Co-ordinatively Unsaturated Diene Complexes of Tungsten(II) and their Reactions with Nucleophiles to give Six- and Seven-co-ordinate Derivatives

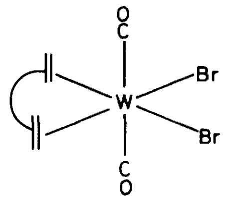
Jack L. Davidson * **and Guiseppe Vasapollo**
Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS

$[\{WBr_2(CO)_4\}_2]$ reacts with the 'dienes' (L′) cyclo-octa-1,5-diene (cod), cyclo-octatetraene (cot), and norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, nbd) to give co-ordinatively unsaturated complexes $[WBr_2(CO)_2L']$. These react with Lewis bases L [= CNBu^t, PMe_2Ph, or $P(OMe)_3$] (1:1 molar ratio) to give co-ordinatively unsaturated diene complexes $[WBr_2(CO)LL']$ *via* intermediate 1:1 adducts $[WBr_2(CO)_2LL']$ isolated in the case of the norbornadiene complexes. With a 3:1 molar ratio of ligand:metal, displacement of cod or cot occurs to give $[WBr_2(CO)_2L_3]$ [L = $P(OMe)_3$, PMe_2Ph, or CNBu^t], while a 4:1 molar ratio (L = CNBu^t) gives $[WBr_2(CO)(CNBu^t)_4]$. In contrast, $[WBr_2(CO)_2(nbd)]$ forms monocarbonyl diene complexes $[WBr_2(CO)L_2(nbd)]$ [L = $P(OMe)_3$ or PMe_2Ph, L_2 = 2,2′-bipyridyl]. Proton and ^{31}P n.m.r. studies of $[WBr_2(CO)_2L_3]$ [L = $P(OMe)_3$ or PMe_2Ph] reveal the presence of two isomeric forms which exhibit dynamic stereochemistry at ambient temperature while the static form of one isomer could be detected at lower temperatures.

In recent years we have been studying the ability of alkynes to stabilise co-ordinative unsaturation at metal centres by involving both sets of C≡C π orbitals in bonding with the metal.[1] Co-ordinative unsaturation in metal complexes can also be stabilised by steric interactions as in $[Mo(CO)_3\{P(C_6H_{11})_3\}_2]$[2] ($C_6H_{11}$ = cyclohexyl) while a combination of steric and electronic (π-donor) interactions may be responsible for the existence of a range of formally 16-electron Mo^{II} and W^{II} halogen and sulphur derivatives, such as $[MX_2(CO)_2L_2]$[3] (X = halogen, L = tertiary phosphine or arsine), $[M(S_2CNR_2)_2(CO)_2]$ (R = Me or Et),[4] and $[M(SBu^t)_2(CNBu^t)_4]$.[5] Interesting features of these types of complex include (*a*) structural distortions from a regular octahedral stereochemistry,[6] (*b*) the ability in some cases to add reversibly CO, *i.e.* to function as carbon monoxide carriers,[3,7] and (*c*) the ability to add other two-electron donor ligands L to give seven-co-ordinate 18-electron complexes which exhibit a variety of structural forms many of which are stereochemically non-rigid.[8] Our recent observations that dimeric dihalogenobis(alkyne) derivatives $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$ (R = R′ = Me or Ph; R = Me, R′ = Ph) in contrast add donor ligands L [L = PPh_3, $P(OMe)_3$, or CNBu^t] to give only six-co-ordinate adducts such as $[WBr_2(CO)L(RC{\equiv}CR')_2]$ and $[WBr_2(CO)L_2(RC{\equiv}CR')]$[1b] (see following paper) prompted us to attempt the synthesis of related co-ordinatively unsaturated alkene complexes in order to investigate the role of π-electron donation in stabilising co-ordinative unsaturation in metal complexes. Preliminary results of this study have been published in an earlier communication.[9]

Results and Discussion

Reactions of $[\{WBr_2(CO)_4\}_2]$[10] with 'dienes' cyclo-octa-1,5-diene (cod), cyclo-octatetraene (cot), and norbornadiene (bicyclo-[2.2.1]hepta-2,5-diene, nbd) in refluxing hexane give black crystalline complexes $[WBr_2(CO)_2L']$ [L′ = cod (**1a**), cot (**1b**), or nbd (**1c**)]. The mass spectra of the complexes exhibit weak ions derived from a parent dimer $[\{WBr_2(CO)L'\}_2]$ and much stronger monomeric ions $P^+ = [WBr_2(CO)L']^+$ and ions $[P - CO]^+$ and $[P - Br]^+$. These data in conjunction with initial analytical results originally suggested a dimeric formulation $[\{WBr_2(CO)L'\}_2]$ similar to that of $[\{WBr_2(CO)(alkyne)_2\}_2]$ obtained from reactions of alkynes with $[\{WBr_2(CO)_4\}_2]$ (see following paper). However, later analytical data are more in accord with a dicarbonyl monomer $[WBr_2(CO)_2L']$ a conclusion subsequently confirmed by single-crystal *X*-ray diffraction studies of $[WBr_2(CO)_2(nbd)]$[11] which revealed structure (**1**). It appears that dimeric ions in the mass spectra result from ion combination in the source chamber, an explanation which accounts for the fact that the intensity of the dimeric ions in the spectrum decreases rapidly with time.



