Carbene Complexes. Part 10.[1] Electron-rich Olefin-based Mono-, Bis-, and Tris-carbene-tungsten(0) Complexes and some Derived Six- and Seven-co-ordinate Mono- and Bis-carbene-dihalogenotungsten(II) and Related Molybdenum(II) Species †

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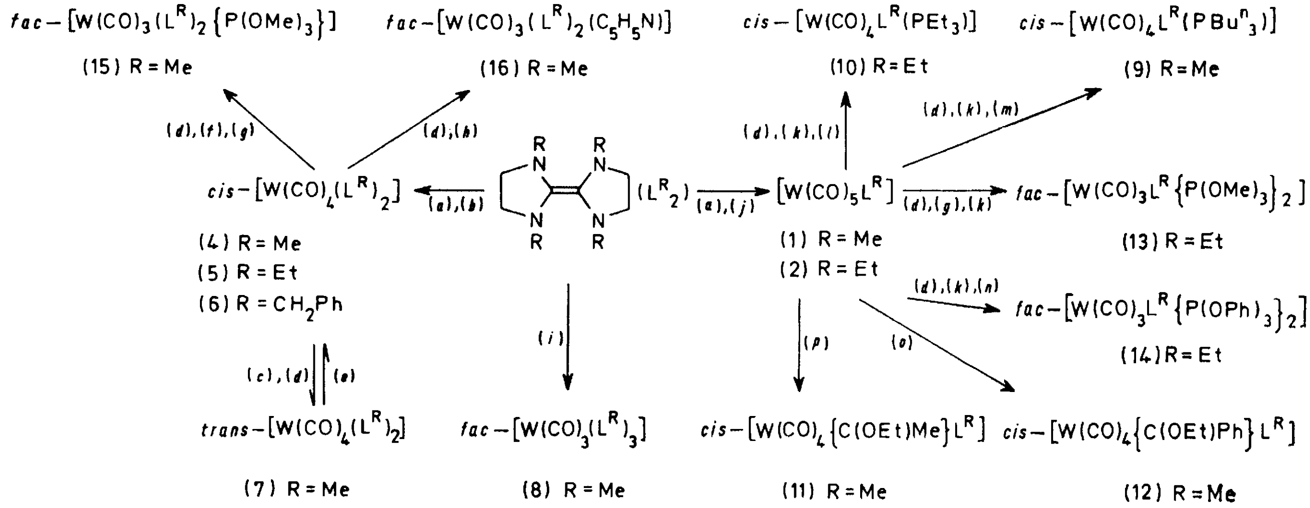
Stable mono- and bis-carbene-tungsten(0) complexes $[W(CO)_5L^R]$ or *cis*-$[W(CO)_4(L^R)_2]$ [L^R = $:CN(R)CH_2CH_2NR$ (R = Me, Et, or CH_2Ph)] are obtained by heating $[W(CO)_6]$ with the electron-rich olefin $[:CN(R)CH_2CH_2NR]_2$, $L^R{}_2$. The six-membered chelate olefin $[:CN(Me)(CH_2)_3NMe]_2$, $L'^{Me}{}_2$, is less reactive, only forming $[W(CO)_5L'^{Me}]$. The *cis*-dicarbenetungsten(0) complexes are isomerised photochemically to the *trans* species, but readily revert thermally to the former. Bases react with (*a*) $[W(CO)_5L^R]$ to yield *cis*-$[W(CO)_4(L^R)Q]$ (Q = PEt_3 or $PBu^n{}_3$), *fac*-$[W(CO)_3L^RQ_2]$ [Q = $P(OMe)_3$ or $P(OPh)_3$], or {using successively LiR' (R' = Me or Ph) and $[OEt_3][BF_4]$} *cis*-$[W(CO)_4\{C(OEt)R'\}L^R]$, or (*b*) *cis*-$[W(CO)_4(L^R)_2]$ to afford *fac*-$[W(CO)_3(L^R)_2Q]$ [Q = C_5H_5N or $P(OMe)_3$]. The tricarbene complex *fac*-$[W(CO)_3(L^{Me})_3]$, obtained from $[W(CO)_3(\eta\text{-mesitylene})]$, is rather unstable. The *cis*-dicarbene complexes *cis*-$[M(CO)_4(L^R)_2]$ (M = Mo or W) with dihalogens give the metal(II) species $[M(CO)_2(L^R)_2X_2]$ (M = Mo, R = Et, X = I, Br, or Cl; M = W, R = Me or Et, X = I) and $[M(CO)_3(L^R)_2X_2]$ (M = W, R = Me or Et, X = I). The latter provides an example of a CO-carrying system, the interconversion of $[W(CO)_3I_2(L^R)_2]$ and $[W(CO)_2I_2(L^R)_2]$ + CO being reversible as a function of temperature. The monocarbene complexes $[M(CO)_5L^R]$ (M = Mo or W) behave differently, yielding respectively $[IL^R][Mo(CO)_4I_3]$ or $[W(CO)_4I_2(L^R)]$ (R = Me). The frequency $\nu(CN_2)$ is at 1 500—1 480 cm^{-1} for the carbene-tungsten(0), but at 1 530—1 500 cm^{-1} for the carbene-molybdenum(II) and -tungsten(II), complexes; values of $\nu(CO)$ are generally low, in accordance with the strong σ-donor character of the carbene ligand. The value of $\Delta G^\ddagger$ for W–$C_{carb.}$ rotation in *cis*-$[W(CO)_4(L^R)_2]$ is *ca.* 10 kcal mol^{-1} and *ca.* 14 kcal mol^{-1} in $[W(CO)_4I_2(L^R)]$. Carbon-13 n.m.r. chemical shifts for $C_{carb.}$ and CO in the tungsten(0) species are comparable, but distinguishable by ^1H decoupling and ^1H off-resonance studies, and are in the range 200—220 p.p.m. downfield from $SiMe_4$. Values for $^1J(^{183}W-^{13}C)$ and $^2J(^{13}C-^{31}P)$ are provided.

IN our previous publication [1] we described the synthesis and some chemistry of zerovalent mono- and bis-carbene-molybdenum(0) complexes. Here we report the preparation of some mono-, bis-, and tris-carbene-tungsten(0) complexes and their reaction with neutral ligands. Additionally, some reactions of mono- and bis-carbene-molybdenum(0) or -tungsten(0) complexes with dihalogens are described, affording interconvertible six- and seven-co-ordinate carbene-molybdenum(II) and -tungsten(II) derivatives. The characterised new compounds are listed in Table 1.



SCHEME 1 Synthesis and reactions with neutral ligands of electron-rich olefin-derived mono-, bis-, and tris-carbene-tungsten(0) complexes. (*a*) Decalin $[W(CO)_6]$; (*b*) >180 °C; (*c*) acetone; (*d*) *hν*, 25 °C; (*e*) solid state, 140—160 °C; (*f*) toluene; (*g*) $P(OMe)_3$; (*h*) OEt_2, pyridine; (*i*) no solvent, 110 °C, $[W(CO)_3(mes)]$; (*j*) decalin, 160—180 °C; (*k*) hexane; (*l*) PEt_3; (*m*) $PBu^n{}_3$; (*n*) $P(OPh)_3$; (*o*) LiPh, OEt_2, 0 °C followed by $[OEt_3][BF_4]$, OEt_2–H_2O, 10 °C; (*p*) LiMe, OEt_2, 0 °C followed by $[OEt_3][BF_4]$, OEt_2–H_2O, 10 °C.

RESULTS AND DISCUSSION

The electron-rich olefin $[:CN(R)CH_2CH_2NR]_2$ ($L^R{}_2$; R = Me, Et, or CH_2Ph) readily reacted under forcing conditions with $[W(CO)_6]$, Scheme 1, to afford $[W(CO)_5L^R]$

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† No reprints available.

[1] Part 9, M. F. Lappert, G. McLaughlin, and P. L. Pye, *J.C.S. Dalton*, preceding paper.

