Carbene Complexes. Part 11.[1] Steric and Conformational Effects upon the Transition-metal Reactivity of Electron-rich Olefins and Derived Species; Heteroatom-donor-olefin–Metal (Cr^0, Mo^0, W^0, or Rh^I) and 2-Imidazoline-*N*-donor–Metal Complexes, and the Crystal and Molecular Structure of Tetracarbonyl[*NN'N''N'''*-tetramethylbi(imidazolidin-2-ylidene)-*NN''*]-chromium(0)

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The electron-rich olefin $[\dot{:}CN(R)CH_2CH_2NR]_2$, $L^R{}_2$ (R = Me or Et), reacts thermally with (*a*) $[Cr(CO)_6]$, forming $[Cr(CO)_5L^R]$ [(1) or (2)] or *cis*-$[Cr(CO)_4(L^R)_2]$ [(3) or (4)] or (*b*) $[Cr(\eta\text{-}C_6H_6)(CO)_3]$, yielding $[Cr(\eta\text{-}C_6H_6)(CO)_2L^{Me}]$, (5); $[Cr(CO)_5L^{Me}]$, (1), forms the mixed ligand complexes *cis*-$[Cr(AsPh_3)(CO)_4L^{Me}]$, (6), or *cis*-$[Cr(CO)_4\{C(OMe)Me\}L^{Me}]$, (7), upon treatment with $AsPh_3$, or LiMe and then $MeOSO_2F$, respectively. The related olefins $[\dot{:}CN(Me)(CH_2)_3NMe]_2(L'^{Me}{}_2)$ and $[\dot{:}C(NMe_2)_2]_2$ (tdae) do not afford carbene complexes with Cr^0. From $[M(CO)_4(bhd)]$ (M = Cr, Mo, or W; bhd = bicyclo[2.2.1]hepta-2,5-diene) each of the three olefins readily affords heteroatom-donor-olefin species $[M(CO)_4(\text{olefin-}NN'')]$. For M = Mo, the latter is transformed thermally into the *N'N''*-carbenemolybdenum complexes, only for olefin = $L^{Me}{}_2$, but not for $L'^{Me}{}_2$ or tdae. Attempted *in situ* syntheses of metal complexes of $L^H{}_2$ or $L^H\text{–}L^{Et}$ [from $HC(OMe)_2NMe_2$, and $H_2NCH_2CH_2NH_2$ or $H_2NCH_2CH_2NHEt$, and a Mo^0 or Rh^I reagent] lead instead to 2-imidazoline $[N{=}C(H)N(R)CH_2CH_2]$ (R = H or Et) *N*-bonded complexes of Mo^0 and Rh^I. Carbon-13 n.m.r. (but also i.r. and ^1H n.m.r.) spectra are diagnostic for differentiating the type of complex (carbene, olefin-*N,N''*, or imidazoline) and its stereochemistry. The crystal and molecular structure of $[Cr(CO)_4(L^{Me}\text{-}NN'')]$ shows the metal to be in an approximately octahedral environment: the mutually-*trans* CO ligands are bent away from the olefin fragment and have Cr–C bond lengths of 1.90 Å compared to 1.82 Å of those *cis*; the C=C bond length is 1.34 Å and there is probably little interaction with the Cr atom, the distance of closest approach being *ca.* 3.0 Å.

IN previous publications [1-4] dealing with the interaction of an electron-rich olefin {generally $[\dot{:}CN(R)CH_2CH_2NR]_2$ (R = alkyl or aryl, $L^R{}_2$)} and a suitable transition-metal complex, we have been much concerned with the use of the olefin as a precursor to the carbene ligand $\dot{:}CN(R)CH_2CH_2NR$ (L^R). Although by describing some carbene–Cr^0 complexes (Scheme 1) we extend this facet of the olefin's reactivity, we are primarily now concerned with the influence of olefin structure and conformation upon a wider range of transition-metal (especially Cr^0, Mo^0, W^0, or Rh^I) chemistry. For this purpose, among the tetrakis(amino)olefins we differentiate between the chelate and non-chelate and, for the former, the five- and six-membered heterocycles. Thus the reference olefins are $[\dot{:}CN(R)(CH_2)_nNR]_2$ ($L^R{}_2$, $n = 2$; $L'^R{}_2$, $n = 3$) and $[\dot{:}C(NMe_2)_2]_2$ (tdae). The method for

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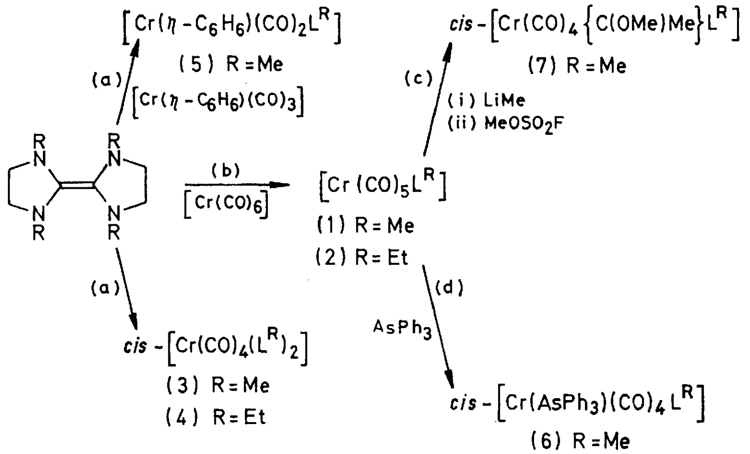
[1] Part 10, M. F. Lappert and P. L. Pye, *J.C.S. Dalton*, 1977, 1283.

[2] Part 9, M. F. Lappert, G. McLaughlin, and P. L. Pye, *J.C.S. Dalton*, 1977, 1272.

[3] M. F. Lappert, *J. Organometallic Chem.*, 1975, **100**, 139, and refs. therein.

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

preparing L^{R}_{2} or L'^{R}_{2} requires heating the appropriate diamine $HN(R)(CH_2)_nN(R)H$ ($n = 2$ or 3) with $HC(OMe)_2NMe_2$ (with loss of $2MeOH + Me_2NH$),[5,6] and the transition-metal chemistry of such an olefin may be explored by its *in situ* generation in the presence of a suitable metal substrate.[7] Extending this procedure to the diamine $H_2NCH_2CH_2NHR$ (R = H or Et) failed to yield an olefin-derived metal complex and instead gave an *N*-bonded 2-imidazoline–metal derivative. The olefins L^{R}_{2}, L'^{R}_{2} and tdae may, in principle, yield olefin-*NN''*–metal or carbenemetal complexes;[8] in practice, tdae goes not give the latter type of complex. A self-consistent rationalisation is offered to account for the variety of reactions observed, and a single-crystal *X*-ray study of $[Cr(CO)_4(L^{Me}_2\text{-}NN'')]$ provides further experimental support.



SCHEME 1 Routes to mono- and bis-carbenechromium(0) complexes. (a) Decalin, 180 °C. (b) Decalin, 150 °C. (c): (i) OEt_2, 0 °C; (ii) OEt_2–H_2O, 5 °C. (d) $C_6H_{11}Me$, 100 °C

Although *cis*-$[Cr(CO)_4(L^{Me})_2]$, (3), has been reported previously,[4] the thermal reaction of L^{Me}_2 (or L^{Et}_2) with $[Cr(CO)_6]$ is the synthesis of choice for this type of carbene complex. The mono-substituted derivatives $[Cr(CO)_5L^{R}]$ [R = Me (1) or Et (2)] may similarly be obtained in high yield by modification of the reaction conditions. Compounds (1)—(3), like their Mo and W analogues,[1,2] are stable to heat or O_2, both as solids and in solution. From $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ and L^{Me}_2, $[Cr(\eta\text{-}C_6H_6)(CO)_2L^{Me}]$ (5) (for which a Fischer-type carbene analogue is known[9]) was isolated, and substantial amounts of (3) were obtained, perhaps *via* the pathway of equation (1). There was no evidence in either of these systems for formation of a *fac*-triscarbenemetal complex, in contrast to results with Mo^0 or W^0.[1,2]

$$\begin{tikzcd} 2[Cr(\eta\text{-}C_6H_6)(CO)_3] \arrow[r] & \{[Cr(\eta^4\text{-}C_6H_6)(CO)_4] + [Cr(\eta\text{-}C_6H_6)(CO)_2]\} \arrow[d, "L^{Me}_2"'] \\ & cis\text{-}[Cr(CO)_4(L^{Me})_2] + [Cr(\eta\text{-}C_6H_6)(CO)_2L^{Me}] + 2C_6H_6 \end{tikzcd} \tag{1}$$

The olefin L^{Me}_2 (unlike PPh_3)[10-13] displaces the Fischer-type carbene ligand from $[Cr(CO)_5\{C(OMe)Me\}]$ to yield (1); nevertheless, the heat- or O_2-labile (especially in halogenated solvents) mixed biscarbene complex *cis*-$[Cr(CO)_4\{C(OMe)Me\}L^{Me}]$, (7), was obtained from $[Cr(CO)_5L^{Me}]$, (1), by reaction with successively LiMe and $MeOSO_2F$. Another mixed complex, *cis*-$[Cr(AsPh_3)(CO)_4L^{Me}]$, (6), was prepared from (1) and $AsPh_3$.

An alternative mode of reaction of L^{R}_2 with a hexacarbonyl derivative of a Group 6 metal is demonstrated by the reaction with $[M(CO)_4(bhd)]$ (M = Cr, Mo, or W; bhd = bicyclo[2.2.1]hepta-2,5-diene) (Scheme 2). Under milder conditions than required for generation of a carbene–chromium, –molybdenum, or –tungsten complex, L^{Me}_2 acts as an olefin-*NN''* donor, without C=C cleavage of the electron-rich olefin,[8] and displaces bhd to form $[M(CO)_4(L^{Me}_2\text{-}NN'')]$ [(8) (M = Cr), (9) (M = Mo), or (13) (M = W)], and similarly from L^{Et}_2, $[Mo(CO)_4(L^{Et}_2\text{-}NN'')]$, (10). Likewise, both L'^{Me}_2 and tdae form compounds of this type. Carbene derivatives (L'^{Me}–metal) are formed from L'^{Me}_2 only with great difficulty (for Mo^0, W^0, Rh^I, or Pt^{II}),[1,2,7] and tdae does not give similar $(Me_2N)_2C$–metal complexes.[14]

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[5] H. E. Winberg, *Chem. Abs.*, 1966, **64**, 15854h.

[6] D. M. Lemal, 'The Chemistry of the Amino Group,' ed. S. Patai, Interscience, 1968, p. 701.

[7] P. L. Pye, D.Phil. Thesis, University of Sussex, 1976.