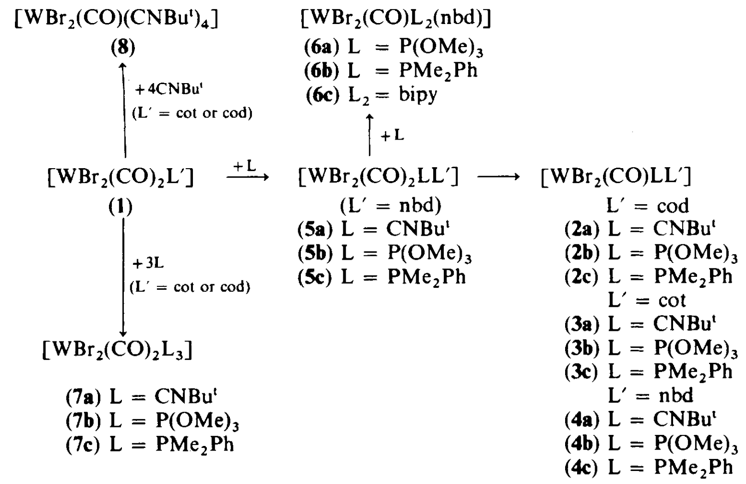
(**1**)

Interestingly, *X*-ray diffraction studies of other six-co-ordinate d^4 metal complexes $[MoBr_2(CO)_2(PPh_3)_2]$,[12] $[Mo(SBu^t)_2(CNBu^t)_4]$,[5] $[Mo(OBu^t)_2(CO)_2(py)_2]$[13a] (py = pyridine), $[Mo(S_2CNMe_2)_2(CO)_2]$,[4] and $[Mo(OPr^i)_2(bipy)_2]$[13b] (bipy = 2,2′-bipyridyl) have revealed that the preferred structure is distorted significantly from a regular octahedron. Extended Hückel calculations[6] suggest that this distortion is a direct consequence of the d^4 electron configuration and not surprisingly a distortion is also found in (**1c**) where the OC–W–CO angle is 172.9(4)°.[11] The ν(CO) region of the i.r. spectra confirms that this is maintained in solution since a strong asymmetric stretch due to *trans* CO ligands is accompanied by a weak band to higher frequency which we attribute to the symmetric stretch activated by the distortion from octahedral geometry. However, the distortion is not revealed by the ^1H n.m.r. spectra of the diene ligands which only exhibit the expected co-ordination shifts of the olefinic protons to higher field. Thus the two planes of symmetry present in the free ligand still persist in the complexes. Interestingly the two ^1H signals of the cot complex confirm that the C_8H_8 ligand is co-ordinated in a 1—4-η-diene manner and the complexes can therefore be compared with d^6 diene complexes $[W(CO)_4L']$ (L′ = cod, cot, or nbd) which presumably have a more regular octahedral geometry.[14] Potentially the cyclo-octatetraene ligand could co-ordinate *via* three olefinic bonds as in $[M(CO)_3(\eta^6\text{-cot})]$ and thus enable the metal ion to achieve an 18-electron configuration. That this does not occur probably

Table 1. Physical and analytical* data for the complexes

Complex	Colour	Analysis (%)					
		C	H	Br	P	N	O
(1a) $[WBr_2(CO)_2(cod)]$	Black	22.4 (23.6)	2.2 (2.4)	31.9 (31.5)			
(1b) $[WBr_2(CO)_2(cot)]$	Black	23.8 (23.8)	1.5 (1.6)	32.4 (31.7)			6.3 (6.3)
(1c) $[WBr_2(CO)_2(nbd)]$	Black	21.7 (22.0)	1.7 (1.6)	33.5 (32.5)			6.5 (6.5)
(2a) $[WBr_2(CO)(CNBu^t)(cod)]$	Dark green	30.0 (29.8)	3.9 (3.7)			2.6 (2.5)	
(2b) $[WBr_2(CO)\{P(OMe)_3\}(cod)]$	Dark green	24.0 (23.8)	3.4 (3.5)				
(2c) $[WBr_2(CO)(PMe_2Ph)(cod)]$	Dark green	33.1 (33.0)	3.9 (4.0)				
(3a) $[WBr_2(CO)(CNBu^t)(cot)]$	Black	29.9 (30.0)	3.7 (3.0)			2.5 {2.5)	
(3b) $[WBr_2(CO)\{P(OMe)_3\}(cot)]$	Black	23.4 (24.0)	2.9 (2.8)				
(3c) $[WBr_2(CO)(PMe_2Ph)(cot)]$	Black	32.7 (33.2)	3.1 (3.4)				
(4a) $[WBr_2(CO)(CNBu^t)(nbd)]$	Dark green	28.9 (28.5)	3.2 (3.10)			2.5 (2.6)	3.4 (2.9)
(4b) $[WBr_2(CO)\{P(OMe)_3\}(nbd)]$	Dark green	22.7 (22.5)	3.0 (2.9)				
(4c) $[WBr_2(CO)(PMe_2Ph)(nbd)]$	Dark green	32.2 (31.9)	3.3 (3.5)				
(5a) $[WBr_2(CO)_2(CNBu^t)(nbd)]$	Orange	30.3 (29.2)	3.2 (3.0)			2.6 (2.4)	5.5 (5.6)
(5b) $[WBr_2(CO)_2\{P(OMe)_3\}(nbd)]$	Orange-yellow	24.4 (23.4)	3.0 (2.8)	26.5 (25.8)	5.1 (5.0)		
(5c) $[WBr_2(CO)_2(PMe_2Ph)(nbd)]$	Orange-yellow	32.5 (32.4)	3.1 (3.3)		5.2 (4.9)		
(6a) $[WBr_2(CO)\{P(OMe)_3\}_2(nbd)]$	Orange	23.1(23.6)	3.6 (3.7)				
(6b) $[WBr_2(CO)(PMe_2Ph)_2(nbd)]$	Orange	39.0 (38.9)	4.0 (4.5)		8.0 (8.4)		
(6c) $[WBr_2(CO)(bipy)(nbd)]$	Red-brown	34.8 (34.7)	2.6 (2.7)			4.7 (4.5)	
(7a) $[WBr_2(CO)_2(CNBu^t)_3]$	Yellow	31.4 (31.4)	4.3 (4.2)				
(7b) $[WBr_2(CO)_2\{P(OMe)_3\}_3]$	Yellow	17.1 (17.1)	3.3 (3.5)	21.1 (20.7)	11.4 (12.0)		
(7c) $[WBr_2(CO)_2(PMe_2Ph)_3]$	Yellow	38.5 (38.3)	4.2 (4.8)		11.5 (11.4)		
(8) $[WBr_2(CO)(CNBu^t)_4]$	Yellow	35.70 (35.8)	5.0 (5.1)	21.40 (22.7)		7.8 (8.0)	