[R = Me (1); or Et (2)] or, with an excess of olefin, *cis*-$[W(CO)_4(L^R)_2]$ [R = Me (4); or Et (5)]. Higher temperatures and longer reaction times are necessary than for the analogous molybdenum(0) species [1,2] because of the greater resistance to CO displacement from the heavier metal, also observed in other, *e.g.* PPh_3, ligand-substitution reactions.[3] As for the molybdenum analogue, u.v. irradiation of *cis*-$[W(CO)_4(L^{Me})_2]$, (4), as a saturated acetone solution, caused precipitation of *trans*-$[W(CO)_4(L^{Me})_2]$, (7); although heating in the solid state or in solution resulted in the eventual reformation of the thermodynamically preferred *cis* isomer, the change was less rapid than for the molybdenum analogue. Related *cis* $\rightleftharpoons$ *trans* isomerisations have been studied in detail for other $[M(CO)_4L_2]$ species [L = $\overline{:\mathrm{CN(Me)CH{=}CHN}}\mathrm{Me}$ or a similar ligand].[4] Other routes to carbenetungsten(0) complexes have been described,[5,6] all yielding relatively stable species. The original Fischer technique {$[M(CO)_6]$ and successively LiR and $[R']^+$}, however, is really only applicable to monocarbene complex formation, even though one bis derivative has been described,[7] obtained in *ca.* 1—2% yield. Some closely related compounds containing the carbene ligand $\overline{:\mathrm{CN(Me)CH{=}CHN}}\mathrm{Me}$ have also been reported.[4,8] The route to the latter type involved dihydrogen elimination [equation (1)], followed by thermal or photochemical disproportionation [equation (2)]. The use of the electron-rich olefin, L^R_2, has the considerable advantage of only requiring one direct step from the readily available hexacarbonyl, either the mono- or bis-carbene derivative being obtained in high yield depending on stoicheiometry.

TABLE 1

Mono- and oligo-carbene complexes of W^0, W^{II}, and Mo^{II}, and some related complexes, and their characterisation

Complex	No.	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis (%) [a]			
					C	H	N	X
$[W(CO)_5L^{Me}]$	(1)	65	118	White	28.2 (28.5)	2.4 (2.4)	6.5 (6.6)	
$[W(CO)_5L^{Et}]$	(2)	75	102	Cream	32.0 (32.5)	3.2 (3.1)	6.4 (6.2)	
$[W(CO)_5L'^{Me}]$	(3)	15	102	Cream	29.6 (30.3)	2.8 (2.8)	6.3 (6.4)	
cis-$[W(CO)_4(L^{Me})_2]$	(4)	100	278 (decomp.)	Yellow	33.8 (34.2)	4.3 (4.1)	11.4 (11.4)	
cis-$[W(CO)_4(L^{Et})_2]$	(5)	95	210—211	Bright yellow	39.5 (39.4)	5.2 (5.2)	10.5 (10.2)	
cis-$[W(CO)_4(L^{Ch_2Ph})_2]$	(6)	70	230—232	Yellow	57.2 (57.3)	4.7 (4.6)	7.1 (7.0)	
trans-$[W(CO)_4(L^{Me})_2]$	(7)	60	*b*	Orange-red	33.9 (34.2)	4.2 (4.1)	11.4 (11.4)	
fac-$[W(CO)_3(L^{Me})_3]$	(8)	70	151 (decomp.)	Pale yellow	37.6 (38.4)	5.4 (5.4)	14.6 (14.9)	
cis-$[W(CO)_4L^{Me}(PBu^n_3)]$	(9)	70	97	Pale yellow	42.3 (42.3)	6.2 (6.2)	4.8 (4.7)	
cis-$[W(CO)_4L^{Et}(PEt_3)]$	(10)	90	118	Pale yellow	38.1 (37.8)	5.4 (5.4)	5.3 (5.2)	
cis-$[W(CO)_4\{C(OEt)Me\}L^{Me}]$	(11)	55	93	Red	32.9 (33.4)	3.8 (3.8)	6.1 (6.0)	
cis-$[W(CO)_4\{C(OEt)Ph\}L^{Me}]$	(12)	60	103	Deep brown	40.9 (40.9)	3.9 (3.8)	5.4 (5.3)	
fac-$[W(CO)_3L^{Et}\{P(OMe)_3\}_2]$	(13)	95	170	White	30.4 (30.0)	5.1 (5.0)	4.4 (4.4)	
fac-$[W(CO)_3L^{Et}\{P(OPh)_3\}_2]$	(14)	85	144	White	54.3 (54.5)	4.3 (4.4)	2.9 (3.1)	
fac-$[W(CO)_3(L^{Me})_2\{P(OMe)_3\}]$	(15)	70	{(slow decomp.) >135	Pale yellow	32.7 (32.6)	5.1 (4.9)	9.3 (9.5)	
fac-$[W(CO)_3(L^{Me})_2(C_5H_5N)]$	(16)	60	175 (decomp.)	Purple	39.4 (39.8)	4.6 (4.6)	12.9 (12.9)	
$[Mo(CO)_3I_2(L^{Me})_2]$ [c]	(17)	*c*	*c*	Yellow				
$[Mo(CO)_2I_2(L^{Me})_2]$	(18)	80	115 (decomp.)	Blue-black	23.9 (23.9)	3.4 (3.4)	9.2 (9.3)	
$[Mo(CO)_2I_2(L^{Et})_2]$	(19)	70	101 (decomp.)	Blue-black	29.3 (29.2)	4.4 (4.3)	8.5 (8.5)	
$[Mo(CO)_2Cl_2(L^{Et})_2]$	(20)	70	114 (decomp.)	Blue	40.2 (40.4)	6.0 (5.9)	11.6 (11.8)	Cl, 15.1 (15.0)
$[MoBr_2(CO)_2(L^{Et})_2]$	(21)	80	135 (decomp.)	Ultramarine	34.2 (34.1)	5.2 (5.0)	9.9 (9.9)	Br, 28.6 (28.4)
$[W(CO)_3I_2(L^{Me})_2]$	(22)	85	123 (decomp.)	Orange-yellow	21.9 (21.8)	2.9 (2.8)	7.6 (7.8)	
$[W(CO)_3I_2(L^{Et})_2]$	(23)	65	104 (decomp.)	Orange-yellow	26.6 (26.3)	3.6 (3.6)	7.2 (7.2)	I, 32.5 (32.8)
$[W(CO)_2I_2(L^{Et})_2]$	(24)	70	104 (decomp.)	Blue-black	25.9 (25.8)	3.8 (3.8)	7.4 (7.5)	I, 34.0 (34.0)
$[W(CO)_4I_2(L^{Me})]$	(25)	40	102 (decomp.)	Orange-yellow	16.8 (16.7)	1.8 (1.5)	4.1 (4.3)	
$[HL^{Et}][WBr_3(CO)_3L^{Et}]$	(26)	50	95	Yellow	26.9 (26.8)	4.0 (3.9)	7.3 (7.4)	Br, 31.3 (31.5)
$[IL^{Me}][Mo(CO)_4I_3]$	(27)	80	96 (decomp.)	Orange-yellow	13.4 (13.3)	1.2 (1.2)	3.4 (3.4)	I, 62.6 (62.4)
$[HL^{Et}]_2[WBr_2(CO)_4]$	(28)	65		Yellow				

[a] Calculated values are given in parentheses. [b] Isomerises to *cis* form, 160—180 °C. [c] Only observed in solution below 0 °C, saturated with CO.