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

[9] E. O. Fischer and H. J. Beck, unpublished results; E. O. Fischer, *Rev. Pure Appl. Chem.*, 1970, **24**, 407.

[10] C. G. Kreiter and K. Öfele, cited by C. G. Kreiter and E. O. Fischer, *Pure Appl. Chem. Suppl.*, 1971, **6**, 151.

[11] E. O. Fischer, M. Fischer, and H. Werner, *Angew. Chem. Internat. Edn.*, 1972, **11**, 644.

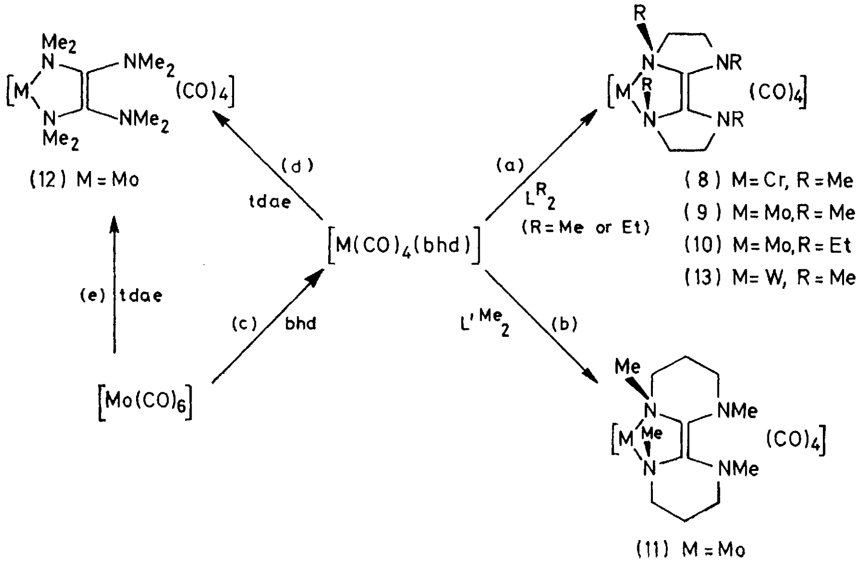
[12] H. Werner and H. Rascher, *Helv. Chim. Acta*, 1968, **51**, 1765.

[13] E. O. Fischer and R. Aumann, *Chem. Ber.*, 1969, **102**, 1495.

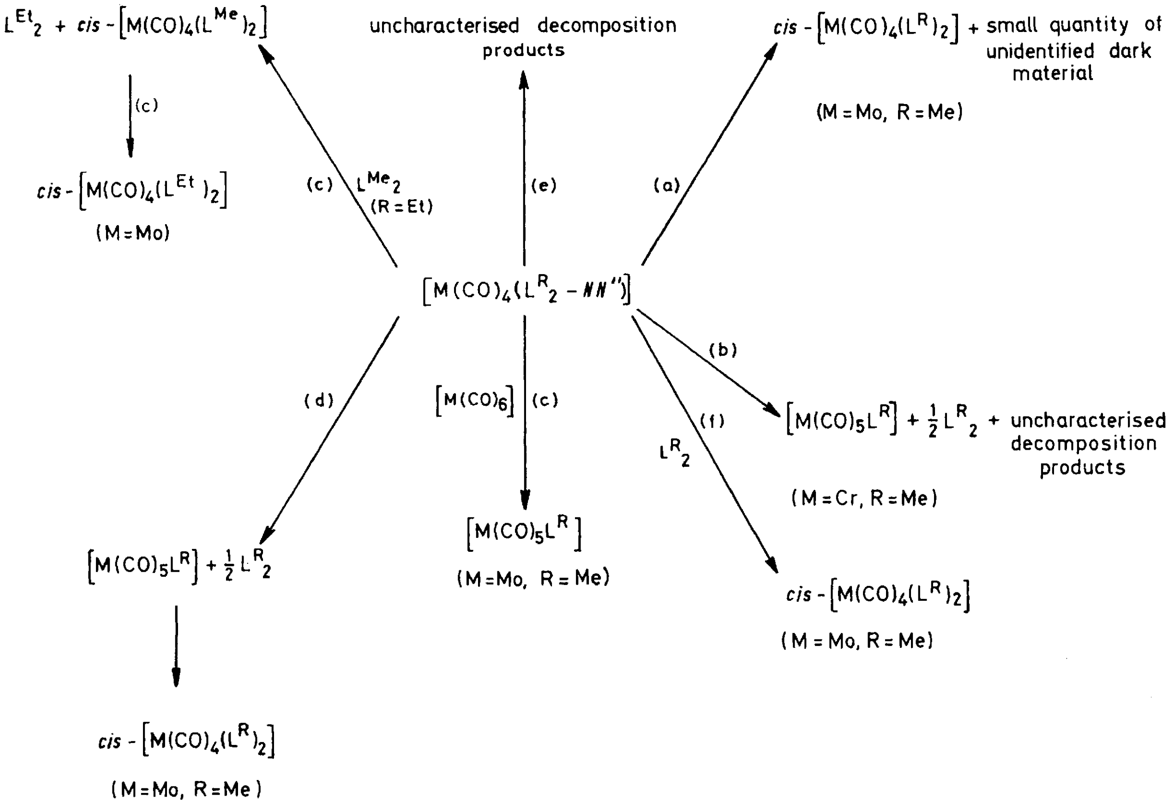
[14] B. Çetinkaya, M. J. Doyle, M. F. Lappert, and P. L. Pye, unpublished results.

The order of olefin reactivity towards formation of this type of olefin-*NN''*-metal complex is identical to that for carbenemetal complex formation, *i.e.*, $L^{Me}_2 \approx L^{Et}_2 > L'^{Me}_2 \gg$ tdae. For example, although L^{Me}_2 or L^{Et}_2 react instantaneously with $[M(CO)_4(bhd)]$ (M = Cr, Mo, or W) below 20 °C to yield (8)—(10) or (13), L'^{Me}_2 requires gentle heating {to yield *cis*-$[Mo(CO)_4(L'^{Me}_2$-*NN''*$)]$, (11)}, and tdae refluxing in toluene {to give $[Mo(CO)_4($tdae-*NN''*$)]$, (12)}.

Under certain conditions (Scheme 3) $[Mo(CO)_4(L^R_2$-*NN''*$)]$, but not the related L'^{Me}_2 or tdae complexes, are transformed into the carbenemolybdenum(0)



SCHEME 2 Synthetic routes to electron-rich olefin *NN''*-bonded complexes (bhd = bicyclo[2.2.1]hepta-2,5-diene). (a) Toluene, 0 °C. (b) Toluene, 35 °C. (c) $C_6H_{11}Me$, 100 °C. (d) Toluene, 110 °C. (e) Decalin, 160 °C

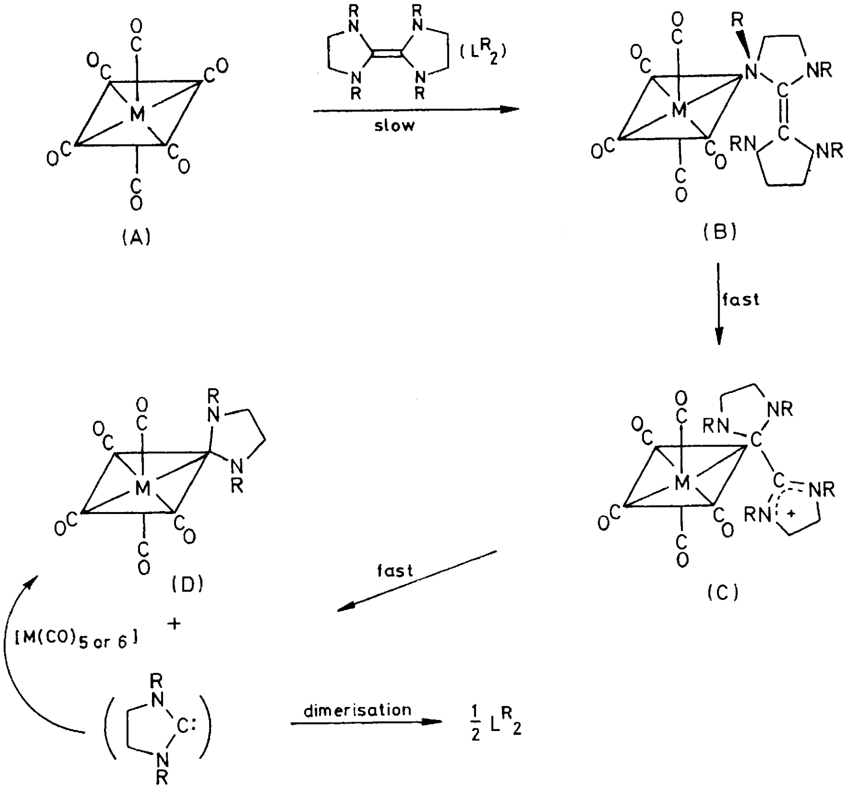


SCHEME 3 Effect of heat on $[M(CO)_4(L^R_2$-*NN''*$)]$ complexes. (a) Sealed pan, d.s.c. experiment, 140 °C. (b) $C_6H_{11}Me$, 100 °C. (c) Sealed n.m.r. tube experiment, C_6H_6, 80 °C. (d) Sealed n.m.r. tube experiment, >100 °C. (e) Solid state, under N_2, open system, or *in vacuo*, >130 °C. (f) C_6H_6, 80 °C, open system under N_2

TABLE I

Cr^0, Mo^0, W^0, and Rh^I heteroatom-donor and electron-rich olefin-derived carbenechromium(0) complexes and their characterisation