* Calculated values are given in parentheses.



Scheme.

reflects the stability of the d^4 16-electron configuration which is conceivably stabilised by π-donation from the two bromine ligands (see below). Interestingly, however, structurally related methyl complexes $[Mo(Me)_2L_2(cod)]$ (L = PMe_3 or PMe_2Ph), which contain no π-donor ligands, have been isolated from the reactions of $[MoCl_3(L)(thf)_2]$ (thf = tetrahydrofuran) with $MgMe_2$ in the presence of cod although cyclo-octatetraene and norbornadiene did not give isolable products.[15] A structure with *trans* phosphines and *cis* methyl groups was deduced from the ^1H n.m.r. spectra and therefore can be compared directly with that of complexes **(1)**.

Previously it has been observed that the complexes $[\{MX_2(CO)_4\}_2]$ (M = Mo or W; X = Cl, Br, or I) react with the ligands EPh_3 (E = P, As, or Sb) to give seven-co-ordinate tricarbonyls $[MX_2(CO)_3(EPh_3)_2]$ which on heating lose CO to produce dicarbonyls $[MX_2(CO)_2(EPh_3)_2]$ (E = P only) analogous to the co-ordinatively unsaturated diene complexes **(1)**.[3,12] In view of the importance of co-ordinative unsaturation in both catalytic and stoicheiometric reactions of metal alkene complexes it was of interest to investigate further the factors controlling the relative stabilities of co-ordinatively unsaturated six-co-ordinate species and saturated seven-co-ordinate derivatives.

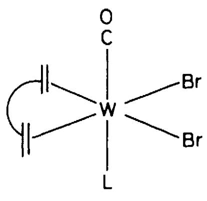
Reactions of **(1a)**, **(1b)**, and **(1c)** with two-electron donor ligands $CNBu^t$, $P(OMe)_3$, and PMe_2Ph were subsequently carried out, the results of which are summarised in the Scheme. Thus with 1:1 molar ratios of reactants dark green six-co-ordinate substitution products **(2)**, **(3)**, and **(4)** were obtained in every case. However, intermediate seven-co-ordinate dicarbonyl complexes $[WBr_2(CO)_2L(nbd)]$ **(5)** of varying stability were obtained with very short reaction times in the case of the norbornadiene complex which were originally thought to be isomeric forms of (**4**).[9] With *ca.* 1:2 molar ratios, (**1c**) and $P(OMe)_3$ and PMe_2Ph gave seven-co-ordinate monocarbonyl complexes $[WBr_2(CO)L_2(nbd)]$ (**6a**) and (**6b**) while bipy and (**1c**) gave a related derivative (**6c**). In contrast, 2:1 molar ratios involving cot and cod complexes led to displacement of the diene giving dicarbonyls $[WBr_2(CO)_2L_3]$ (**7**) which were isolated in larger yield when 3:1 molar ratios of ligand were employed. Larger excesses of t-butyl isocyanide led to the monocarbonyl complex $[WBr_2(CO)(CNBu^t)_4]$ (**8**). In a number of cases 1:1 molar ratios gave mixtures of six-co-ordinate species (**2**) or (**3**) and small amounts of (**7**), particularly when the ligand L was added quickly, whereas slow addition led to optimum yields of the former.

The key step in all of these transformations appears to be the initial formation of seven-co-ordinate dicarbonyl intermediates exemplified by the isolation of (**5a**)—(**5c**). These complexes are unstable with respect to CO loss giving six-co-ordinate monocarbonyls (**4**) on standing in diethyl ether solution at ambient temperature [L = $P(OMe)_3$ or PMe_2Ph] or on refluxing in hexane (L = $CNBu^t$). Related seven-co-ordinate Mo^{II} and W^{II} carbonyls, *e.g.* $[Mo(S_2CNMe_2)_2(CO)_3]$[7] and $[MoCl_2(CO)_3(PPh_3)_2]$,[3,12] have also been observed to undergo CO loss in solution, in some cases reversibly, and therefore act as carbon monoxide carriers; (**5a**)—(**5c**) clearly react in an analogous manner.

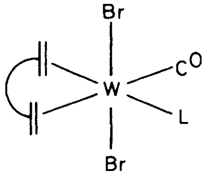
It is not possible to assign a definite structure to (**5a**)—(**5c**) on the basis of spectroscopic data available but the similarity of the ν(CO) region of the i.r. spectra to that of (**1**) suggests *trans* CO ligands with a OC–M–CO angle somewhat less than 180 °. The simplicity of the ^1H n.m.r. spectra, only three diene resonances, is consistent with a symmetric pentagonal-bipyramidal arrangement with axial CO or Br groups but in view of a preponderance of alternative structures based on a capped octahedron or a capped trigonal prism[8] it seems more probable that a less symmetric structure exists in which fluxional behaviour averages out inequivalent norbornadiene ^1H sites. This may be the case in complexes $[MoBr_2(CO)_2\{Me_2AsC(CF_3){=}C(CF_3)AsMe_2\}L]$ [L = $P(OEt)_3$, $P(OMe)_3$, $P(OMe)_2Ph$, PMe_2Ph, or $PMePh_2$] where ^1H and ^{13}C n.m.r. spectroscopy consistently revealed a symmetric environment for the ligands down to −70 °C[16] indicating a low barrier to ligand site exchange. The same conclusion applies to complexes (**5**) where no changes occur in the ^1H n.m.r. spectra down to −70 °C. However the PMe_2Ph doublet of (**5c**) broadened significantly below this temperature indicating the slowing down of a low-energy exchange process.