Despite being unavailable directly from $[W(CO)_6]$, the unusual neutral triscarbene complex, *fac*-$[W(CO)_3(L^{Me})_3]$ (8), can be obtained by displacement of mesitylene from $[W(CO)_3(mes)]$ (mes = η-mesitylene) in the absence of solvent (Scheme 1), the basic method found useful for the synthesis of other trisubstituted metal(0) derivatives.[3,9,10] Unlike the other carbenetungsten(0) complexes, (8) is rather labile and readily decomposes in various solvents, including Me_2CO, $CHCl_3$, or dimethyl sulphoxide (dmso), but only slowly (*ca.* 1 h) in CH_2Cl_2 or in the solid state; the only identified decomposition product is the biscarbene complex (4), this also being formed from L^{Me}_2, and $[W(CO)_3(cht)]$ (cht = η-cyclo-

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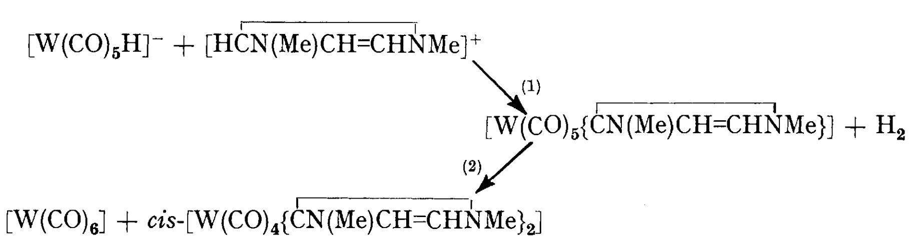
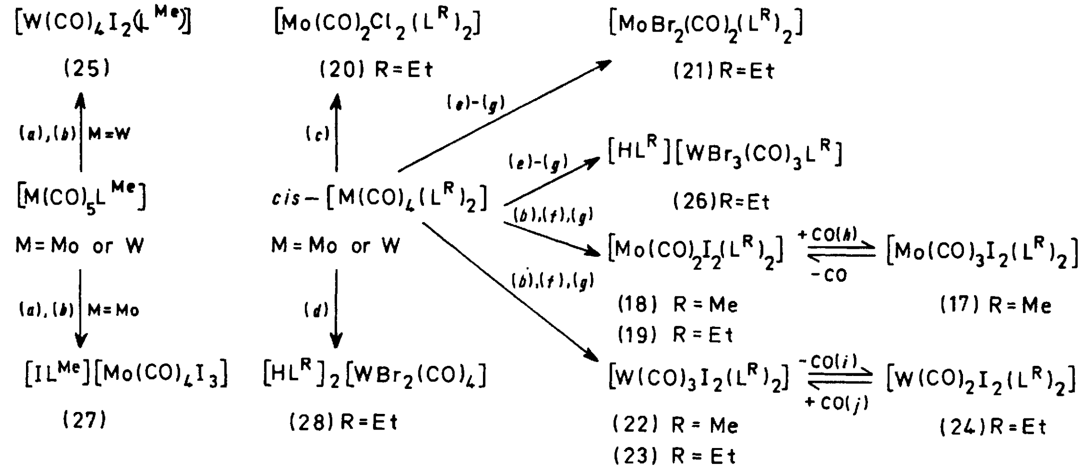
hepta-1,3,5-triene) in solution. Similar decomposition to a bis(ligand) complex has been observed for other nucleophiles, including PPh_3[11] and MeCN;[12] however, in general the tris complexes are more stable for W than for Mo.[1]

Although the thermal reactions of either $[W(CO)_5L^R]$, (2) or (3), or *cis*-$[W(CO)_4(L^R)_2]$ (4; R = Me) with a neutral donor to form mixed-ligand complexes have generally been unsuccessful, photochemical syntheses with PR'_3 (R' = Et or Bu^n) are facile, (1) or (2) affording *cis*-$[W(CO)_4L^R(PR'_3)]$, (9) or (10). The better π-acceptor ligands, $P(OR'')_3$ (R'' = Me or Ph), readily yield *fac*-$[W(CO)_3L^R\{P(OR'')_3\}_2]$, (13) or (14). From (4), *fac*-$[W(CO)_3(L^{Me})_2Q]$ [Q = $P(OMe)_3$ (15), or C_5H_5N (16)] can be obtained. The unusual mixed biscarbene complexes (11) and (12) were synthesised from (1) by a Fischer-type carbene synthesis.





SCHEME 2 Some reactions of mono- and bis-carbene-molybdenum(0) and -tungsten(0) complexes with dihalogens. (*a*) OEt_2, −10 °C; (*b*) I_2; (*c*) Cl_2, CCl_4, −10 °C; (*d*) HBr, C_6H_6, 5 °C; (*e*) Br_2; (*f*) CH_2Cl_2; (*g*) −20 °C; (*h*) < −30 °C; (*i*) >30 °C; (*j*) <30 °C.

All the new tungsten(0) complexes, except the triscarbene (8), are moderately stable to oxygen both in the solid state and in solution, although (13) and (14) slowly lose $P(OR'')_3$.

Biscarbonylhalogeno(neutral ligand)metal(II) complexes have previously been synthesised for the Group 6 metals by two basic methods:[13] (*i*) addition of ligand to the halide-bridged dimer $[\{M(CO)_4X_2\}_2]$,[14-16] or (*ii*) reaction of dihalogen[17,18] with, *e.g.*, $[M(CO)_4(PPh_3)_2]$. Such metal(II) products have been studied in detail, notably by Colton and his co-workers.[13] Of these two preparative routes, only the latter was synthetically useful for L^R. Addition of I_2 to a cold solution of the *cis*-dicarbene complex (4) or (5) in CH_2Cl_2 resulted in the rapid evolution of CO and the eventual formation of yellow-orange $[W(CO)_3I_2(L^R)_2]$ [R = Me (22) or Et (23)] (Scheme 2). The molybdenum analogues were not preparable, the corresponding reaction continuing a stage further to give the deep blue dicarbonyl derivative $[Mo(CO)_2I_2(L^R)_2]$, (17) or (18). Similar six-co-ordinate tungsten(II) complexes, (24) or (25), required more forcing conditions. The readily reversible quantitative gain and loss of CO to form respectively seven- or six-co-ordinate metal species, particularly for the less-labile tungsten complexes, parallels the chemistry of the PPh_3[13,14,16-20] analogues, but with several significant differences. Generally, and especially for the molybdenum(II) derivatives for which the seven-co-ordinate state could not be isolated [although an example, (17), was identified in a cold solution saturated with CO], the metal(II) (M = Mo or W) bis(carbene)tricarbonyl complexes afford the deep blue dicarbonyl complexes much

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more readily; for W^{II}, this is slow in solution or in the solid state at 25 °C and rapid at 40 °C (especially *in vacuo*). The PPh_3 analogues required prolonged heating in solution, or *in vacuo* [16] as the solid, for CO loss to occur but the seven-co-ordinate derivatives of $AsPh_3$ or $SbPh_3$ are stable.[14,15,19] These observations appear consistent primarily with the steric rather than electronic requirements of the ligands. If the latter were the more significant, then, because of the higher σ-donor : π-acceptor ratio of L^R compared with EPh_3 (E = P, As, or Sb), $[M(CO)_3I_2(L^R)_2]$ might have been expected to be preferred over $[M(CO)_2I_2(L^R)_2]$ in order to maximise electroneutrality.

Table 2

Selected ^1H n.m.r. spectroscopic data for electron-rich olefin-derived complexes of Mo^{II}, W^0, and W^{II}

		Resonance (τ) [a]				
Complex	Solvent	ring CH_2	*N*–CH_3	*N*–CH_2–CH_3 (*N*–C*H*₂)	*N*–CH_2–CH_3 (C*H*₃)	Others
(1)	$CDCl_3$	6.40	6.67			
(2)	$CDCl_3$	6.35		6.15 (q)	8.72 (t)	
(3)	C_6H_6		6.85	7.8 (t)		9.0 (p) [b]
(4)	$CDCl_3$	6.50	6.75			
(5)	$CDCl_3$	6.50		6.20 (q)	8.84 (t)	
(6)	$CDCl_3$	6.79		4.88		2.71 [c]
(7)	$CDCl_3$	6.41	6.60			
(8)	CH_2Cl_2	6.65	6.90			
(9)	C_6H_6	7.46	7.0			
(10)	C_6H_6	7.30		6.31 (q)	8.90 (t)	
(11)	C_6H_6	7.53	7.15			
(12)	C_6D_6	7.67	7.20			
(13)	C_6H_6	7.20		6.05 (q)	8.85 (t)	
(14)	$CDCl_3$	6.83		6.15 (q)	8.85 (t)	
(15)	C_6H_6	7.25	6.75			
(16)	C_5D_5N	7.60	7.60			
(17)	CH_2Cl_2	6.43	7.03			
(18)	CH_2Cl_2	6.41	7.13			
(19)	CH_2Cl_2	6.40		6.90 (q)	8.95 (t)	
(20)	CH_2Cl_2	6.35		6.80 (q)	9.0 (t)	
(21)	CH_2Cl_2	6.38		6.80 (q)	8.95 (t)	
(22)	CH_2Cl_2	6.40	6.73			
(23)	CH_2Cl_2	6.40		6.36 (q)	8.80 (t)	
(24)	CH_2Cl_2	6.35		6.81 (q)	8.90 (t)	
(25)	CH_2Cl_2	6.30 (m)	6.72, 6.76			
(26)	CH_2Cl_2	6.4 (6.05) [d]		6.35 (q) [6.25 (q)] [d]	8.80 (t) [8.65 (t)] [d]	0.91 [d,e]
(27)	CH_2Cl_2	5.90	6.70			
(28)	CH_2Cl_2	6.05 [d]		6.25 (q) [d]	8.70 (t) [d]	0.91 [d,e]

[a] Relative to $SiMe_4$ (τ 10); all resonances are singlets unless otherwise stated in parentheses, t = triplet, m = multiplet, q = quartet, p = pentet. [b] C–C*H*₂–C. [c] Aryl–*H*. [d] Values for $[HL^{Et}]^+$. [e] $>\overset{+}{C}$–*H*.