Compound	Yield (%)	M.p. (θ_c/°C)	Colour	Found (required) (%)		
				C	H	N
$[\mathrm{Cr(CO)_5L^{Me}}]$ (1)	65	108—109	White	41.2 (41.1)	3.2 (3.4)	9.5 (9.6)
$[\mathrm{Cr(CO)_5L^{Et}}]$ (2)	60	100—102	White	45.6 (45.3)	4.5 (4.4)	8.9 (8.8)
cis-$[\mathrm{Cr(CO)_4(L^{Me})_2}]$ (3)	100	255 (decomp.)	Yellow	46.4 (46.7)	5.6 (5.5)	15.4 (15.6)
cis-$[\mathrm{Cr(CO)_4(L^{Et})_2}]$ (4)	100	201	Yellow	52.1 (51.9)	6.9 (6.7)	13.5 (13.5)
$[\mathrm{Cr(\eta\text{-}C_6H_6)(CO)_2(L^{Me})}]$ (5)	15	202	Orange	55.2 (54.9)	5.8 (5.7)	9.9 (10.1)
cis-$[\mathrm{Cr(AsPh_3)(CO)_4(L^{Me})}]$ (6)	35	176—178 (decomp.)	Yellow	56.9 (57.0)	4.5 (4.4)	5.0 (4.9)
cis-$[\mathrm{Cr(CO)_4\{C(OMe)Me\}L^{Me}}]$ (7)	40	82 (decomp.)	Crimson	44.8 (45.0)	5.0 (5.0)	9.0 (8.8)
$[\mathrm{Cr(CO)_4(L^{Me}{}_2\text{-}}NN'')]$ (8)	45	154—155 (decomp.)	Orange	46.7 (47.6)	5.6 (5.5)	15.5 (15.6)
$[\mathrm{Mo(CO)_4(L^{Me}{}_2\text{-}}NN'')]$ (9)	45	140—144 (decomp.)	Yellow	41.7 (41.6)	5.0 (5.0)	13.8 (13.8)
$[\mathrm{Mo(CO)_4(L^{Et}{}_2\text{-}}NN'')]$ (10)	60	135 (decomp.)	Yellow	46.7 (46.9)	6.1 (6.1)	12.2 (12.2)
$[\mathrm{Mo(CO)_4(L'^{Me}{}_2\text{-}}NN'')]$ (11)	30	160 (decomp.)	Yellow	44.2 (44.4)	5.6 (5.6)	12.8 (12.9)
$[\mathrm{Mo(CO)_4(tdae\text{-}}NN'')]$ (12)	40	160 (decomp.)	Yellow	41.4 (41.2)	6.1 (5.9)	13.7 (13.7)
$[\mathrm{W(CO)_4(L^{Me}{}_2\text{-}}NN'')]$ (13)	35	127 (decomp.)	Yellow	33.6 (34.1)	4.2 (4.1)	11.1 (11.4)
$[\mathrm{Mo(CO)_5\{N{:}C(H)N(Et)CH_2CH_2\}}]$ (14)	30	41—42	Pale yellow	32.3 (32.3)	3.4 (3.0)	8.5 (8.4)
cis-$[\mathrm{Mo(CO)_4\{N{:}C(H)N(Et)CH_2CH_2\}_2}]$ (15)	45	102—104	Bright yellow	41.5 (41.6)	5.0 (5.0)	14.1 (13.8)
cis-$[\mathrm{Mo(CO)_4\{N{:}C(H)N(H)CH_2CH_2\}_2}]$ (16)	20		Yellow	34.3 (34.5)	3.6 (3.4)	16.0 (16.1)
fac-$[\mathrm{Mo(CO)_3\{N{:}C(H)N(H)CH_2CH_2\}_3}]$ (17)	75	150 (decomp.)	Pale yellow	36.7 (36.7)	4.7 (4.6)	21.5 (21.5)
$[\mathrm{RhCl(1,5\text{-}cod)\{N{:}C(H)N(H)CH_2CH_2\}}]$ (18)	55	180 (decomp.)	Yellow	41.3 (41.7)	5.6 (5.7)	9.1 (8.9)
$\mathrm{N{:}C(H)N(H)CH_2CH_2}$ (19)	80	56 (sublimes)	White	51.2 (51.4)	8.6 (8.6)	39.8 (40.0)



SCHEME 4a Proposed pathway to carbenemetal complex formation (M = Cr, Mo, or W)

species $[\mathrm{Mo(CO)_5L^R}]$ and *cis*-$[\mathrm{Mo(CO)_4(L^R)_2}]$. However, these reactions require more forcing conditions than those used for the synthesis of such carbenemolybdenum(0) complexes from $[\mathrm{Mo(CO)_6}]$ and $\mathrm{L^R{}_2}$ and therefore the olefin-*NN''* species are unlikely to be implicated in a major pathway to the carbene complexes.

It has previously been suggested[15] that the initial approach to an electrophile {and we may include $[\mathrm{M(CO)_6}]$ or a derivative in this class} is *via* a nitrogen atom for tdae but an ethylenic carbon atom for $\mathrm{L^{Me}{}_2}$. This seems unlikely, because $\mathrm{L^{Me}{}_2}$ reacts with $[\mathrm{M(CO)_4(bhd)}]$ (M = Cr, Mo, or W) more readily at nitrogen than does tdae. We propose (Scheme 4a) that the carbene-

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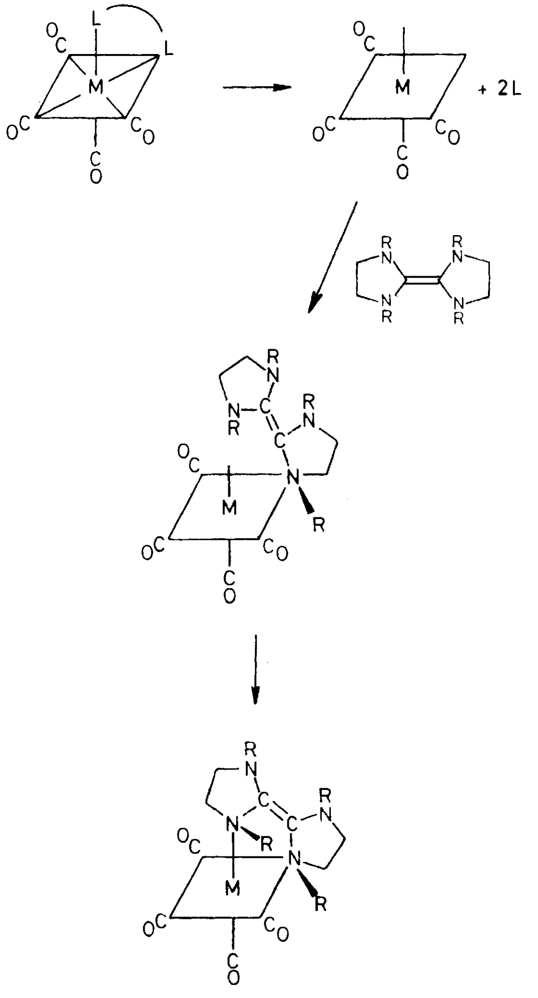
[15] N. Wiberg, *Angew. Chem. Internat. Edn.*, 1968, **7**, 766.

metal complex is formed by (i) initial olefin-*N*-metal complex formation, then (ii) subsequent rearrangement to a *C*-bonded species, which may then (iii) fragment to form the carbenemetal complex with expulsion of a resonance-stabilised carbene fragment, $\dot{\mathrm{L}}^{\mathrm{R}}$. The latter may be free and dimerise or be captured by another metal centre by [M(CO)$_n$] (n = 5 or 6). Alternatively, free $\dot{\mathrm{L}}^{\mathrm{R}}$ is removed by attack of [M(CO)$_n$] upon the complex from (*ii*). The olefin-*NN''* complex is formed if, after initial monohapto *N*-co-ordination, spontaneous vacation of a second site occurs. This is clearly the case with [M(CO)$_4$(bhd)], upon displacement of bhd (Scheme 4b).[16]



SCHEME 4b The formation of *NN''*-bonded electron-rich olefin metal complexes. M = Cr, Mo, or W; 2L = bicyclo[2.2.1]-hepta-2,5-diene

It is noteworthy that when vacation of co-ordination sites is sequential,[17] *e.g.* loss of CO from [M(CO)$_6$] or bhd [16] from [Fe(CO)$_3$(bhd)], then carbenemetal, and not olefin-*NN''*-metal complexes are formed from $\mathrm{L^{Me}}_2$. For $\mathrm{L'^{Me}}_2$ and especially tdae, however, the activation energy for the required olefin-*N* to olefin-*C* metal-complexes isomerisation [(B) ⟶ (C) in Scheme 4a] appears to be excessive; hence, from [M(CO)$_6$], the loss of a second CO molecule is preferred and olefin-*NN''*-metal complexation results. These differences in reactivity of the various olefins with respect to the Group 6 metal-carbonyl derivatives can be rationalised in terms of steric and conformational variations.

A comparison of the electron-rich olefins with *N*-methyl substituents (Figure 1) shows that in all cases, assuming coplanarity, there is a close non-bonded contact (*d*) between the vicinal Me groups at either end of the double bond. The distance (*d*) increases from the acyclic tdae to the (at present unknown) four-membered ring species, (**19**).

Assuming reasonable bond lengths and angles, and a planar arrangement at the double bond and nitrogen atoms, the distances can be calculated as $d_1 \approx d_2 \approx 1.29$ Å, $d_3 \approx 1.63$ Å, and $d_4 \approx 2.29$ Å. All these are much shorter than the usual contact distances of *ca.* 3.5 Å between Me groups [18] and therefore substantial non-planarity of the molecules must be expected, particularly for the shortest calculated contacts. (It is noted that five-membered cyclic olefins containing bulky *N*-substituents such as Bu^t, Pr^i, or cyclohexyl are impossible to prepare *via* the procedure used for $\mathrm{L^{Me}}_2$.[6,7]) A corresponding situation occurs in perchlorodifulvalene (20) (Figure 1) where the non-bonded contacts between Cl atoms force the two rings of the molecule to be rotated with respect to each other.[19] In the case of the electron-rich olefins, the distortion will probably take the form of making the nitrogen atoms more tetrahedral with the Me substituents above and below the plane of the molecule and retaining the planar arrangement at the double bond. Two possible arrangements of $\mathrm{L'^{Me}}_2$ are shown in (21) and (22); in both cases all Me groups are equivalent and give rise to the observed singlet in the ^{1}H n.m.r. spectrum. In $\mathrm{L^{Me}}_2$, a similar (but less pronounced) distortion is probable and is indeed seen in the Me substituents of the two nitrogen atoms not co-ordinated to Cr in [Cr(CO)$_4$-($\mathrm{L^{Me}}_2$-*NN''*)] (see below), and in tdae a large number of non-planar arrangements is possible.

A probable consequence of the non-planarity of the nitrogen substituents is a steric blocking of access by a metal atom to the ethylenic carbon atoms. It may well be relevant that the rates of olefin reaction (including the chemiluminescence of the olefins in air) are very different. Thus $\mathrm{L^{Me}}_2$ reacts with exceeding rapidity and chemiluminesces brilliantly in air.[6,15,20] Similarly tdae chemiluminesces in air,[6,15,20] but reacts more slowly with O$_2$; $(\mathrm{Et_2N})_2\mathrm{C{:}C}(\mathrm{NEt_2})_2$ does not chemiluminesce at all [21] and can be handled (for limited periods) in the air. In

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[16] D. F. Hunt, L. P. Lillya, and M. D. Rausch, *Inorg. Chem.*, 1969, **8**, 446.

[17] F. Zingales, M. Graziani, and U. Belluco, *J. Amer. Chem. Soc.*, 1967, **89**, 256; F. Zingales, F. Canziani, and F. Basolo, *J. Organometallic Chem.*, 1967, **7**, 461.

[18] A. I. Kitaigorodskii, 'Organic Chemical Crystallography,' Heywood, 1961.