The structures of (**2**), (**3**), and (**4**) are probably based on a distorted octahedron as found with $[WBr_2(CO)_2(nbd)]$. Although several isomeric forms are possible in every case only one isomer is observed in solution except for (**3b**) where n.m.r. data indicate that two forms exist [(i) and (ii)]. Spectroscopic data do not enable unequivocal structural assignments to be made in every case but tentative conclusions can be reached on the basis of ^1H n.m.r. spectra. Thus all the PMe_2Ph complexes exhibit one methyl-group doublet indicating that the metal centre is non-chiral and a plane of symmetry is present in the complexes. As with (**1**) the CO ligand will dominate the metal $d\pi$ electrons and it might be expected that back donation to the diene and ligand L will be maximised if the CO is *trans* to L and *cis* to the diene. On this basis a structure (**I**) related to (**1**) but with ligand L replacing one axial CO will be favoured although a second structure containing a plane of symmetry (**II**) is also possible.

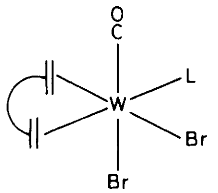
The norbornadiene adducts (**4a**) and (**4c**) exhibit the five ^1H resonances expected for a symmetric structure with three sets of two equivalent protons and two inequivalent single proton environments. Significantly in one case the CH_2 proton resonance appears as a barely resolved triplet [similar to (**1c**)] consistent with structure (**I**) where the two protons are equivalent by symmetry. This is also the case with (**4b**) implying a similar isomeric form although five separate norbornadiene resonances were not observed in this case due to signal overlap. The ^1H n.m.r. of (**2a**) exhibits the six separate cyclo-octadiene resonances expected for a symmetric structure [probably (**I**)] but signal overlap leads to a reduced number of peaks in the spectra of (**2b**) and (**2c**). Cyclo-octatetraene complexes (**3**) with such a structure should give two co-ordinated alkene resonances near δ 4 and two free alkene resonances near δ 7.5 in the ^1H n.m.r. spectrum. This is observed with (**3a**) and since coupling is observed between the two sets of co-ordinated alkene protons structure (**I**) is again indicated. A similar spectrum is observed with the minor isomer (ii) of (**3b**) whereas although the major isomer and (**3c**) exhibit the same number of peaks one of the co-ordinated alkene resonances in each case consists of a partially resolved doublet of doublets. This may reflect a small distortion in the structure or alternatively a less symmetric form such as (**III**) or less likely, (**IV**).



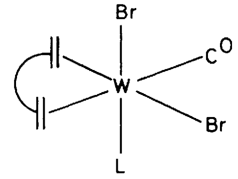
(I)



(II)



(III)



(IV)

The formation of seven-co-ordinate complexes (**6**) by addition of 2:1 molar excess of ligand to $[WBr_2(CO)_2(nbd)]$ appears to depend on the nature of the ligand since t-butyl isocyanide, unlike $P(OMe)_3$ and PMe_2Ph, only gives the 1:1 adduct (**4a**) obtained on addition of one mole of isocyanide. Spectroscopic data indicate that only one isomeric form of the $P(OMe)_3$ derivative (**6a**) is formed whereas the PMe_2Ph complex (**6b**) exists in solution as an equilibrium mixture of two isomers (ratio 3:1) according to i.r. and n.m.r. spectroscopic studies. Compound (**6a**) and the major isomer of (**6b**) exhibit similar spectroscopic features, *viz.* four norbornadiene resonances in the ^1H n.m.r. spectrum, the CH_2 resonance appearing as an AB quartet indicating inequivalence of the two protons. The phosphorus ligands give rise to virtual triplets suggesting a *trans* arrangement.[17] In the case of the PMe_2Ph derivative two triplets are observed due to the diastereotopic nature of the two methyl groups while the single resonance in the ^{31}P n.m.r. spectrum confirms that only one phosphorus environment exists. No significant changes were observed in the spectra down to −70 °C.

The minor isomer of (**6b**) exhibits a ν(CO) mode in the i.r. spectrum some 80 cm^{-1} to low frequency of the major isomer suggesting a substantial increase in W–CO π back-donation relative to the latter. Five distinct norbornadiene resonances are observed, ratio 1:1:2:2:2, while two PMe_2Ph multiplets are observed consisting of a broad resonance lying between a 1:1

