F_o, calculated by the analytical method of De Meulenauer and Tompa,[52] varied from 0.6323 to 0.8464. Extinction corrections did not appear to be significant and were not applied.

Structure Analysis.—The structure was solved by conventional heavy-atom techniques and refined to R 0.023 and R' 0.028 {where $R' = [\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|$} by full-matrix least-squares. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. Atomic scattering factors were taken from ref. 53, those for hydrogen from ref. 54, with corrections for anomalous dispersion (f', f'') for molybdenum from ref. 55. After all non-hydrogen atoms had been included and refined with anisotropic thermal parameters, a resulting difference map clearly indicated all hydrogen atom positions which were subsequently included with isotropic thermal parameters and successfully refined. On the final cycle of refinement, no parameter shifted by >0.04σ. The adequacy of the weighting scheme was indicated by an analysis of $w(|F_o| - |F_c|)^2$ *vs.* F_o and sinθ/λ which showed no systematic trends. The standard deviation of an observation of unit weight was 1.40. There were no peaks in the final difference map >0.2 eÅ^{-3}. Final atom parameters are shown in Table 8, and observed and calculated structure factors, details of least-squares planes, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21961 (12 pp., 1 microfiche).*

The ANUCRYS (1975) System of Crystallographic programmes as implemented on the UNIVAC 1108 at A.N.U. by P. O. Whimp and D. Taylor was used throughout the structure solution.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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