[19] H. L. Ammon, G. L. Wheeler, and L. Agranat, *Tetrahedron*, 1973, **29**, 2695.

[20] R. N. Hoffmann, *Angew. Chem. Internat. Edn.*, 1968, **7**, 754.

[21] J. W. Scheeren and R. J. F. Nivard, *Rec. Trav. chim.*, 1969, **88**, 289.

each case, a metal atom could bond relatively easily to a nitrogen atom of the electron-rich olefin, but probably less readily for tdae than $L^{Me}{}_2$. The more non-planar the olefin, the more the Me groups above and below the plane block the subsequent transfer of the metal from a nitrogen to a carbon atom of the olefin.

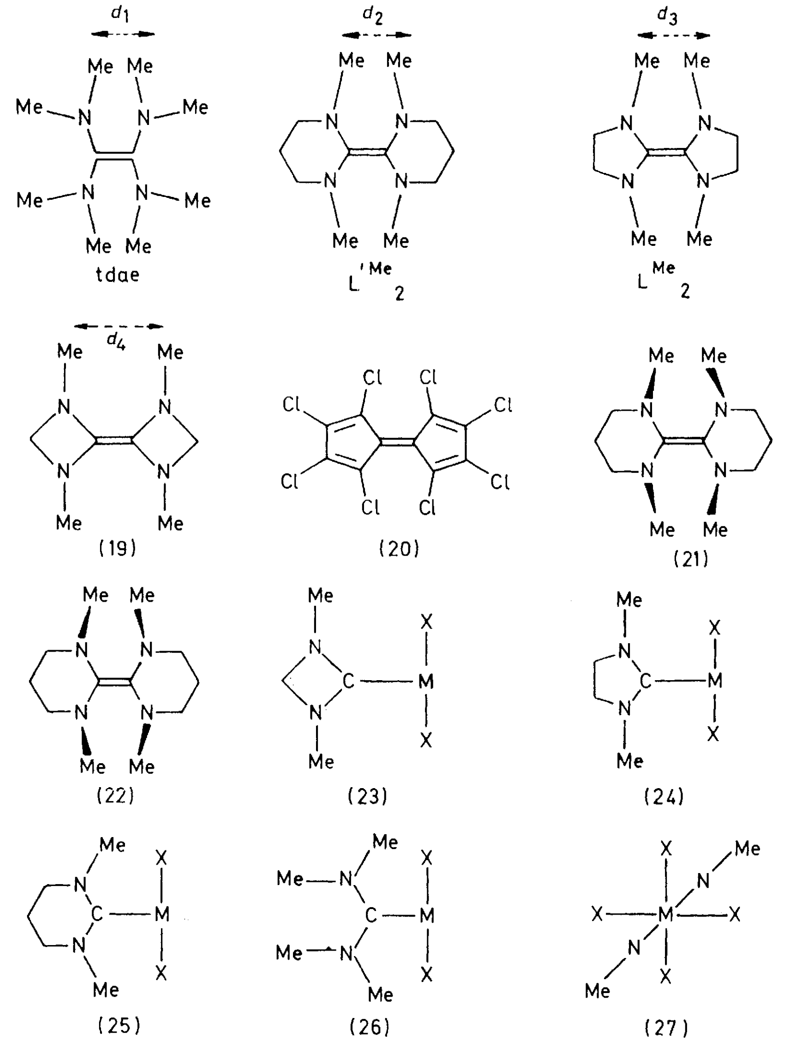

FIGURE 1 Diagrammatical representation of non-bonded interactions in electron-rich olefins and related species

Consideration of the structures of the carbenemetal complexes derived from electron-rich olefins leads to a similar argument. In an octahedral metal complex *cis*-[$M(CO)_4(L^{Me})_2$] with a planar ring carbene ligand L^{Me}, so as to bring the nitrogen substituent about half-way between the two *cis*-ligands, (27), as seen in the crystal structure of *cis*-[$Mo(CO)_4(L^{Me})_2$] [2] and *trans*-[$RuCl_2(L^{Et})_4$].[22] Even so, non-bonding repulsions in an octahedral carbenemetal complex of L'^{Me} [*i.e.* (25)] are appreciable. In the complexed carbene, the strength of the M–C bond is dependent on a trigonal-planar arrangement of the nitrogen atoms allowing the observed interaction between the filled p_π orbitals on the nitrogen atoms with the empty p_π orbital of the carbene carbon. With *X*-ray analysis shows that the *N*-Me substituents closely approach the *cis* ligands. This is illustrated by low-temperature ^1H and ^{13}C n.m.r. spectra in *cis*-[$M(CO)_4(L^R)_2$] [1,2] and related complexes [10] and such non-bonding interactions should increase in the order: (i) cyclic carbene ligand < acyclic carbene ligand, (26), and (ii) within the cyclic series,.(the unknown) four-membered (23) < five-membered (24) < six-membered (25) ligand complex. These strains can be alleviated by rotating the plane of the carbene ligand (around the M–C bond) regard to stability of the metal complex, relief of steric strain *via* distortion of the carbene ligand (as in the original olefin) is offset by a concomitant decrease in electron stabilisation of the $M-CN_2$ system. Thus the various steric requirements of the different nitrogen-atom substituents can explain trends in ease of formation of the olefin-*NN''*-metal or carbenemetal complex from the several electron-rich olefins. The following further

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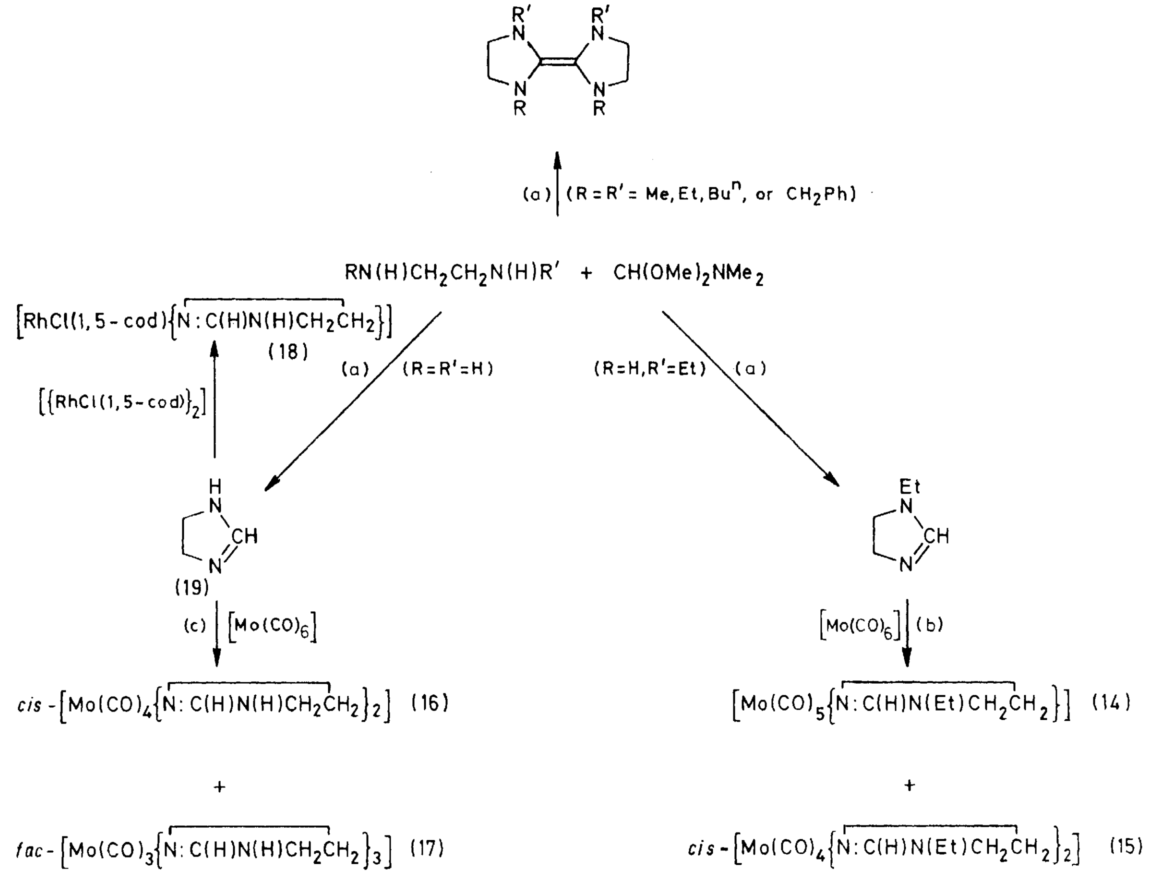
[22] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Chem. Comm.*, 1976, 644.

predictions are made: (i) replacement of the *N*-R substituents with bulkier R groups (such as Ph or Bu^t) will lower the olefin reactivity and carbenemetal stability; (ii) acyclic electron-rich olefins may yield carbenemetal complexes if non-bonded contacts are minimised, as in the unknown $[(CH_2)_2N]_2C{:}C[N(CH_2)_2]_2$, and (iii) in a square-planar metal environment the relative ease of formation of carbenemetal complexes will be less affected by the ring size or bulk of the nitrogen substituents, since these can be accommodated above and below the co-ordination plane, although the argument concerning the reactivity of the original electron-rich olefin will still apply. As for (i), with R = Ph, L^{Ph}–Mo derivatives have not yet been obtained, and we have failed even to synthesise the olefin $L^{Bu^t}{}_2$. As for (iii), taking Rh^I as an example, from *trans*-$[Rh(CO)Cl(PPh_3)_2]$, $L^{Me}{}_2$, $L'^{Me}{}_2$, and $L^{Ph}{}_2$ give respectively $[Rh(CO)(L^{Me})_3]Cl$,[23] *trans*-$[Rh(CO)Cl(L'^{Me})_2]$,[7] and *trans*-$[Rh(CO)Cl(L^{Ph})PPh_3]$,[24] and tdae does not react (all reactions in xylene, 140 °C, 3 h with an excess of olefin).

A further prediction, (iv), that replacement of *N*-Me by the much smaller H should make all the octahedral carbenemetal complexes easier to form since the carbene can be planar with little steric strain, led to attempts to synthesise $[{:}CN(H)CH_2CH_2NH]_2$. These instead afforded (Scheme 5) 2-imidazoline, $N{:}C(H)N(H)CH_2CH_2$, (19), which reacted readily with $[Mo(CO)_6]$ affording *fac*-$[Mo(CO)_3\{N{:}C(H)N(H)CH_2CH_2\}_3]$, (17), as the major product. As the spatial requirements of (19) as an *N*-bonded ligand should be similar to the isomeric *C*-bonded carbene ${:}CN(H)CH_2CH_2NH$, and as *stable fac*-$[M(CO)_3(L^{Me})_3]$ (M = Cr or Mo)[1] cannot be obtained, we may regard this as circumstantial evidence for proposition (iv).