There is evidence (^1H or ^{13}C n.m.r.) for significant intramolecular *cis*-ligand repulsions in *cis*-$[M(CO)_4(L^R)_2]$ (M = Cr, Mo, or W). In the M^{II}–L^R species, because of (*i*) the decrease in radius of the metal and (*ii*) its increased co-ordination number, this repulsion may well increase, thus favouring the six-co-ordinate complex. Introduction of CO gas either on to the solid or above the solution of the deep blue dicarbonyl complex, especially at low temperatures (< −20 °C), resulted in rapid uptake and regeneration of the yellow-orange tricarbonyl complex. A similar observation for the PR_3 complexes has led to the suggestion [18,21] that the blue complexes are monomeric, rather than the halide-bridged seven-co-ordinate dimers,[15,22] following the 18-electron rule. It seems that the colour is diagnostic of structure. It is worth noting that the apparently six-co-ordinate $[M(CO)_4X_2]$ are in fact halide-bridged seven-co-ordinate dimers,[14,15] and are yellow and not dark blue. Similarly, $[MoBr_2(CO)_2(PEt_3)_2]$ is blue and monomeric, whereas $[\{Mo(CO)_2Cl_2(PMe_2Ph)_2\}_2]$ is yellow and dimeric.[18] For both the PPh_3 and L^R derivatives the observed diamagnetism of the blue complexes is in marked contrast to the paramagnetism of $[Mo(CO)_2X_2(C_5H_5N)_2]$ [23] and can only be explained by a large distortion from a basic octahedral symmetry.[21] For $[MoBr_2(CO)_2(PPh_3)_2]$, X-ray crystallography has confirmed [21] this, and indeed also the monomeric nature of the complex. The diamagnetism must therefore arise by partial lifting of the degeneracy of the t_{2g}-orbital manifold causing spin pairing of the four *d* electrons in the presence of a strong ligand field. There must presumably be a fine balance depending on the ligand(s) other than CO or X, as *N*-donor analogues (py or phen) are often paramagnetic.[23,24]

For the biscarbene complexes there are several variables affecting the carbon monoxide gain for $[M(CO)_2(L^R)_2X_2]$ and CO loss from $[M(CO)_3(L^R)_2X_2]$. Comparison of M, X, and R leads to the conclusion that (*i*) W > Mo, (*ii*) I > Br > Cl, and (*iii*) Me > Et in terms of stability of the seven- over the six-co-ordinate complex. A similar trend, for halides, has been observed

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[21] M. G. B. Drew, I. B. Tomkins, and R. Colton, *Austral. J. Chem.*, 1970, **23**, 2517.

[22] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 1143.

[23] R. Colton and C. J. Rix, *Austral. J. Chem.*, 1968, **21**, 1155.

[24] R. Colton and I. B. Tomkins, *Austral. J. Chem.*, 1967, **20**, 13.

in the PPh_3 analogues,[16] but here all the six- and seven-co-ordinate complexes of Mo^{II} and W^{II} could be isolated.

The reaction of *cis*-$[W(CO)_4(L^{Et})_2]$, (5), with Br_2 led unexpectedly to the ionic product $[\overline{CHN(Et)CH_2CH_2N}Et][WBr_3(CO)_3L^{Et}]$, (26) (the cation may be written as $[HL^{Et}]^+$), whereas the molybdenum analogue, *cis*-$[Mo(CO)_4(L^{Et})_2]$, afforded $[MoBr_2(CO)_2(L^{Et})_2]$, (21), in high yield. Relevant to the former observation, are reactions (3) [11] and (4).[16] Formation of these cations

$$[W(CO)_4(PPh_3)_2] + Br_2 \longrightarrow [PPh_3H][WBr_3(CO)_3(PPh_3)] \quad (3)$$

$$[\{Mo(CO)_4I_2\}_2] + PPh_3 \longrightarrow [PPh_3H][Mo(CO)_3I_3(PPh_3)] \quad (4)$$

may arise by initial reaction with HX. Thus, the *cis*-dicarbenetungsten complex (5) reacts with HBr (Scheme 2) to yield $[HL^{Et}]_2[WBr_2(CO)_4]$, (28), a reaction related to that described by Fischer *et al.*[25] for some Group 6 metal (aminocarbene)pentacarbonyl complexes [equation (5)]. In our case, the HBr may be produced by prior

$$[M(CO)_5\{C(NRR')R''\}] + HX \longrightarrow [R'(R)N{=}CHR''][M(CO)_5X] \quad (5)$$

interaction of Br_2 and the solvent CH_2Cl_2 (although a reaction in C_6H_6 afforded the same compound), or the carbene *N*-alkyl side chain.

Monosubstituted seven-co-ordinate tetracarbonyl complexes of Mo^{II} or W^{II} have previously received little attention, and a low stability of these species might have been expected. The presence of a strong σ-donating carbene ligand was expected to enhance the stability by partially alleviating the electron deficiency of the metal and increasing the degree of M–CO d_π–$p_{\pi*}$ back bonding. With $[W(CO)_5L^{Me}]$, (1), a fairly thermally stable complex was isolated on reaction with I_2, $[W(CO)_4I_2(L^{Me})]$, (25), but for $[Mo(CO)_5L^{Me}]$ carbene displacement occurred affording the known anion [26] $[Mo(CO)_4I_3]^-$, the counter cation being $[IL^{Me}]^+$. This, and closely related anions, have previously been isolated and characterised as their $[NEt_4]^+$ salts.[27]

TABLE 3

Variable-temperature ^1H n.m.r. $\Delta G^\ddagger$ and T_c data

Complex [a]	Solvent	Observed signal	T_c [b]/ °C	$\Delta G^\ddagger$ [c,d]/ kcal mol^{-1}
cis-$[Cr(CO)_4(L^{Me})_2]$	$(CD_3)_2CO$	N–CH_3	−40.5	11.6
cis-$[Cr(CO)_4(L^{Et})_2]$	$(CD_3)_2CO$	N–CH_2CH_3	−42	11.7
cis-$[Mo(CO)_4(L^{Me})_2]$ [e]	$(CD_3)_2CO$	N–CH_3	−66	10.4
cis-$[W(CO)_4(L^{Me})_2]$	$(CD_3)_2CO$	N–CH_3	−64	10.4
cis-$[W(CO)_4(L^{Et})_2]$	$(CD_3)_2CO$	N–CH_2CH_3	−66	10.0
$[W(CO)_4I_2(L^{Me})]$	$(CD_3)_2CO$	N–CH_3	+17	14.4
$[Mo(CO)_2I_2(L^{Et})_2]$	CD_2Cl_2	N–CH_2–CH_3	<−85	
$[W(CO)_3I_2(L^{Et})_2]$ [f]	CD_2Cl_2	N–CH_2–CH_3	<−85	

[a] Run as saturated solutions. [b] Calibrated *via* ethylene glycol. [c] ±0.5 kcal mol^{-1}. [d] For the method of calculation see: 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. [e] From ref. 1. [f] No change observed on cooling to at least −85 °C.