Table 2. Hydrogen-1 n.m.r. data (δ) for the complexes*

Complex	Solvent	
(1a)	$CDCl_3$	4.41 (d, J = 2.1, 4 H), 3.74 (m, 4 H), 3.02 (m, 4 H)
(1b)	$CDCl_3$	7.38 (m, 4 H), 4.18 (m, 4 H)
(1c)	$CDCl_3$	4.42 (t, J = 2.7, 4 H), 3.98 (br m, 2 H), 0.79 (t, J = 1.45, 2 H)
(2a)	$CDCl_3$	4.90 (m, 2 H), 3.98 (m, 2 H), 3.76 (m, 2 H), 3.68 (m, 2 H), 3.04 (m, 2 H), 2.84 (m, 2 H) (C_8H_{12}); 1.78 (s, 9 H, $CNBu^t$)
(2b)	$CDCl_3$	5.05 (m, 2 H), 3.81 (m, 6 H), 3.05 (m, 2 H), 2.81 (m, 2 H) (C_8H_{12}); 3.98 [d, J_{PH} = 9.8, 9 H, $P(OMe)_3$]
(2c)	$CDCl_3$	5.0 (m, 2 H), 3.78 (m, 4 H), 3.10 (m, 4 H), 2.05 (m, 2 H) (C_8H_{12}); 7.94 (m), 7.45 (m) (total 5 H, C_6H_5), 2.20 (d, J_{PH} = 8.0, 6 H, CH_3)
(3a)	$CDCl_3$	7.61 (s, 2 H), 7.49 (s, 2 H), 4.52 (d, J = 12, 2 H), 3.51 (d, J = 2.1, 2 H) (C_8H_8); 1.70 (t, J = 1.3, 9 H, $CNBu^t$)
(3b) (i)	$CDCl_3$	7.51, 7.50 (overlapping s, 4 H), 4.64 (d, J = 12.2, 2 H), 3.58 (dd, J = 10.2, 2 H) (C_8H_8); 3.95 [d, J = 9.6, 9 H, $P(OMe)_3$]
(ii)	$CDCl_3$	7.93 (s, 2 H), 7.67 (s, 2 H), 5.65 (d, J = 11.65, 2 H), 3.31 (d, J = 10.95, 2 H) (C_8H_8); 3.99 [d, J = 11.50, 9 H, $P(OMe)_3$]
(3c)	$CDCl_3$	7.41 (s, 2 H), 7.34 (s, 2 H), 4.53 (d, J = 12.4, 2 H), 2.80 (dd, 2 H) (C_8H_8); 7.90 (m), 7.40 (m) (total 5 H, C_6H_5), 2.16 (d, J_{PH} = 8.3, 6 H, CH_3)
(4a)	$CDCl_3$	4.73 (m, 2 H), 3.88 (br m, 1 H), 3.86 (m, 2 H), 3.76 (br m, 1 H), 0.57 (br s, 2 H) (C_7H_8); 1.71 (br, s, 9 H, $CNBu^t$)
(4b)	$CDCl_3$	4.74 (m, 2 H), 3.96 (m, 2 H), 3.77 (m, 2 H), 0.53 (br s, 2 H) (C_7H_8); 3.93 [d, J_{PH} = 9.8, 9 H, $P(OMe)_3$]
(4c)	$CDCl_3$	4.69 (br s, 2 H), 3.84 (br s, 1 H), 3.46 (br m, 1 H), 3.23 (br m, 2 H), 0.43 (t, J = 1.4, 2 H) (C_7H_8); 7.94 (m), 7.48 (m) (total 5 H, C_6H_5), 2.15 (d, J_{PH} = 9.6, 6 H, CH_3)
(5a)	$CDCl_3$	4.11 (m, 4 H), 3.71 (br s, 2 H), 1.39 (t, J = 1.4, 2 H) (C_7H_8); 1.57 (s, 9 H, $CNBu^t$)
(5b)	$CDCl_3$	4.45 (m, 2 H), 3.49 (m, 4 H), 1.20 (AB quartet, 2 H) (C_7H_8); 3.68 [d, J_{PH} = 11.0, 9 H, $P(OMe)_3$]
(5c)	$CDCl_3$	4.06 (t, J = 2.6, 4 H), 3.63 (br s, 2 H), 1.42 (br s, 2 H) (C_7H_8); 7.60 (m), 7.40 (m) (total 5 H, C_6H_5), 2.24 (d, J_{PH} = 9.4, 6 H, CH_3)
(6a)	$CDCl_3$	3.81 (br m, 2 H), 3.38 (br m, 2 H), 2.53 (br m, 2 H), 0.87 (AB quartet, 2 H) (C_7H_8); 3.92 [t, J = 4.95, 18 H, $P(OMe)_3$]
(6b)	$CDCl_3$	7.65 (m), 7.40 (m) (C_6H_5). Major Isomer: 2.91 (m, 2 H), 1.96 (br s, 2 H), 1.75 (br s, 2 H), 0.40 (AB quartet, 2 H) (C_7H_8); 2.2 (t, J = 3.75, 6 H), 2.17 (t, J = 4.15, 6 H) [PMe_2Ph]
		Minor Isomer: 3.43 (m, 1 H), 3.34 (m, 1 H), 2.93 (m, 2 H), 2.71 (m, 2 H), 0.71 (br s, 2 H) (C_7H_8); 2.09 (m, 6 H), 1.97 (m, 6 H) [PMe_2Ph]
(6c)	$CDCl_3$	4.35 (t, J = 4.3, 2 H), 3.96 (br s, 1 H), 3.78 (br s, 1 H), 3.43 (t, J = 4.3, 2 H), 1.46 (br s, 2 H) (C_7H_8); 9.91 (d, J = 5.5, 1 H), 9.68 (d, J = 5.2, 1 H), 8.29 (d, J = 8.3, 1 H), 8.10 (m, 3 H), 7.60 (m, 2 H) (bipy)
(7a)	$CDCl_3$	0.96 (s, $CNBu^t$)
(7b)	$CDCl_3$	3.77 [m, $P(OMe)_3$]
(7c)	CD_2Cl_2	1.96 (br m), 1.76 (d, J_{PH} = 9.60), 1.64 (br m,), 1.55 (s), 1.26 (d, J_{PH} = 8.60) [PMe_2Ph]
(8)	$CDCl_3$	1.51 (s, $CNBu^t$)

* J Values are in Hz; br = broad, m = multiplet.

doublet. This is consistent with the spectra predicted for a $H_nPP'H'_n$ system when ^{31}P–^{31}P coupling is intermediate between large and small thus indicating *cis* phosphine ligands[17,18] a suggestion supported by the similarity of the norbornadiene resonances in the ^1H n.m.r. spectrum of the complex **(6c)** where *cis* nitrogens are obligatory. The presence of two PMe_2Ph multiplets again indicates diastereotopic methyl groups since only one ^{31}P n.m.r. resonance is found. However, the data do not allow us to assign structures to the complexes, a conclusion which also applies to the bipy complex **(6c)** which has similar spectroscopic features to those of the minor isomer of **(6b)**.