SCHEME 5 2-Imidazoline *N*-donor complexes of Mo^0 and Rh^I: the dependence of R and R' upon electron-rich olefin and subsequent carbenemetal complex formation. (a) 100—140 °C, no solvent. (b) $C_6H_{11}Me$, 100 °C. (c) Toluene, 110 °C

Spectroscopic Properties.—The i.r. spectrum of each compound (Table 2) shows bands attributable to terminal ν(CO), consistent with the formulations; ν(CO) for the carbenechromium complexes are very low (compared, *e.g.* to their PPh_3 analogues) due to the higher σ-donor : π-acceptor ratio of the carbene ligand.[1,2] The *NN''*-bonded olefin–metal complexes have ν(CO) very similar in frequency to the reported ethylenediamine derivatives.[25] One major difference between the

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[23] M. J. Doyle, D.Phil. Thesis, University of Sussex, 1974.

[24] M. J. Doyle and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 679.

[25] *Cf.*, D. M. Adams, ' Metal–Ligand and Related Vibrations,' Arnold, 1967, and refs. therein.

carbene– and olefin-*NN''*–metal complexes is the absence of the ν(CN)$_2$ band observed in the former species between 1 500 and 1 480 cm^{-1}. This may be due to the lower $\overset{\frown}{\mathrm{N}}$–C p_π-p_π interaction for the latter.

TABLE 2

Selected i.r. spectroscopic data [a] of Cr^0, Mo^0, W^0, and Rh^I heteroatom-donor, and electron-rich olefin-derived Cr^0 complexes

Compound	ν(CO)	ν(CN$_2$) [b]
(1)	2 061m, 1 928vs [c]	1 495m
(2)	2 056m, 1 924vs [c]	1 482m
(3)	1 984m, 1 865s, 1 856s, 1 833s [d]	1 498m
(4)	1 983m, 1 866s, 1 855s, 1 833s [d]	1 482m
(5)	1 840s, 1 764s [b]	1 495m
(6)	1 997s, 1 885s, 1 875s, 1 833s [b]	1 503m
(7)	2 004m, 1 914s, 1 895s, 1 888s [c]	1 505m
(8)	2 005m, 1 884s, 1 864s, 1 839s [c]	
(9)	2 005m, 1 895s, 1 870s, 1 836s [e]	
(10)	2 007m, 1 899s, 1 873s, 1 834s [c]	
(11)	2 015m, 1 910s, 1 881s, 1 839s [c]	
(12)	2 009m, 1 898s, 1 871s, 1 822 [b]	
(13)	2 005m, 1 896s, 1 874s, 1 830 [b]	
(14)	2 071vw, 1 935vs, 1 911m [c]	1 618s
(15)	2 009m, 1 865vs, 1 816s [e]	1 611s
(16)	1 994s, 1 855s, 1 820s, 1 781s [b]	1 600s
(17)	1 875vs, 1 730vs [b]	1 600s
(18)		1 597s

[a] Spectra calibrated against polystyrene (1 801.5 and 1 601 cm^{-1}) and all figures quoted are ν(max.) cm^{-1}. [b] Dilute Nujol mull between CsI plates. [c] Hexane solution. [d] Tetrahydrofuran solution. [e] Toluene solution.

Carbon-13 n.m.r. spectra (Table 3) appear to be the most useful spectroscopic probe for structure elucidation and differentiation of the carbene–, olefin-*NN''*–, and 2-imidazoline–metal derivatives. Compared with the *C*(carbene) resonance in complexes of the type [Cr(CO)$_5${*C*(OR)R'}] [26] that of L^R (R = Me or Et) is found at relatively high field (for a carbene carbon), *ca.* 230—215 p.p.m. from SiMe$_4$, although in the related *cis*-[Cr(CO)$_4${CN(Me)CH:CHNMe}$_2$], the *C*(carbene) resonance is at 198 p.p.m.;[27] the additional high-field shift is presumably due to the increased delocalisation afforded by the planar aromatic nature of the dedihydroimidazolidin-2-ylidene ring. It is interesting to note that L^{Me} *cis* to {C(OMe)Me} in [Cr(CO)$_4${C(OMe)Me}L^{Me}], (7), has no effect upon the chemical shift of the Fischer-type carbene carbon compared with a *cis*-CO group, whereas in *cis*-[Cr(CO)$_4$(L^{Me})$_2$], (3), L^{Me} *cis* to L^{Me} causes a downfield shift of *ca.* 10 p.p.m. in this carbene carbon (as compared with [1,2] Mo^0 and W^0 analogues).

In the olefin-*NN''*–metal complexes, the ethylenic carbon atoms are at 148—134 p.p.m., in a similar region to that of the parent olefins (131—125 p.p.m.). This is consistent with (i) the intact nature of the ethylenic linkage and (ii) the absence of any metal–(C:C) interaction. If the latter were operative, even to a small extent, a shift to higher field compared with the parent olefin would be expected (as observed in η-arene–, bhd–, or ethylene–metal complexes).[26] The lower-field shift of the ethylenic carbon atoms in the tdae-*NN''* complex (12) (148 p.p.m., compared with 131 p.p.m. in free tdae) than in the L$^{Me}{}_2$-*NN''* complexes [(8) or (9)] (134 p.p.m. compared with 129 p.p.m. in free L$^{Me}{}_2$) is not readily explained. However, there may be some electron density removal from the ethylenic carbon atoms in (12); in the dication [L$^{Me}{}_2$]$^{2+}$, the ethylenic carbon resonance is also at 148 p.p.m.[2] The *syn*-orientation of the donor *N*-Me

TABLE 3

Selected ^{13}C n.m.r. spectroscopic data [a] of Cr^0, Mo^0, W^0, and Rh^I heteroatom-donor and electron-rich olefin-derived Cr^0 complexes

			mutually			
Compound	Solvent	*C*$_2$ [b]	*cis*-CO	*trans*-CO	N–*C*H$_2$ (ring)	N–*C*H$_3$
(1)	C$_6$D$_6$	219.6	221.1	218.7	51.3	38.3
(2)	C$_6$D$_6$	217.6	222.5	218.4	47.4	
(3) [c]	CDCl$_3$	228.4	230.0	222.6	51.9	38.3
(4)	CD$_2$Cl$_2$	226.9	228.7	222.2	47.9	
(7) [d]	C$_6$D$_6$	224.9	227.6, 233.0	222.9	51.3	38.2
(8)	C$_6$D$_6$	134.5	227.9	213.9, 214.5	51.4, 62.6 [e]	38.9, 53.0 [e]
(9)	C$_6$D$_6$	134.6	222.4	206.6, 206.8	51.0, 62.7 [e]	38.6, 52.7 [e]
(11)	C$_6$D$_6$	134.1	223.0	207.3, 207.8	49.7, 60.8 [e]	45.0, 47.1 [e]
(12)	C$_6$D$_6$	148.0	222.6	206.8		45.1, 54.2 [e]
(15)	C$_6$D$_6$	160.6	221.2	207.1	48.0, 58.7 [e]	
(18)	CDCl$_3$	159.9			43.4, 50.8 [c]	
[:CN(Me)CH$_2$CH$_2$NMe]$_2$ (L$^{Me}{}_2$)	C$_6$D$_6$	129.6			52.7	40.1
[:CN(Et)CH$_2$CH$_2$NEt]$_2$ (L$^{Et}{}_2$)	C$_6$D$_6$	125.6			49.1	
[:C(NMe$_2$)$_2$]$_2$ (tdae)	C$_6$D$_6$	132.0				

[a] All values quoted in p.p.m. relative to internal SiMe$_4$, or calculated from solvent resonance at 25 °C. [b] Carbene, ethylenic, or imino-carbon. [c] Spectrum obtained at 50 °C. [d] Me(MeO)*C*(carbene), 359.6 p.p.m. [e] *N*-donor atom substituent.

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[26] *Cf.*, B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135, and refs. therein.

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

substituents in [$\mathrm{Cr(CO)_4(L^{Me}{}_2}$-*NN''*)], (8), and the related $\mathrm{L'^{Me}{}_2}$ and $\mathrm{MoL^{Me}{}_2}$ complexes (11) and (9), is indicated by the doublet signal for the mutually-*trans* CO ligands [see below, for confirmation from *X*-ray data for (13)].

The nature of the bonding in the 2-imidazoline derivatives [(15) and (18)] was also readily shown by ^{13}C n.m.r. techniques. The imino-carbon N:*C*H is found as a singlet in the ^{1}H-decoupled mode (*ca.* 160 p.p.m. is general for this type of carbon atom),[28] but a doublet in the ^{1}H off-resonance spectrum; and in (18) no ^{103}Rh coupling is observed, indicating an *N*-bonded species. It is interesting that a related *C*-bonded complex is known for $\mathrm{Ru^{II}}$, *trans*-[Ru(CO)$(\mathrm{NH_3})_4${CN(H)CR:CRNH}]$^{2+}$.[29]

The carbenechromium complexes show simple first-order ^{1}H n.m.r. spectral characteristics at 25 °C (Table 4). Variable-temperature studies for the complexes *cis*-[$\mathrm{M(CO)_4(L^R)_2}$] (M = Cr, Mo, or W; R = Me or Et),[1,2] show trends in activation parameters for $\mathrm{M}\overset{\curvearrowleft}{-}\mathrm{C}$(carbene) rotation which are consistent with the above discussion of non-bonded interactions.