Spectroscopic Properties.—All the tungsten(0) complexes exhibited simple first-order ^1H n.m.r. spectra at room temperature; the data are given in Table 2. Variable low-temperature studies (Table 3) on *cis*-$[M(CO)_4(L^R)_2]$ (M = Cr,[28] Mo,[1] or W; R = Me or Et) complexes show the free energy of activation ($\Delta G^\ddagger$) to M–$C_{carb.}$ rotation of the mutually *cis*-carbene ligands to be slightly higher than in the dedihydro-analogues, *cis*-$[M(CO)_4\{\overline{CN(Me)CH{:}CHN}Me\}_2]$ (M = Cr, Mo, or W),[8] and this is considered to be due to the change in hybridisation of the ring carbon atoms.[1] The values for M = Cr are higher than for Mo or W (which are similar to each other) due to the smaller covalent radius of Cr^0 compared with those of Mo^0 or W^0.

The six-co-ordinate complexes of Mo^{II} and W^{II} all exhibited sharp n.m.r. signals illustrating their diamagnetic character (also no e.s.r. signals were observed in the range −95 to +25 °C). Table 2 contains the ^1H n.m.r. spectroscopic data for these and also the seven-co-ordinate species. All the bis(carbene)metal(II) complexes examined exhibited simple spectra and no change was observed on cooling $[W(CO)_3I_2(L^{Et})_2]$, (23), or $[Mo(CO)_2I_2(L^{Et})_2]$, (19), to −85 °C. However, the seven-co-ordinate complex $[W(CO)_4I_2L^{Me}]$, (25), did show a marked temperature-dependent spectrum; at 30 °C the ring methylene protons and N–CH_3 resonances were observed as broad singlets, but at lower temperatures were seen as an AA'BB' multiplet and doublet, respectively.

From the additional evidence available from i.r. studies (Table 4), which show (*i*) the CO groups to be at least in an approximately mutually *cis* configuration in all the metal(II) complexes, and (*ii*) that in $[M(CO)_2Cl_2(L^{Et})_2]$, (20), chloride ligands are mutually *trans*, we consider the seven-co-ordinate bis(carbene)metal complex may have a structure related to that of $[Mo(CO)_3I_2(pdma)]$ [pdma = *o*-phenylenebis(dimethylarsine)] [29] and the six-co-ordinate complexes a structure similar to that of $[MoBr_2(CO)_2(PPh_3)_2]$.[21]

For the seven-co-ordinate monocarbenetungsten derivative (25), a similar stereochemistry to that of complex (22), but with CO replacing one L^R ligand, might be

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[25] E. O. Fischer, K. R. Schmid, W. Kalbfus, and C. G. Kreiter, *Chem. Ber.*, 1973, **106**, 3893.

[26] J. A. Bowden and R. Colton, *Austral. J. Chem.*, 1968, **21**, 2657.

[27] M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 3494.

[28] M. F. Lappert and P. L. Pye, unpublished work.

[29] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1960, 1806.

expected not to show a temperature dependence of its ^{1}H n.m.r. spectrum, whereas this possibility is more likely for a geometry in which the halide ligands are mutually *cis*, provided there is restricted rotation about the M–C$_{\text{carb.}}$ bond. That this is likely is shown by the ready loss of CO from the seven-co-ordinate bis(carbene) complexes, although here the halide ligands are considered to be mutually *trans*. The precise geometry adopted (capped octahedral, pentagonal bipyramidal, or capped trigonal bipyramidal) will depend on the relative ligand–ligand repulsions, crystal-lattice energies, and ligand-field strengths, and little free-energy difference between the three basic polyhedra is expected.[29–31]

TABLE 4

Selected i.r. spectroscopic data for electron-rich olefin-derived complexes of Mo$^{\text{II}}$, W^0, and W$^{\text{II}}$

		Band maxima (cm^{-1})	
Complex	Solvent	ν(CO) [a]	ν(CN$_2$) [b]
(1)	n-C_6H_{14}	2 063w, 1 932vs	1 496m
(2)	n-C_6H_{14}	2 060w, 1 927vs	1 485m
(3)	n-C_6H_{14}	2 058w, 1 922vs	1 506m
(4)	*b*	1 991m, 1 879s, 1 854s, 1 818s	1 497m
(5)	thf	1 988m, 1 865s, 1 853s, 1 836s	1 482m
(6)	*b*	1 992m, 1 881s, 1 869s, 1 822s	1 490m
(7)	*b*	1 845vs	1 497m
(8)	*b*	1 885s, 1 765s, 1 754s	1 490m
(9)	$C_6H_{11}Me$	2 003s, 1 895s, 1 870vs	1 503m
(10)	$C_6H_{11}Me$	2 004s, 1 897s, 1 872vs	1 492m
(11)	n-C_6H_{14}	2 011s, 1 913s, 1 897s, 1 885s	1 504m
(12)	n-C_6H_{14}	2 012s, 1 916s, 1 899s, 1 888s	1 502m
(13)	$C_6H_{11}Me$	1 968s, 1 856s, 1 843s	1 491m
(14)	CH_2Cl_2	1 958s, 1 855vs	1 496m
(15)	CH_2Cl_2	1 912s, 1 806s, 1788s	1 500m
(16)	*b*	1 890s, 1 761s, 1 740s	1 490m
(17)	*c*	*c*	*c*
(18)	*b*	1 970s, 1 887s	1 512m
(19)	CH_2Cl_2	1 965s, 1 879s	1 498m
(20)	*b*	1 970s, 1 875s	1 501m
(21)	*b*	1 969s, 1 878s	1 500m
(22)	*b*	2 021s, 1 939s, 1 896s	1 520m
(23)	CH_2Cl_2	2 023s, 1 936s, 1 914s	1 498m
(24)	CH_2Cl_2	1 958s, 1 868s	1 497m
(25)	C_6H_6	2 095m, 2 041s, 1 982s, 1 958s	1 512m
(26)	*b*	2 030s, 1 914s, 1 876s	1 648s,[d] 1 522w,[d] 1 498m
(27)	C_6H_6	2 076s, 2 007vs, 1 950s	1 595s [e]
(28)	CH_2Cl_2	1 984m, 1 913s, 1 881s, 1 863s	1 650s,[d] 1 520w [d]

[a] Spectra were recorded on a X10 expanded scale and calibrated against a polystyrene film at 1 801 cm^{-1}. [b] Dilute Nujol mull. [c] Unstable in solution at 25 °C. [d] Asym and sym from [HL$^{\text{Et}}$]$^+$. [e] From [IL$^{\text{Me}}$]$^+$.

The ^{13}C n.m.r. spectroscopic data (Table 5) for the new mono- and bis-carbenetungsten(0) complexes show, as noted for their molybdenum analogues,[1,2] a relatively high field position for C$_{\text{carb.}}$ at *ca.* 110 p.p.m. upfield from that of a Fischer-type carbene carbon [32–36] [see (11) and (12)], and comparable to that of the carbonyl carbon atoms, but at lower field (*ca.* 20—30 p.p.m.) compared with related complexes containing the pseudo-aromatic carbene ligands :CN(Me)CH=CHNMe or :CN(Me)N=CHNMe.[37] The chemical shift of the four mutually *cis*-carbonyl carbons in the monocarbene complexes (1) and (2) are similar to those found in [W(CO)$_5${C(NHMe)Me}] [35] or many Group 5 element donor compounds,[38] but the values of CO (*trans* to C$_{\text{carb.}}$) are at a slightly higher field. In the bis(carbene) complexes (4) and (5) there is little variation in the values of δ(CO) (mutually *trans*) compared to the bis(phosphine) complexes *cis*-[W(CO)$_4$(PEt$_3$)$_2$] [39] or *cis*-[W(CO)$_4$(dppe)] (dppe = Ph$_2$P[CH$_2$]$_2$PPh$_2$),[40] but δ(CO)