Unlike $[WBr_2(CO)_2(nbd)]$ the corresponding cod and cot complexes **(1a)** and **(1b)** react with excess of ligand L [= $P(OMe)_3$ or PMe_2Ph] to give complexes **(7b)** and **(7c)** respectively, resulting from displacement of diene (L′). Assuming that a seven-co-ordinate dicarbonyl $[WBr_2(CO)_2LL']$ is an intermediate in such reactions it appears that in the subsequent reaction with excess ligand substitution of the diene is preferred to the carbonyl displacement reaction observed with the norbornadiene derivatives. This possibly reflects the greater stability of metal–norbornadiene bonding resulting from the release of strain associated with co-ordination and subsequent rehybridisation of the four sp^2 carbon atoms. Complexes of this stoicheiometry have been isolated previously from reactions of phosphorus nucleophiles with $[\{MX_2(CO)_4\}_2]$ (M = Mo or W; X = Cl, Br, or I), the reactions proceeding *via* isolable tricarbonyl intermediates.[3]

Isocyanides undergo a more complex sequence of reactions which give, amongst other products, $[MX_2(CO)_2(CNR)_3]$ and $[MX_2(CO)(CNR)_4]$ (X = halide).[19] It is not surprising therefore to find that 2:1 or 3:1 ratios of $CNBu^t$ and $[WBr_2(CO)_2L']$ (L′ = cot or cod) give $[WBr_2(CO)_2(CNBu^t)_3]$ **(7a)** while >3:1 excess of isocyanide gives $[WBr_2(CO)(CNBu^t)_4]$ **(8)**, reflecting the greater ability of isocyanides to displace CO ligands. The spectroscopic features of **(7a)** and **(8)** are similar to those of related complexes $[WI_2(CO)_2(CNBu^t)_3]$ and $[WI_2(CO)(CNBu^t)_4]$ the structures of which have been elucidated by single-crystal *X*-ray diffraction studies.[20] Several solid-state forms of the former have been isolated, three of which have been found to contain molecular structures approximating to a 4:3 ligand 'piano stool' geometry. The structure of $[WI_2(CO)(CNBu^t)_4]$ has been shown to approximate to that of a capped octahedron with the carbonyl group as the capping ligand and the two iodines on the uncapped face. It is conceivable that such structures are adopted by the bromo-analogues **(7a)** and **(8)** but spectroscopic data do not allow us to confirm this.

The PMe_2Ph complex **(7c)** has been reported previously[21] but limited n.m.r. data were obtained and consequently a structural assignment not attempted. The appearance of two sets of ^{31}P n.m.r. peaks at 20 °C, one of which suggested fluxional behaviour, prompted us to carry out full variable-temperature ^1H and ^{31}P n.m.r. studies. As with $[MX_2(CO)_2(PMe_3)_3]$ (M = Mo or W; X = Cl, Br, or I)[22] the ^1H spectra are too complex to provide structural information whereas ^{31}P-$\{^1H\}$ spectra obtained over the range −90 to +95 °C (see the Figure) are particularly revealing. Two isomers are clearly present, one of which (A) exhibits an AX_2 triplet and doublet with ^{183}W satellites indicating one unique and two equivalent phosphine ligands. However, the doublet shows signs of broadening at −90 °C suggesting that the equivalence may be due to a two-site exchange process with a very low barrier to

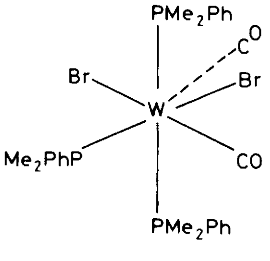
Table 3. I.r. and $^{31}P-\{^1H\}$ n.m.r.* data for the complexes