TABLE 4

Selected ^{1}H n.m.r. spectroscopic data [a] of $\mathrm{Cr^0}$, $\mathrm{Mo^0}$, $\mathrm{W^0}$, and $\mathrm{Rh^I}$ heteroatom-donor and electron-rich olefin-derived chromium(0) complexes

Compound	Solvent	N–C*H*$_2$ (ring)	N–C*H*$_3$	Others
(1)	$\mathrm{CDCl_3}$	6.41	6.63	
(2)	$\mathrm{CDCl_3}$	6.45		6.15q,[b] 8.75t [c]
(3) [d]	$\mathrm{C_6H_6}$	7.45	6.95	
(4)	$\mathrm{CDCl_3}$	6.52		6.20q,[b] 8.80t [c]
(5)	$\mathrm{CDCl_3}$	6.53	6.62	5.4 [e]
(6)	$\mathrm{CDCl_3}$	6.55	6.75	
(7)	$\mathrm{C_6H_6}$	7.53	7.17	5.63,[f] 7.27 [g]
(8)	$\mathrm{C_6H_6}$	6.6—7.3m	7.30, 7.40	
(9)	$\mathrm{C_6H_6}$	6.8—7.4m	7.40, 7.50	
(10)	$\mathrm{C_6H_6}$	6.8—7.6m		8.75t,[c] 9.05t [c]
(11)	$\mathrm{CDCl_3}$	6.5—7.3m	6.88, 7.30	
(12)	$\mathrm{C_6H_6}$		6.70, 7.15	
(13)	$\mathrm{CDCl_3}$	6.5m	6.70, 7.15	
(14)	$\mathrm{C_6D_6}$	7.3m		3.9,[h] 7.8q,[b] 9.5t [c]
(15)	$\mathrm{C_6D_6}$	6.85m		3.75,[h] 7.46q,[b] 9.3t [c]
(16)	*i*			
(17)	*i*			
(18)	$\mathrm{CDCl_3}$	6.50s		2.3,[h] 3.7 [j]

[a] All values quoted in τ measured from internal $\mathrm{SiMe_4}$, or calculated from the corrected solvent resonance; all signals singlets unless stated: m = multiplet, q = quartet, t = triplet. [b] N–C*H*$_2$–CH$_3$. [c] N–CH$_2$–C*H*$_3$. [d] N–CH$_2$ (ring) = 7.35, N–CH$_3$ = 6.54, *trans*-isomer. [e] η-$\mathrm{C_6H_6}$. [f] O–CH$_3$. [g] C–CH$_3$. [h] =CH. [i] Insoluble in non-reacting solvents. [j] =NH (disappeared upon addition of $\mathrm{D_2O}$).

The Crystal and Molecular Structure of Tetracarbonyl-[NN'N''N'''-*tetramethylbi(imidazolidin-2-ylidene)*-NN'']-*chromium*(0).—Figure 2 is an ORTEP[30] drawing of the molecule showing the 50% thermal-vibration ellipsoids and the atom numbering scheme. The bond lengths, bond angles, and torsion angles are listed in Table 5. The electron-rich olefin is seen to act as a bidentate ligand with its two donor-nitrogen atoms occupying *cis*-positions of an octahedral zero-valent carbonylchromium complex. The two halves of the molecule, related by a plane through O(1), O(2), and bisecting the olefin, show good agreement between equivalent bond lengths.

We do not, as yet, know the conformation of the electron-rich olefin in its unco-ordinated state, but conjecture that it is substantially planar around the double bond except for the methyl substituents on the nitrogens. The co-ordination of the two nitrogen atoms N(1) and N(4) to the chromium is associated with substantial non-planarity of the olefinic ligand. In particular N(1) and N(4) are brought closer together, twisting the two ends of the molecule towards the chromium atom. Also C(7) and C(10) are twisted up out of the plane of the olefin on the opposite side to the methyl groups C(12) and C(11). The effect of these two distortions is to bring the lone pairs on N(1) and N(4) into approximately sp^3 hybrid orbitals directed along the Cr–N bond axis. The two non-co-ordinated nitrogen atoms N(2) and N(3) have shorter bond lengths and a rather flattened tetrahedral geometry, presumably indicating partial conjugation involving the nitrogen lone-pair orbitals and the π orbitals on C(5)–C(6). In fact the bond length of 1.337(7) Å for C(5)–C(6) is that expected for an isolated double bond, and the average length of 1.41(1) Å for the N(2)–C(5) and N(3)–C(6) bonds is that expected for a single bond between sp^2-hybridised C and N atoms. Other bond lengths within the olefinic ligand are consistent with single bonds between atoms where C(5), N(2), C(6), and N(3) are sp^2 hybridised and the rest are sp^3 hybridised. The reason why N(2) and

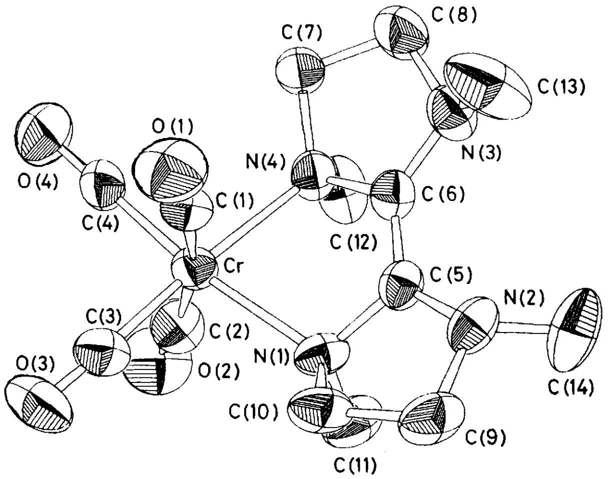

FIGURE 2 View of [$\mathrm{Cr(CO)_4(L^{Me}{}_2}$-*NN''*)] showing the bond lengths and numbering system used and thermal motion of atoms refined (50% probability ellipsoids)

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[28] G. Clevy and G. L. Nelson, '^{13}C n.m.r. for Organic Chemists,' Wiley–Interscience, 1972, and refs. therein.

[29] R. J. Sundberg, R. F. Bryan, I. F. Taylor, jun., and H. Taube, *J. Amer. Chem. Soc.*, 1974, **96**, 381.

[30] C. K. Johnson, Publication ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

N(3) do not have trigonal planar bonding, as seen for instance in amides, is presumably due to the need to minimise non-bonded contacts between methyl groups C(13) and C(14).

The average Cr–N and Cr–C(O) (*trans* to N) bond lengths of 2.20(1) and 1.82(1) Å may be compared to those in *fac*-[Cr(CO)$_3${NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$}] [31] where Cr–C(O) is 1.817(4) Å and Cr–N is 2.185(4) Å. The average bond length for Cr–C(*trans* to CO) is 1.90(1) Å, consistent with the effect of competition for Cr–CO π bonding between the two mutually-*trans* carbonyl ligands giving Cr–C bond lengths comparable to those [1.92(4) Å] in [Cr(CO)$_6$].[32] Presumably for steric reasons, the two *trans* carbonyls are bent away from the olefinic ligand such that the angle C(1)–Cr–C(2) is 169.1(2)°, and the Cr–C–O moieties themselves are slightly bent with angles of 173.3(5) at C(1) and 170.7(5)° at C(2). Similar effects in both bond lengths and bonding in carbonyl ligands are seen in the structures of *cis*-[Mo(CO)$_4$(diphos)] [33] and *cis*-[Mo(CO)$_4$(L^{Me})$_2$].[2]

TABLE 5

Intramolecular distances and angles, with estimated standard deviations in parentheses

(a) Bonds (Å)

Cr–C(1)	1.895(7)	N(1)–C(10)	1.491(6)
Cr–C(2)	1.899(8)	N(4)–C(7)	1.502(7)
Cr–C(3)	1.817(6)	N(1)–C(5)	1.457(8)
Cr–C(4)	1.823(5)	N(4)–C(6)	1.447(7)
Cr–N(1)	2.188(4)	C(7)–C(8)	1.520(10)
Cr–N(4)	2.209(4)	C(9)–C(10)	1.521(9)
C(1)–O(1)	1.137(8)	N(3)–C(8)	1.465(7)
C(2)–O(2)	1.143(10)	N(2)–C(9)	1.457(7)
C(3)–O(3)	1.157(7)	N(3)–C(6)	1.402(8)
C(4)–O(4)	1.151(7)	N(2)–C(5)	1.410(7)
N(1)–C(11)	1.497(7)	N(3)–C(13)	1.436(12)
N(4)–C(12)	1.481(7)	N(2)–C(14)	1.446(7)
C(5)–C(6)	1.337(7)		

(b) Angles (°)

N(1)–Cr–N(4)	77.3(3)	N(1)–C(10)–C(9)	104.5(4)
C(3)–Cr–C(4)	90.0(3)	C(10)–C(9)–N(2)	103.0(4)
C(4)–Cr–N(4)	95.1(3)	C(9)–N(2)–C(5)	107.9(5)
C(3)–Cr–N(1)	97.6(3)	N(2)–C(5)–N(1)	110.6(4)
C(1)–Cr–C(2)	169.1(2)	C(6)–N(4)–C(7)	100.6(5)
C(1)–Cr–N(4)	91.6(3)	N(4)–C(7)–C(8)	103.9(4)
C(1)–Cr–N(1)	91.7(3)	C(7)–C(8)–N(3)	103.1(5)
Cr–C(1)–O(1)	173.3(5)	C(8)–N(3)–C(6)	107.7(5)
Cr–C(2)–O(2)	170.7(5)	N(3)–C(6)–N(4)	111.2(4)
Cr–C(3)–O(3)	177.6(5)	C(9)–N(2)–C(14)	116.4(4)
Cr–C(4)–O(4)	177.9(5)	C(5)–N(2)–C(14)	118.3(4)
Cr–N(1)–C(5)	106.7(4)	N(2)–C(5)–C(6)	129.5(6)
Cr–N(4)–C(6)	105.4(4)	N(1)–C(5)–C(6)	119.3(5)
Cr–N(1)–C(11)	114.9(5)	C(8)–N(3)–C(13)	111.4(5)
Cr–N(4)–C(12)	114.8(4)	C(6)–N(3)–C(13)	117.6(5)
C(10)–N(1)–C(11)	108.0(4)	N(3)–C(6)–C(5)	130.4(6)
C(7)–N(4)–C(12)	108.5(4)	N(4)–C(6)–C(5)	118.5(5)
C(5)–N(1)–C(10)	100.2(5)		

(c) Torsion angles (°)

C(10)–N(1)–C(5)–N(2)	30	C(13)–N(3)–C(6)–C(5)	−44
C(10)–N(1)–C(5)–C(6)	−142	C(6)–N(3)–C(8)–C(7)	15
C(11)–N(1)–C(5)–N(2)	−84	C(13)–N(3)–C(8)–C(7)	−116
C(11)–N(1)–C(5)–C(6)	105	C(7)–N(4)–C(6)–N(3)	−28
C(5)–N(1)–C(10)–C(9)	−37	C(7)–N(4)–C(6)–C(5)	151
C(11)–N(1)–C(10)–C(9)	77	C(12)–N(4)–C(6)–N(3)	86
C(9)–N(2)–C(5)–N(1)	−10	C(12)–N(4)–C(6)–C(3)	−94
C(9)–N(2)–C(5)–C(6)	160	C(6)–N(4)–C(7)–C(8)	36
C(14)–N(2)–C(5)–N(1)	125	C(12)–N(4)–C(7)–C(8)	−80
C(14)–N(2)–C(5)–C(6)	−65	N(1)–C(5)–C(6)–N(3)	171
C(5)–N(2)–C(8)–C(10)	−14	N(1)–C(5)–C(6)–N(4)	−8
C(14)–N(2)–C(9)–C(10)	−149	N(2)–C(5)–C(6)–N(3)	2
C(8)–N(3)–C(6)–N(4)	9	N(2)–C(5)–C(6)–N(4)	−178
C(8)–N(3)–C(6)–C(5)	−171	N(4)–C(7)–C(8)–N(3)	−32
C(13)–N(3)–C(6)–N(4)	136	N(2)–C(9)–C(10)–N(1)	32

The distance of the chromium atom from the centre of the C:C bond is 2.94 Å, suggesting that there is unlikely to be any direct interaction involving the filled *d* orbitals on the metal, particularly since there do not appear to be any such orbitals suitably directed for overlap with unfilled π* orbitals on the olefinic ligand.