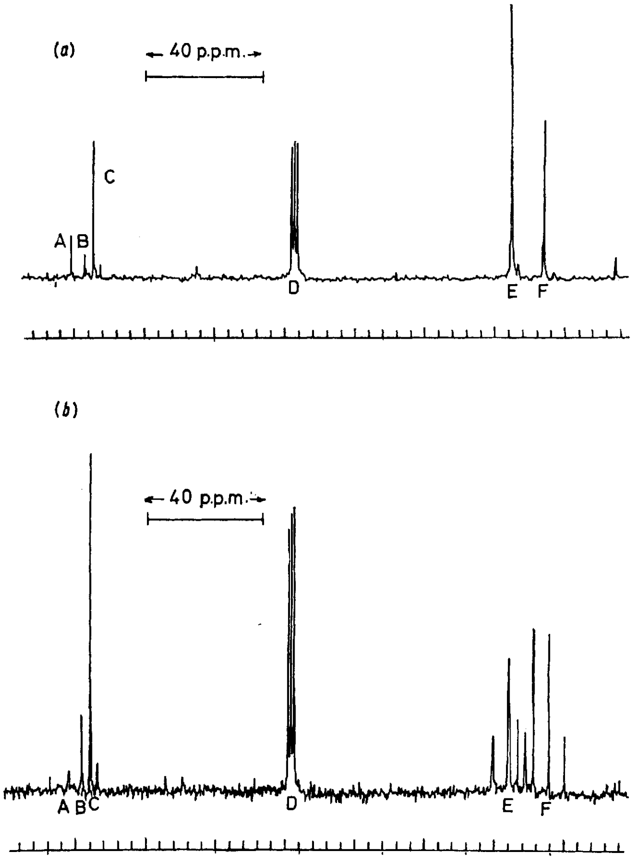

FIGURE 1 Carbon-13 n.m.r. spectrum of [W(CO)$_5$L$^{\text{Me}}$] in C$_6$D$_6$: (*a*) ^{1}H decoupled; (*b*) ^{1}H off-resonance. A = *C*$_{\text{carb.}}$, B = *CO trans* to C$_{\text{carb.}}$, C = 4 × *CO cis* to C$_{\text{carb.}}$, D = solvent resonance, E = ring *C*H$_2$, and F = N–*C*H$_3$

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[30] M. G. B. Drew and J. Wilkins, *J.C.S. Dalton*, 1973, 2664.

[31] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

[32] G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. F. Wuller, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 1071.

[33] D. J. Ciapenelli, F. A. Cotton, and L. Kruczynski, *J. Organometallic Chem.*, 1973, **50**, 171.

[34] J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1972, 2419.

[35] C. G. Kreiter and V. Formaček, *Angew. Chem. Internat. Edn.*, 1972, **11**, 141.

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

[37] F. H. Köhler, H. J. Kalder, and E. O. Fischer, *J. Organometallic Chem.*, 1976, **113**, 11.

[38] O. A. Gansow, B. Y. Kimura, G. R. Dobson, and R. A. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5922.

[39] B. E. Mann, *J.C.S. Dalton*, 1973, 2012.

[40] P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1027.

(mutually *cis*) is at a significantly lower field, possibly a reflection of the difference in the σ-donor : π-acceptor ratio of the tertiary phosphine ligand compared to L^R (R = Me or Et), the latter causing an increased electron density in the antibonding orbital of the *trans*-W–C_{CO} bond. As noted previously,[1] ^1H off-resonance experiments provide a basis for assignments, the broadening of the $C_{carb.}$ resonance (Figures 1 and 2) and the decrease in intensity of the mutually *trans*-carbonyl groups relative to those *cis* being more pronounced than in the analogous molybdenum(0) complexes.

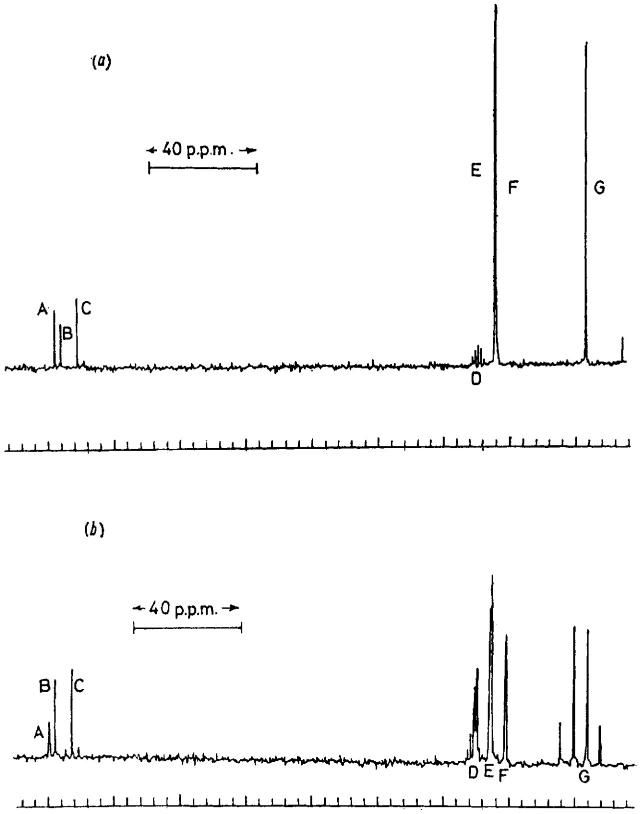

FIGURE 2 Carbon-13 n.m.r. spectrum of *cis*-$[W(CO)_4(L^{Et})_2]$ in CD_2Cl_2 at 35 °C: (*a*) ^1H decoupled; (*b*) ^1H off-resonance. A = $C_{carb.}$, B = 2 × mutually *cis* CO, C = 2 × mutually *trans* CO, D = solvent resonance, E = ring CH_2, F = N–CH_2 and G = N–CH_3

The coupling constants $^1J(^{13}C-^{183}W)$ (Table 5) are very similar to previous values for the coupling of carbonyl carbon to W^0 [36,37,41] (in the 129—124 Hz region), but coupling with $C_{carb.}$ is significantly lower (*ca.* 30 Hz). This is undoubtedly associated with changes in hybridisation at C for carbonyl and carbene ligands. A similar variation in ^1J values has been observed in some related carbenetungsten(0) complexes by Köhler *et al.*[37] For $[W(CO)_5\{\overline{CN(Me)CH{:}CHNMe}\}]$, ^1J is 100.1 Hz compared with 94.6 Hz in (2). The difference may indicate small variations in *s* character in the W–$C_{carb.}$ bonds. However, insufficient results [*e.g.* there are no data for complexes (1) or (4)—(6) due to the proximity of other signals to the satellite resonances] are available to make a firm conclusion. There is also a clear variation in the values of $^2J(^{13}C-^{31}P)$, with *trans* coupling being greater than *cis* (*cf.* refs. 36 and 39), and although the difference is rather small, unlike that observed in the platinum-group metals, we have found it can provide a useful probe for determining stereochemistry.

The resonances of $C_{carb.}$ in complexes containing Fischer-type carbene ligands have been extensively quoted.[32-36] Data obtained here for the mixed dicarbene complexes (11) and (12) show that the presence of the electron-rich olefin-derived carbene ligand, L^{Me}, has only a minor effect on the position of $C_{carb.}$ in C(OMe)Me, causing only a very small upfield shift; the opposite might have been expected as we have found that replacement of one or more CO ligands by donors of a higher σ-donor : π-acceptor ratio causes $C_{carb.}$ of L^R to move to lower field [*e.g.* in the pairs of complexes (2) and (5), or (1) and (13), Table 5]. This small shift has also been observed [28] in *cis*-$[Cr(CO)_4\{C(OMe)Me\}L^{Me}]$, where δ($C_{carb.}$) is 359.6 compared with 360.4 p.p.m. in $[Cr(CO)_5\{C(OMe)Me\}]$.[36]

It has not yet been possible to obtain satisfactory ^{13}C n.m.r. spectra of the metal(II) (M = Mo or W) complexes; their insolubility, relatively high molecular weight, and lability in solution (concentrated solutions appear to decompose remarkably quickly) has prevented the unambiguous observation of signals assignable to $C_{carb.}$ or CO, although for complexes (19), (21), or (22), signals assignable to the *N*-substituents and ring methylene atoms have been observed.[28]

TABLE 5

Selected ^{13}C n.m.r. spectroscopic data for electron-rich olefin-derived complexes of W^0