Complex	I.r. solvent	ν(CO)/cm^{-1}	ν(CN)/cm^{-1}	δ	J_{WP}		Temperature (°C)
(**1a**)	$CHCl_3$	2 074w, 2 018s					
(**1b**)	CCl_4	2 088w, 2 037s					
(**1c**)	CH_2Cl_2	2 070w, 2 000s					
(**2a**)	CCl_4	2 000s	2 182m				
(**2b**)	$CHCl_3$	1 983s		105.50	292		−20
(**2c**)	$CHCl_3$	1 978s		−23.75	165		−20
(**3a**)	$CHCl_3$	2 025s	2 198m				
(**3b**)	$CHCl_3$	2 015s		99.60	293		−20
(**3c**)	$CHCl_3$	2 010s		−24.50	160		−20
(**4a**)	$CHCl_3$	1 985s	2 180m				
(**4b**)	$CHCl_3$	1 984s		117.35	309		−20
(**4c**)	$CHCl_3$	1 974s		−14.3	176		−20
(**5a**)	CCl_4	2 058w, 1 976s	2 218m				
(**5b**)	$CHCl_3$	2 060w, 1 983s, 1 960 (sh)		96.05	293		−20
(**5c**)	$CHCl_3$	2 020w, 1 955s		−27.95	150		−10
(**6a**)	$CHCl_3$	1 980s		107.4	380	(Major isomer)	−10
(**6b**)	$CHCl_3$	1 979s, 1 896m,		−26.2	224.5	(Minor isomer)	−10
		1 896m		−20.0	137.4		−10
(**6c**)	CH_2Cl_2	1 908s					
(**7a**)	$CHCl_3$	1 979s	2 180s				
		1 914s	2 160s		J_{PP}		
(**7b**)	$CHCl_3$	1 961s		δ_1 125.13 (d, 2 P)	14.8	Isomer (**A**)	−30
		1 880s		δ_2 99.6 (t, 1 P)	14.6		
				δ_1 117.86 (d, 1 P)	J_{13} = 198.4	Isomer (**B**)	
				δ_2 117.79 (d, 1 P)	J_{23} = 163.6		
				δ_3 106.6 (dd, 1 P)	J_{31} = 199.5		
					J_{32} = 163.6		
(**7c**)	$CHCl_3$	1 922s		δ_1 −10.41 (d, 2 P)	12.6	Isomer (**A**)	−90 (CD_2Cl_2)
		1 830s		δ_2 −30.77 (t, 1 P)	12.8		
				δ_1 −14.80 (dd, 1 P)	J_{12} = 17.8	Isomer (**B**)	
					J_{13} = 162.3		
				δ_2 −23.31 (dd, 1 P)	J_{21} = 17.8		
					J_{23} = 44.2		
				δ_3 −29.05 (dd, 1 P)	J_{31} = 162.3		
					J_{32} = 44.3		
(**8**)	$CHCl_3$	1 980w	2 156s,				
		1 890s	2 136s,				
			2 199s,				
			2 090m (sh)				

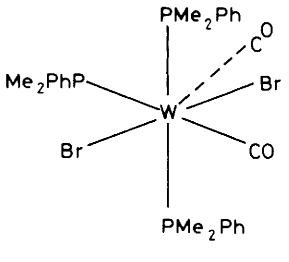
* Measured in $CDCl_3$ unless stated otherwise; J values in Hz.

exchange. The $^{31}P-\{^1H\}$ spectrum of the second isomer (**B**) varies significantly with temperature. At −90 °C three phosphorus multiplets are observed, each a doublet of doublets accompanied by ^{183}W satellites. At higher temperatures P^2 and P^3 undergo site exchange leading to a broad distorted doublet at 20 °C while the P^1 resonance consists of distorted triplet. Above 20 °C these peaks broaden again and coalesce at *ca.* 95 °C. Thus two separate dynamic processes are indicated, the lower energy one involving equilibration of two phosphine sites, the higher energy process leading to exchange between all three phosphine sites. These data can be compared with the $^{31}P-\{^1H\}$ spectra of $[MX_2(CO)_2(PMe_3)_3]$ (M = Mo, X = Cl, Br, I, or CNO; M = W, X = Cl, I, or CNO) where in most cases an AX_2 pattern [*cf.* isomer (**A**)] was observed.[22b] However, two isomers of $[MoBr_2(CO)_2(PMe_3)_3]$ and $[WCl_2(CO)_2(PMe_3)_3]$ were found, each exhibiting AX_2 spectra apart from the major isomer of the latter which exhibited a singlet between −60 and +50 °C indicating fluxional behaviour as found with (**7c**), isomer (**B**).

The n.m.r. data for (**7c**) do not allow us to define the isomeric forms (**A**) and (**B**) unambiguously but *X*-ray diffraction studies of related complexes $[MoCl_2(CO)_2(PMe_2Ph)_3]\cdot MeOH$[23] and $[MoBr_2(CO)_2(PMe_2Ph)_3]\cdot Me_2CO$[24] provide information concerning possible structures. Both exhibit distorted octahedral geometry with a CO ligand capping one of the octahedral faces: the latter has three phosphines occupying the capped face and two bromine atoms and a CO the uncapped face, while in the former two PMe_2Ph ligands and a CO occupy the capped face and two chlorines and the remaining phosphine the uncapped face. Tentatively we can conclude that the data for (**7c**) [isomer (**A**)] are explicable in terms of structure (**V**) as found for $[MoCl_2(CO)_2(PMe_2Ph)_3]$ in which flipping of the



(V)



(VI)