Calculation of intermolecular contacts shows that there are none significantly shorter than the sum of the relevant van der Waals radii.

EXPERIMENTAL

General Procedures.—All reactions were carried out under an atmosphere of dry dinitrogen. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use and chlorinated solvents were distilled from P_2O_5. 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 dilute Nujol mulls or as dilute solutions using a Perkin-Elmer 457 grating spectrophotometer and ^{1}H n.m.r. spectra were recorded on Varian Associates HA-100, A60, or T60 spectrometers. Melting points were determined in evacuated sealed tubes and are uncorrected. The electron-rich olefins were prepared by literature methods.[5,34] Other starting materials were prepared by standard literature procedures [35-37] and [M(CO)$_6$] (M = Cr, Mo, or W) were used as purchased from Alfa Ventron Ltd.

Crystal Data.—$C_{14}H_{20}CrN_4O_4$, $M = 360.3$, Monoclinic, $a = 9.883(3)$, $b = 15.806(3)$, $c = 12.83(2)$ Å, $\beta = 118.87(2)°$, $U = 1\,694.6$ Å^3, $Z = 4$, $F(000) = 752$. Mo-K_α radiation, $\lambda = 0.709\,26$ Å, μ(Mo-$K\bar{\alpha}$) = 8.9 cm^{-1}. Space group $P2_1/c$ (No. 14) from the systematic absences of $0k0$ for k odd and $h0l$ for l odd.

A flat needle-shaped crystal of orange colour and approximate size 0.5 × 0.25 × 0.12 mm was used for data collection on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell parameters were derived by least-squares treatment of setting angles for 12 reflections. Intensity data out to $\theta = 20°$ were measured using the ω—2θ step scan technique with Mo-K_α radiation (graphite-crystal monochromator). Reflections were scanned in 80 steps of 0.5 s each with background counts of 20 s at each end of the scan. Three standard reflections were remeasured after every 100 reflections and showed no significant changes. After correction for Lorentz and polarisation effects, but not for absorption, data with $I < 3\sigma(I)$ based on counting statistics were classified as unobserved, leaving 1 225 significant reflections which were used in the structure analysis.

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[31] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

[32] L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1350.

[33] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc. (A)*, 1971, 1644.

[34] H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, 1966, **88**, 850; *J. Org. Chem.*, 1966, **31**, 3427.

[35] R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

[36] W. R. Boon, *J. Chem. Soc.*, 1947, 309.

[37] R. B. King, 'Organometallic Syntheses,' Academic Press, 1965, vol. 1.

The positions of all non-hydrogen atoms were located by the usual Patterson and Fourier techniques and their positions and anisotropic thermal parameters refined by full-matrix least squares to a R 0.06 using a unit-weighting scheme. At this stage a difference-Fourier synthesis revealed the positions of all the hydrogen atoms which were included in further refinement with fixed positions and temperature factors of $B = 4.0$ Å^2. Refinement of the structure was continued with an empirical weighting scheme defined as $\omega = 1/[1 + \{(F_o - 26)/56\}^2]$ and converged at $R = 0.034$, $R' = 0.039$, with a maximum shift: error ratio of 0.0002. The estimated standard deviation of an observation of unit weight was 1.64. A final difference-Fourier synthesis was everywhere <0.2eÅ^{-3}.

Initial data processing was with local programmes, and the structure solution and refinement was carried out using the '*X*-RAY '72' programme system.[38] Scattering factors for neutral atoms and dispersion corrections for chromium were taken from ref. 39. The final atom parameters are listed in Table 6. The anisotropic temperature factors and hydrogen atom positions, together with a list of final structure factors have been deposited as Supplementary Publication No. SUP 22096 (10 pp.).*

TABLE 6

Final atom co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
Cr	−0 221(1)	1 305(1)	2 273(1)
N(1)	−2 280(5)	2 106(2)	1 454(3)
N(2)	−4 421(5)	2 309(3)	1 776(4)
N(3)	−4 077(5)	0 374(3)	2 431(4)
N(4)	−2 097(4)	0 397(2)	1 896(4)
O(1)	0 429(5)	1 639(3)	4 888(4)
O(2)	0 135(5)	1 070(3)	−0 007(4)
O(3)	2 140(5)	2 637(3)	2 804(4)
O(4)	2 325(5)	0 051(3)	3 449(5)
C(1)	0 091(6)	1 512(3)	3 885(6)
C(2)	−0 125(6)	1 133(2)	0 794(6)
C(3)	1 197(7)	2 131(3)	2 584(5)
C(4)	1 326(7)	0 527(3)	2 975(6)
C(5)	−3 417(5)	1 701(3)	1 713(4)
C(6)	−3 268(5)	0 880(3)	2 005(4)
C(7)	−1 733(6)	−0 265(3)	2 871(5)
C(8)	−3 283(7)	−0 444(3)	2 802(6)
C(9)	−3 793(7)	3 144(3)	1 780(5)
C(10)	−2 157(6)	2 948(3)	2 038(5)
C(11)	−2 977(7)	2 236(4)	0 091(5)
C(12)	−2 752(6)	−0 029(3)	0 681(6)
C(13)	−4 363(9)	0 718(4)	3 376(7)
C(14)	−6 064(7)	2 203(4)	0 984(6)

$[Cr(CO)_5L^R]$ (R = Me or Et).—Hexacarbonylchromium(0) (1.10 g, 5.0 mmol) and bi(1,3-dimethylimidazolidin-2-ylidene) (0.558 g, 3.0 mmol) were heated together in decalin (10 cm^3) at 150 °C (2 h). CO was evolved and a small quantity of yellow powder precipitated. The mixture was cooled to 40 °C, filtered, and the volume of decalin was reduced to *ca.* 2 cm^3 by vacuum distillation, and to dryness under high vacuum at 20 °C. The residue was extracted with ether (20 cm^3) and hexane (10 cm^3) was added. This was filtered and the filtrate cooled (−30 °C) for several days to afford white crystals of *pentacarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*chromium*(0) (0.94 g, 65%). The same procedure with bi(1,3-diethylimidazolidin-2-ylidene) gave the ethyl analogue.

cis-$[Cr(CO)_4(L^R)_2]$ (R = Me *or* Et).—Hexacarbonylchromium(0) (1.10 g, 5.0 mmol) and bi(1,3-diethylimidazolidin-2-ylidene) (1.89 g, 7.5 mmol) were heated together in decalin (20 cm^3) to 180 °C (3 h). CO was evolved and the solution slowly became yellow, and on cooling (below 120 °C) yellow microcrystals of cis-*tetracarbonylbis*(1,3-*diethylimidazolidin*-2-*ylidene*)*chromium*(0) (2.08 g, 100%) were deposited. These were filtered and washed with hexane (6 × 5 cm^3) and dried under vacuum. The same procedure with bi(1,3-dimethylimidazolidin-2-ylidene) gave the methyl analogue.

$[Cr(\eta\text{-}C_6H_6)(CO)_2L^{Me}]$.— η-Benzenetricarbonylchromium(0) (0.40 g, 1.87 mmol) and bi(1,3-dimethylimidazolidin-2-ylidene) (0.59 g, 3.0 mmol) were heated together in decalin (5 cm^3, 180 °C, 2 h). The solution became deep orange in colour and on cooling a yellow precipitate formed {*cis*-$[Cr(CO)_4(L^{Me})_2]$}. Hexane (5 cm^3) was added and the mixture cooled (−30 °C, 48 h). The solid product was filtered off and extracted with ether (3 × 10 cm^3) to give an orange solution. The volume of ether was reduced to *ca.* 15 cm^3 and cooling (−25 °C, 7 d) yielded orange crystals of η-*benzene*(*dicarbonyl*)(1,3-*dimethylimidazolidin*-2-*ylidene*)-*chromium*(0) (0.025 g, 15%).

cis-$[Cr(AsPh_3)(CO)_4L^{Me}]$.—$[Cr(CO)_5L^{Me}]$ (0.11 g, 0.38 mmol) and $AsPh_3$ (0.40 mmol) in methylcyclohexane (10 cm^3) were refluxed (15 h) and then cooled (−15 °C, 24 h) to afford yellow crystals of cis-*tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylarsine*)*chromium*(0) (0.075 g, 35%).

cis-$[Cr(CO)_4\{C(OMe)Me\}L^{Me}]$.—To $[Cr(CO)_5L^{Me}]$ (0.60 g, 2.07 mmol) in diethyl ether (10 cm^3), LiMe (3.2 cm^3, 0.7 mol dm^{-3}) in ether was added dropwise (0 °C, 1 h) to form a yellow-orange precipitate. $MeOSO_2F$ (0.24 g, 2.1 mmol) was added and the mixture stirred (5 °C, 30 min). Degassed H_2O (10 cm^3) was then added and the stirring continued (15 min). The ether layer was separated and the aqueous residue extracted with diethyl ether (3 × 5 cm^3), the extracts combined, dried over anhydrous magnesium sulphate, and filtered. Diethyl ether was removed *in vacuo* and the residue dissolved in diethyl ether–hexane (10 cm^3, 1 : 1) and filtered. Cooling (−25 °C, 7 d) afforded crimson crystals of cis-*tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(1-*methoxyethylidene*)*chromium*(0) (0.27 g, 40%).

$[M(CO)_4(L^R{}_2\text{-}NN'')]$ (M = Cr, Mo, or W, R = Me; M = Mo, R = Et).—To bicyclo[2.2.1]hepta-2,5-dienetetracarbonylchromium(0) (0.18 g, 0.7 mmol) in toluene (10 cm^3) bi(1,3-dimethylimidazolidin-2-ylidene) (0.16 g, 0.86 mmol) in hexane (10 cm^3) was added dropwise (0 °C, 10 min). The solution changed colour to orange and a small quantity of dark material precipitated. The mixture was filtered, and hexane was added until a slight cloudiness developed. Cooling (−20 °C, 72 h) afforded orange-yellow crystals of cis-[*bi*(1,3-*dimethylimidazolidin*-2-*ylidene*-*NN''*)-*tetracarbonylchromium*(0) (0.18 g, 70%). Several recrystallisations were necessary before the material was analytically pure, and the sample used for the crystal structure determination was obtained by cooling (−25 °C) a saturated solution in diethyl ether(10 cm^3).