		δ^a/p.p.m.		
Complex	Solvent	$C_{carb.}$	mutually CO_{trans} CO_{cis}	ring CH_2
(1)	C_6D_6	206.6	198.8,[b] 201.8	51.1
(2)	C_6D_6	205.4 [c]	198.7,[b] 201.7	47.5
(4)	CD_2Cl_2	211.4	205.3, 214.0	51.8
(5)	CD_2Cl_2	213.6	204.8,[d] 211.1	47.7
(7)	CD_2Cl_2	215.4	210.8 [e]	51.9
(10)	C_6D_6	213.2 [f]	204.0;[g] 207.8,[h] 208.4 [i]	47.6
(11)	C_6D_6	212.7 (328.7) [j]	205.0; 209.6 215.2	51.0
(12)	C_6D_6	212.4 (313.9) [k]	204.9; 209.4, 215.4	51.2
(13)	C_6D_6	214.9 [l]	210.6,[m] 210.7 [n]	47.8
(16)	C_5D_5N	226.5	224.1, 230.7	51.9

[a] Relative to $SiMe_4$ (δ 0); ^2H lock signal. [b] $^1J(^{183}W-^{13}C)$ 126.7 Hz. [c] $^1J(^{183}W-^{13}C)$ 94.6 Hz. [d] $^1J(^{183}W-^{13}C)$ 128.2 Hz. [e] Four equivalent CO groups. [f] $^2J(^{13}C-^{31}P)$ 9.2 Hz. [g] $^2J(^{13}C-^{31}P)$ 9.1 Hz. [h] *trans* to PEt_3, $^2J(^{13}C-^{31}P)$ 22.9. [i] *trans* to $C_{carb.}$, $^2J(^{13}C-^{31}P)$ < 1.5 Hz. [j] *C*(OEt)Me. [k] *C*(OEt)Ph. [l] $^2J(^{13}C-^{31}P)$ 10.7 Hz. [m] *trans* to $C_{carb.}$, $^2J(^{13}C-^{31}P)$ 9.9 Hz. [n] *trans* to $P(OMe)_3$, $^2J(^{13}C-^{31}P)$ 19.1, $^1J(^{183}W-^{13}C)$ 103.7 Hz.

EXPERIMENTAL

General Procedures.—All the reactions were carried out under an atmosphere of dry dinitrogen or argon. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use and chlorinated solvents were distilled

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[41] *Cf.*, L. J. Todd and J. R. Wilkinson, *J. Organometallic Chem.*, 1974, **77**, 1.

from P_4O_{10}. Photochemical experiments were performed in a Pyrex vessel using a water-cooled, medium-pressure, mercury 100-W Hanovia u.v. lamp. Analyses were carried out in our microanalytical laboratory by Mr. and Mrs. A. G. Olney. The ^{13}C n.m.r. spectra were obtained by Mr. T. M. Sivers on a JEOL PFT-100 Fourier-transform spectrometer. All the compounds were run as saturated solutions in 8-mm or 10-mm tubes at 30 °C using a 1-s repetition rate and a sweep width of 6 250 Hz.

Infrared spectra (250—4 000 cm^{-1}) were examined as *dilute* Nujol mulls using a Perkin-Elmer 457 grating spectrophotometer and ^1H n.m.r. spectra were recorded on Varian Associates HA100 or T60 spectrometers. Melting points were determined in evacuated sealed tubes and are uncorrected. The electron-rich olefins were prepared by literature methods[42] from the relevant diamine. Other starting materials were prepared by standard literature procedures[43] and $[W(CO)_6]$ was used as purchased from Alfa-Ventron Organometallics Ltd.

$[W(CO)_5L^R]$ (R = Me *or* Et).—Hexacarbonyltungsten(0) (3.51 g, 10 mmol) and bi(1,3-diethylimidazolidin-2-ylidene) (1.3 g, 5 mmol) were heated together in decalin (20 cm^3) at 160 °C (2 h). Carbon monoxide was evolved and the solution became pale yellow. The mixture was cooled to 30 °C, filtered, and the solvent removed by vacuum distillation. The residue was extracted with cold (0—10 °C) OEt_2 (2 × 15 cm^3), filtered, and the solvent reduced in volume to *ca.* 10 cm^3. Hexane (10 cm^3) was added and cooling (−25 °C) for several days afforded cream crystals of *pentacarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)*tungsten*(0) (3.1 g, 70%).

$[W(CO)_5L'^{Me}]$.—Hexacarbonyltungsten(0) (0.7 g, 2 mmol) and bi(1,3-dimethylperhydropyrimidin-2-ylidene) (0.45 g, 2.0 mmol) in decalin (10 cm^3) were heated (180 °C, 2 h). The solution became yellow and oily, the solvent was removed by vacuum distillation, and the residue was extracted with OEt_2 (2 × 5 cm^3), cooled to −20 °C, and filtered. The volume of OEt_2 was reduced to 5 cm^3, hexane (10 cm^3) was added, and cooling (−25 °C, 24 h) afforded a yellow solid which was twice recrystallised from diethyl ether–hexane at −20 °C to give cream crystals of *pentacarbonyl*(1,3-*dimethylperhydropyrimidin*-2-*ylidene*)-*tungsten*(0) (0.13 f, 15%).

cis-$[W(CO)_4(L^R)_2]$ (R = Me, Et, *or* CH_2Ph).—Hexacarbonyltungsten(0) (1.76 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 (2 h). Carbon monoxide was evolved, the solution became yellow, and on cooling yellow microcrystals of cis-*tetracarbonylbis*(1,3-*diethylimidazolidin*-2-*ylidene*)*tungsten*(0) (2.6 g, 95%) were deposited. These were filtered off, washed with OEt_2 (4 × 5 cm^3) and pentane (4 × 10 cm^3), and dried *in vacuo*.

trans-$[W(CO)_4(L^{Me})_2]$.—*cis*-Tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)tungsten(0) (0.74 g, 1.5 mmol) was dissolved in acetone (15 cm^3) to form a saturated solution which was irradiated at 25 °C (10 h), during which time orange microcrystals of trans-*tetracarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*tungsten*(0) (0.43 g, 58%) precipitated. These were removed at intervals (3 h) by filtration, and the filtrate was concentrated to maintain a saturated solution. The complex was recrystallised from toluene–hexane (−20 °C), but in solution isomerisation to the *cis* complex slowly occurred.

fac-$[W(CO)_3(L^{Me})_3]$.—Tricarbonyl(η-mesitylene)tungsten(0) (0.39 g, 1.0 mmol) and bi(1,3-dimethylimidazolidin-2-ylidene) (0.45 g, 2.3 mmol) were heated together slowly to 110 °C *in vacuo* (5 mmHg).* The liquid mass became semi-solid (10 min) and heating was discontinued after a further 5 min. The mixture was cooled to 20 °C and washed with OEt_2 (2 × 5 cm^3), C_6H_6 (1 × 5 cm^3), and OEt_2 (2 × 5 cm^3) and dried *in vacuo* to leave a pale yellow powder, fac-*tricarbonyltris*(1,3-*dimethylimidazolidin*-2-*ylidene*)*tungsten*(0) (0.40 g, 72%).

cis-$[W(CO)_4L^R(PR'_3)]$ (R = Et, R′ = Et; R = Me, R′ = Bu^n).—Typically, pentacarbonyl(1,3-diethylimidazolidin-2-ylidene)tungsten(0) (0.45 g, 1 mmol) and triethylphosphine (0.24 g, 2.1 mmol) in hexane solution (10 cm^3) were irradiated for 8 h, after which time a pale yellow precipitate had formed. This was removed by filtration and recrystallised from toluene–hexane at −20 °C, forming pale yellow microcrystals of cis-*tetracarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*tungsten*(0).

cis-$[W(CO)_4\{C(OEt)R\}L^{Me}]$ (R = Me *or* Ph).—Typically, to pentacarbonyl(1,3-dimethylimidazolidin-2-ylidene)tungsten(0) (0.42 g, 1.0 mmol) in OEt_2 (10 cm^3), phenyllithium (1.5 cm^3, 0.8 mol dm^{-3}) solution in OEt_2 was added dropwise at 0 °C to form an orange precipitate. To this triethyloxonium tetrafluoroborate (0.22 g, 1.2 mmol) followed by degassed water (15 cm^3) were added and the resulting dark brown mixture was stirred (18 h); the OEt_2 layer was separated, the aqueous residue extracted with diethyl ether (2 × 5 cm^3), and the combined extracts were dried over $Mg[SO_4]$ and filtered. The volume of OEt_2 was reduced *in vacuo* to 5 cm^3 and pentane (10 cm^3) was added. Cooling (−20 °C, 5 d) afforded dark brown crystals of cis-*tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*ethoxybenzylidene*)*tungsten*(0) (0.31 g, 60%), which were further recrystallised from diethyl ether–pentane (−20 °C, 5 d).