$[Mo(CO)_4(L'^{Me}{}_2\text{-}NN'')]$.—To bicyclo[2.2.1]hepta-2,5-dienetetracarbonylmolybdenum(0) (0.55 g, 1.83 mmol) in toluene

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

[38] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, 'The *X*-ray System,' version of July 1972; Technical Report TR 72-192 of the Computer Science Center, University of Maryland, 1972.

[39] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17; D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

(5 cm^3), bi(hexahydro-1,3-dimethylpyrimidin-2-ylidene) (0.45 g, 2.0 mmol) in toluene (5 cm^3) was added dropwise (40 °C, 30 min); the initial straw-coloured solution became orange-yellow, and was then filtered. Hexane (5 cm^3) was added to the filtrate and after cooling (−15 °C, 5 h) it was refiltered, more hexane (5 cm^3) was added, and it was further cooled (−25 °C, 72 h) to afford yellow microcrystals of cis-*[bi(hexahydro-1,3-dimethylpyrimidin-2-ylidene)*-NN″*]tetracarbonylmolybdenum*(0) (0.40 g, 50%). This material was recrystallised three times from toluene–hexane to obtain an analytically pure sample.

TABLE 7

Distances (Å) of atoms from mean planes through various sets of atoms with equations to the planes in the form $pX + qY + rZ = s$ where X, Y, and Z are co-ordinates in Å with respect to the axis set *a,b,c*.

Atoms not defining the plane are designated †

Plane 1 $0.398\,9X - 0.169\,9Y - 0.901\,1Z = 0.714\,6$

[Cr 0.03, C(3) −0.01, C(4) 0.00, N(1) 0.00, N(4) −0.01, C(7) † −0.87, C(10) † −0.89, N(3) † −1.43, N(2) † −1.29]

Plane 2 $-0.205\,1X - 0.198\,1Y - 0.958\,5Z = 3.4948$

[N(1) −0.06, N(2) 0.01, N(3) −0.05, N(4) 0.03, C(5) 0.06, C(6) 0.02]

Plane 3 $-0.140\,8X - 0.349\,6Y - 0.026\,3Z = -3.268\,2$

[N(3) 0.0, C(6) 0.0, C(8) 0.0, C(13) † −1.02, N(4) † 0.20, C(7) † −0.38]

Plane 4 $-0.043\,9X + 0.023\,8Y - 0.998\,8Z = -2.032\,0$

[N(2) 0.0, C(5) 0.0, C(9) 0.0, N(1) † 0.24, C(10) † −0.35, C(14) † 0.90]

[Mo(CO)$_4$(tdae-*NN*″)].—(*a*) To bicyclo[2.2.1]hepta-2,5-dienetetracarbonylmolybdenum(0) (0.44 g, 1.46 mmol) in toluene (7 cm^3) tetrakisdimethylaminoethylene (0.30 g, 1.5 mmol) was added and the mixture heated (110 °C, 2 h). After cooling, hexane (5 cm^3) was added and the mixture filtered through Celite to give a deep yellow solution. Further addition of hexane (5 cm^3) and cooling (−20 °C, 14 d) afforded yellow crystals of cis-*tetracarbonyl[tetrakisdimethylaminoethylene*-NN″*]molybdenum*(0) (0.24 g, 40%).

(*b*) Hexacarbonylmolybdenum(0) (0.26 g, 1.0 mmol) and tetrakisdimethylaminoethylene (0.22 g, 1.1 mmol) were heated together in decalin (5 cm^3) (180 °C, 30 min) to form a dark solution. The solvent was removed *in vacuo*, excess [Mo(CO)$_6$] was removed by sublimation, and the residue washed with cold (0 °C) hexane (2 × 10 cm^3) and then extracted with warm (70 °C) toluene (2 × 5 cm^3) to give a deep yellow solution. Addition of hexane, followed by filtration, and cooling (−20 °C, 7 d) afforded yellow crystals of *cis*-tetracarbonyl[tetrakisdimethylaminoethylene-*NN*″]-molybdenum(0) (0.13 g, 32%).

2-*Imidazoline*.—Redistilled ethylenediamine (6.0 g, 0.1 mol) and *NN*-dimethylformamide dimethyl acetal (11.9 g, 0.1 mol) were heated together (100 °C, 2 h). NMe$_2$H and MeOH were allowed to escape *via* a hot water condenser into a cold (−78 °C) trap. When the collection was quantitative the heating was stopped and the oily residue was distilled *in vacuo* to afford, upon cooling, white waxy crystals of 2-imidazoline (6.0 g, 85%).

cis-[Mo(CO)$_4${N:C(H)N(H)CH$_2$CH$_2$}$_2$] *and* fac-[Mo(CO)$_3$-{N:C(H)N(H)CH$_2$CH$_2$}$_3$].—To hexacarbonylmolybdenum(0) (0.12 g, 0.45 mmol) in toluene (10 cm^3) 2-imidazoline (0.09 g, 1.3 mmol) was added and the mixture warmed (100 °C, 10 min). CO was liberated, the solution became yellow, and a pale yellow solid precipitated. The mixture was filtered, and to the filtrate hexane (10 cm^3) was added. Cooling (−20 °C, 48 h) afforded a small quantity of yellow crystals, cis-*tetracarbonylbis(2-imidazoline*-N)*molybdenum*(0) (0.03 g, 20%). The pale yellow residue, after filtration, was washed with ether (4 × 5 cm^3) and dried *in vacuo* to afford fac-*tricarbonyltris(2-imidazoline*-N)*molybdenum*(0) (0.13 g, 75%).

cis-[Mo(CO)$_4${N:C(H)N(Et)CH$_2$CH$_2$}$_2$] and [Mo(CO)$_5$-{N:C(H)N(Et)CH$_2$CH$_2$}].—A mixture of *N*-ethyldiaminoethane (0.60 g, 6.7 mmol) and *NN*-dimethylformamide dimethyl acetal (0.90 g, 7.5 mmol) was warmed (50 °C, 10 min) in C$_6$H$_{11}$Me (10 cm^3) and then [Mo(CO)$_6$] (1.31 g, 5.0 mmol) was added and the mixture refluxed (1 h). Evolution of CO occurred and on cooling a yellow solid precipitated. This was removed by filtration, and recrystallised twice from toluene–hexane (−20 °C, 48 h) to afford deep yellow crystals of cis-*tetracarbonylbis*(N′-*ethyl-2-imidazoline*-N)-*molybdenum*(0) (0.88 g, 44%). The C$_6$H$_{11}$Me filtrate was evaporated to dryness *in vacuo* and the residue extracted with warm hexane (2 × 5 cm^3, 40 °C). Cooling (−30 °C) afforded pale yellow crystals of *pentacarbonyl*(N′-*ethyl*-2-*imidazoline*-N)*molybdenum*(0) (0.45 g, 27%).

[RhCl(1,5-cod){N:C(H)N(H)CH$_2$CH$_2$}].—A mixture of di-μ-chloro-bis[1,5-cyclo-octadienerhodium(I)] (0.49 g, 1.0 mmol) and 2-imidazoline (0.14 g, 2.0 mmol) was refluxed in toluene (10 cm^3, 1 h). Cooling (−20 °C) afforded small orange-yellow crystals and addition of hexane (10 cm^3) gave a second crop of crystals. These were collected by filtration, washed with diethyl ether (5 × 5 cm^3), and dried *in vacuo* to afford *chloro(cyclo-octa-*1,5-*diene)*(2-*imidazoline*-N)*rhodium*(I) (0.31 g, 55%).

The Effect of Heat on [M(CO)$_4$(L$^{\text{R}}_2$-*NN*″)].—(*a*) (M = Cr *or* Mo; R = Me). [M(CO)$_4$(L$^{\text{Me}}_2$-*NN*″)] (M = Mo or Cr) (0.08 mmol) in dry benzene (5 cm^3) was warmed to 80 °C (30 min) under N$_2$ in a Schlenk tube. The colour of the solution changed from orange to pale yellow and some dark oily solid precipitated. Solution i.r. spectroscopy showed the presence of a pentacarbonyl species. The solvent was reduced in volume and a ^{1}H n.m.r. spectrum was recorded which showed the presence of [M(CO)$_5$L$^{\text{Me}}$] (M = Cr and Mo) and also that of the free electron-rich olefin, L$^{\text{Me}}_2$.

(*b*) M = Mo, R = Me: *a differential-scanning calorimetric experiment*. [Mo(CO)$_4$(L$^{\text{Me}}_2$-*NN*″)] (0.02 g, 0.05 mmol) was sealed in a differential-scanning calorimetric aluminium pan and heated at 5 °C min^{-1} to 140 °C under N$_2$, at which point an exothermic transition occurred. After cooling, the residual solid in the sample pan was examined by i.r. and ^{1}H n.m.r. spectroscopy, and identified as substantially *cis*-[Mo(CO)$_4$(L$^{\text{Me}}$)$_2$], but with a small quantity of a dark unidentified material. Similar experiments with the Cr and W analogues, [Mo(CO)$_4$(L$'^{\text{Me}}_2$-*NN*″)], and [Mo(CO)$_4$(tdae-*NN*″)] only afforded dark unidentified materials; no products containing a co-ordinated carbene fragment were observed.

(*c*) (*i*) M = Mo, R = Et: ^{1}*H n.m.r. sealed-tube experiments*. To [Mo(CO)$_4$(L$^{\text{Et}}_2$-*NN*″)] (0.112 g, 0.24 mmol) in a ^{1}H n.m.r. tube, 0.4 cm^3 of C$_6$H$_6$ was distilled in and the tube sealed *in vacuo*, and allowed to warm to room temperature. The initial spectrum was recorded and then the tube was slowly heated in an oven up to 90 °C (48 h) whilst spectra were recorded periodically.

(*ii*) M = Mo, R = Et, +L^{Me}_2. To [$Mo(CO)_4$(L^{Et}_2-*NN''*)] (0.110 g, 0.24 mmol) in a ^1H n.m.r. tube, L^{Me}_2 (0.050 g) in C_6H_6 (0.4 cm^3) was added and the tube sealed *in vacuo* and allowed to warm to room temperature. The initial spectrum was recorded and then the tube was slowly heated to 60 °C (10 h) and then to 90 °C (10 h) whilst spectra were recorded periodically.

(*iii*) M = Mo, R = Et, +[$Mo(CO)_6$]. To [$Mo(CO)_4$-(L^{Et}_2-*NN''*)] (0.112 g, 0.24 mmol) in a ^1H n.m.r. tube [$Mo(CO)_6$] (0.066 g, 0.25 mmol) and C_6H_6 (0.4 cm^3) were added and the tube sealed under vacuum and slowly heated, eventually to 100 °C (48 h), whilst ^1H n.m.r. spectra were periodically recorded.

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