fac-$[W(CO)_3L^{Et}\{P(OR)_3\}_2]$ (R = Me *or* Ph).—A mixture of pentacarbonyl(1,3-diethylimidazolidin-2-ylidene)-tungsten(0) (0.45 g, 1.0 mmol) and trimethyl phosphite (0.62 g, 5.0 mmol) was irradiated in hexane (10 cm^3) for 8 h, whereupon a cream-white solid precipitated. This was removed by filtration and recrystallised from toluene–hexane (−25 °C) to afford white crystals of fac-*tricarbonyl*-(1,3-*diethylimidazolidin*-2-*ylidene*)*bis*(*trimethyl phosphite*)-*tungsten*(0) (0.58 g, 91%).

fac-$[W(CO)_3(L^{Me})_2\{P(OMe)_3\}]$.—To a solution of *cis*-tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)tungsten(0) (0.49 g, 1.0 mmol) in toluene (10 cm^3), was added a large excess of $P(OMe)_3$ (5.0 g, 40 mmol) and the mixture was irradiated for 8 h. Addition of hexane caused the precipitation of a pale yellow powder; recrystallisation from toluene–diethyl ether afforded pale yellow microcrystals of fac-*tricarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*trimethyl phosphite*)*tungsten*(0) (0.41 g, 70%).

fac-$[W(CO)_3(L^{Me})_2(C_5H_5N)]$.—*cis*-Tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)tungsten(0) (0.38 g, 0.78 mmol) was dissolved in pyridine (10 cm^3). Diethyl ether (30 cm^3) was added and the mixture was irradiated (25 °C, 18 h). The solution became dark and a purple crystalline solid slowly precipitated. This was removed by filtration,

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

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washed with OEt_2 (2×5 cm^3), and dried *in vacuo* to afford purple air-sensitive crystals of fac-*tricarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*pyridinetungsten*(0) (0.25 g, 60%).

$[Mo(CO)_2(L^R)_2X_2]$ (R = Et, X = Br *or* I; R = Me, X = I).—To a solution of *cis*-tetracarbonylbis(1,3-diethylimidazolidin-2-ylidene)molybdenum(0) (0.46 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3), cooled to −20 °C, a solution of dibromine (0.16 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise (4 h). After the addition was complete, stirring was continued (2 h) whilst the temperature rose to 0 °C. The solution was filtered, diethyl ether (10 cm^3) added, and the mixture was cooled (−20 °C, 2 d) to deposit ultramarine crystals of *dibromodicarbonylbis*(1,3-*diethylimidazolidin*-2-*ylidene*)*molybdenum*(II) (0.45 g, 80%). For X = Cl, a similar procedure was followed, except that Cl_2 was added as a CCl_4 solution, the product precipitating as a blue solid which was recrystallised from CH_2Cl_2–OEt_2 (−25 °C, 48 h).

$[W(CO)_3I_2(L^R)_2]$ (R = Me *or* Et).—To a cooled (−10 °C) solution of *cis*-tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)tungsten(0) (0.43 g, 0.89 mmol) in CH_2Cl_2 (10 cm^3), was added dropwise (2 h) a solution of I_2 (0.23 g, 0.9 mmol) in CH_2Cl_2 (10 cm^3) with rapid stirring. Carbon monoxide was slowly evolved and the solution became yellow-green. After complete addition of di-iodine, stirring was continued (5 h), and the resulting green solution was filtered under a CO atmosphere, whereupon the solution became bright orange. Addition of OEt_2 (20 cm^3) and cooling (−20 °C, 5 d) afforded yellow-orange crystals of *tricarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*di-iodotungsten*(II) (0.52 g, 80%). For M = Mo, R = Me, and X = I, the tricarbonyl derivative could not be isolated, but was observed spectroscopically by saturation of a solution of the dicarbonyl complex with CO below −20 °C. For M = Mo, R = Et, and X = Cl, Br, or I, the tricarbonyl species could not be observed spectroscopically at −30 °C.

$[W(CO)_2I_2(L^{Et})_2]$.—Tricarbonylbis(1,3-diethylimidazolidin-2-ylidene)di-iodotungsten(II) (0.39 g, 0.5 mmol) was dissolved in cold CH_2Cl_2 (15 cm^3) and the solution was stirred (4 h) whilst the temperature was increased (20 min) to 40 °C. The initial orange colour soon became green and finally blue-black. The solution was cooled, filtered, and an equal volume of OEt_2 was added. Cooling (−25 °C, 24 h) afforded deep blue-black crystals of *dicarbonylbis*(1,3-*diethylimidazolidin*-2-*ylidene*)*di-iodotungsten*(II) (0.27 g, 70%).

$[W(CO)_4I_2(L^{Me})]$.—To pentacarbonyl(1,3-dimethylimidazolidin-2-ylidene)tungsten(0) (0.17 g, 0.4 mmol) in benzene (10 cm^3), was added dropwise di-iodine (5 °C, 1 h) (0.10 g, 0.4 mmol) in benzene (5 cm^3). After complete addition the solution was stirred (20 °C, 20 min), diethyl ether (10 cm^3) was added, and the mixture was cooled (−5 °C, 24 h) to deposit a yellow precipitate. This was removed by filtration, and recrystallisation from dichloromethane–hexane afforded small yellow-orange crystals of *tetracarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*di-iodotungsten*(II) (0.10 g, 40%).

$[HL^{Et}][WBr_3(CO)_3L^{Et}]$.—To *cis*-tetracarbonylbis(1,3-diethylimidazolidin-2-ylidene)tungsten(0) (0.29 g, 0.54 mmol) in CH_2Cl_2 (10 cm^3), was added dropwise (0 °C, 1 h) dibromine (0.13 g, 0.8 mmol) in CH_2Cl_2 (5 cm^3) and the yellow solution was stirred (20 °C, 1 h). The solvent was removed *in vacuo* and the residue was extracted with warm toluene (50 °C, 10 cm^3) and filtered. Diethyl ether (5 cm^3) was added and cooling (−20 °C, 72 h) afforded yellow crystals of 1,3-*diethylimidazolidin*-2-*ylidinium tribromotricarbonyl*-(1,3-*diethylimidazolidin*-2-*ylidene*)*tungstate*(II) (0.21 g, 50%).

$[IL^{Me}][Mo(CO)_4I_3]$.—To pentacarbonyl(1,3-dimethylimidazolidin-2-ylidene)molybdenum(0) (0.29 g, 0.86 mmol) in benzene (5 cm^3), was added dropwise (0 °C) di-iodine (0.24 g, 0.95 mmol) in benzene (10 cm^3). Carbon monoxide was evolved, the solution became yellow, and on continued stirring a yellow precipitate formed (25 °C, 2 h). Diethyl ether (10 cm^3) was added, the mixture was cooled (0 °C, 18 h), and the yellow solid so obtained was recrystallised from CH_2Cl_2–OEt_2 to afford yellow-orange crystals of 2-*iodo*-1,3-*dimethylimidazolidin*-2-*ylidinium tetracarbonyltri-iodomolybdate*(II) [0.30 g, 80% (based on di-iodine)].

$[HL^{Et}]_2[WBr_2(CO)_4]$.—To a solution of *cis*-tetracarbonylbis(1,3-diethylimidazolidin-2-ylidene)tungsten(0) (0.16 g, 0.30 mmol) in CH_2Cl_2 (5 cm^3), was added dropwise a solution of HBr in OEt_2 (14 cm^3, 0.05 mol dm^{-3}). A yellow oil was slowly precipitated and this was washed with OEt_2 after the reaction was complete. The oil was dissolved in acetone; the addition of a few drops of OEt_2 and cooling (−20 °C, 24 h) afforded yellow crystals of *bis*(1,3-*diethylimidazolidin*-2-*ylidinium*) *dibromotetracarbonyltungstate*(0) (0.14 g, 65%).

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