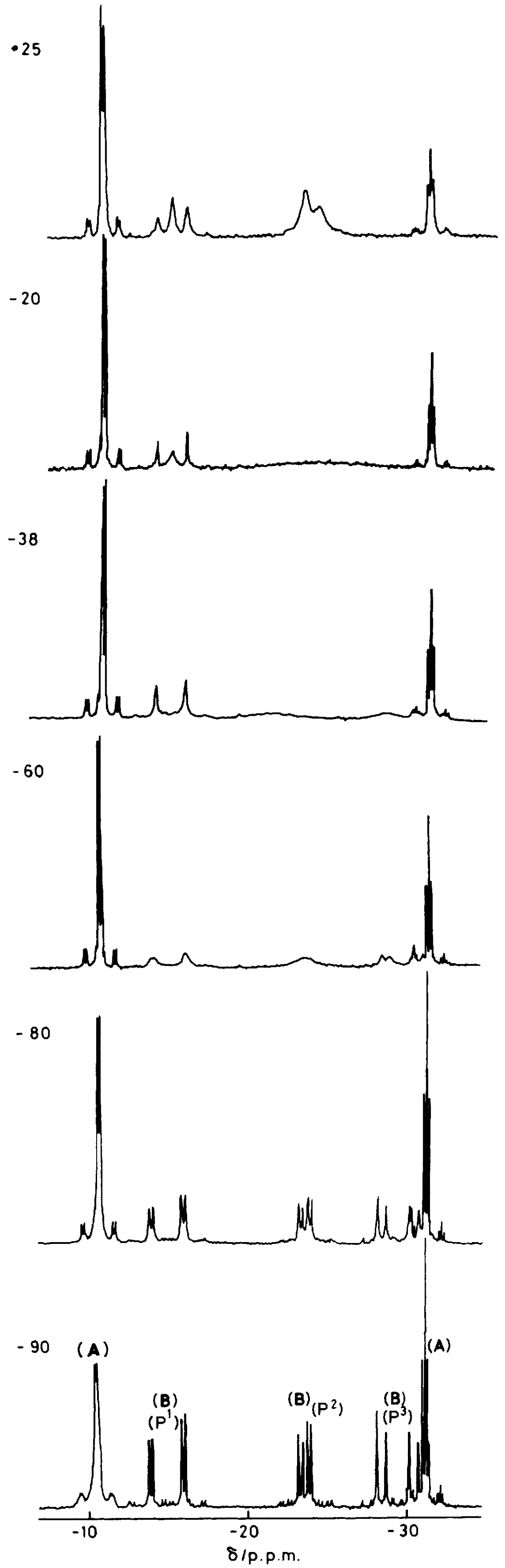


Figure. Variable-temperature (°C) $^{31}P-\{^1H\}$ n.m.r. spectra of $[WBr_2(CO)_2(PMe_2Ph)_3]$ (**7c**)

capping CO ligand between equivalent sites above and below the $WBr_2(CO)(PMe_2Ph)$ plane averages two observable PMe_2Ph environments. Such a process has been proposed to explain the dynamic n.m.r. data for arsine complexes $[MoBr_2(CO)\{P(OMe)_3\}_2\{Me_2AsC(CF_3)=C(CF_3)AsMe_2\}]$.[16] Conceivably isomer (**B**) possesses a related structure, *e.g.* (**VI**) but with a significantly lower energy barrier for the first site-exchange process.

$[WBr_2(CO)_2\{P(OMe)_3\}_3]$ (**7b**) appears to be less stable in solution than the PMe_2Ph complex (**7c**) and n.m.r. spectral samples were prepared at low temperatures (0 °C) to minimise decomposition. As with (**7c**), two ν(CO) modes are observed in the i.r. spectrum while the ^1H n.m.r. spectrum at 20 °C exhibits a filled-in doublet due to a $H_nPP'H'_n$ system.[17,18] At lower temperatures this deceptively simple resonance did not change markedly and hence provides little structural information. In contrast the $^{31}P-\{^1H\}$ n.m.r. spectrum at −30 °C indicates that as with (**7c**) two isomers are present in solution. The first resembles (**7c**) [isomer (**A**)], exhibiting a doublet and triplet with tungsten satellites, while the spectrum of the second consists of a distorted doublet of doublets ($^2J_{PP}$ = *ca.* 199 and 163.6 Hz) and two distorted overlapping doublets with corresponding J values. Thus two large coupling constants are observed while two of the $P(OMe)_3$ groups appear to be uncoupled. As the temperature was raised to 25 °C all of the peaks broadened significantly and this, in conjunction with the observed instability of the complex in solution, possibly suggests exchange between co-ordinated and free $P(OMe)_3$ generated by dissociative equilibria or decomposition.

Conclusions

The chemistry of the d^4 tungsten(II) complexes $[WBr_2(CO)_2L']$ (**1**) described in the present work is basically similar to that of related phosphine and arsine complexes $[MX_2(CO)_2(ER_3)_2]$[3] in that six- and seven-co-ordinate derivatives can be obtained in reactions with two-electron donor ligands. Detailed differences are apparent upon closer examination since the diene complexes do not form tricarbonyls $[WBr_2(CO)_3L']$ whereas stable complexes $[MX_2(CO)_3(ER_3)_2]$ are well known. Since seven-co-ordinate norbornadiene adducts $[WBr_2(CO)_2L(nbd)]$ and $[WBr_2(CO)L_2(nbd)]$ are readily obtainable it appears that the effect of diene co-ordination is to activate the CO groups to substitution, *i.e.* a combination of the π-acceptor diene and more than one π-acceptor CO ligand on the same metal leads to instability. This is confirmed by the ease with which diene loss occurs on reaction of (**1**) (L' = cod or cot) with excess ligand to give dicarbonyls $[WBr_2(CO)_2L_3]$ (**7**). It appears that the metal centre can only accommodate a relatively narrow range of electron density donated to it by the ligands and as a consequence only certain combinations of acceptor and donor ligands are possible.

It is not absolutely clear whether or not π-electron donation from the halogen ligands is important in this respect, particularly in the six-co-ordinate complexes. At the present time stabilisation of formally 16-electron Mo^{II} and W^{II} d^4 configurations by π donation from the π-perpendicular orbitals of an alkyne appears to be reasonably well established[1,4,5] (see following paper). Convincing arguments have also been presented that π donation from oxygen and sulphur ligands occurs in a similar manner in complexes such as $[Mo(OBu^t)_2(CO)_2(py)_2]$[13a] and $[M(S_2CNMe_2)_2(CO)_2]$[4] (M = Mo or W) while π donation from the halogen ligand has been cited as a central factor in determining the rate of CO dissociation from manganese complexes $[MnX(CO)_5]$ (X = Cl, Br, or I).[25] Stabilisation of six-co-ordinate species (**1**)—(**4**) by bromine ligands seems equally plausible but in view of the fact that divalent Group 6A metal complexes such as $[Cr(Me)_2(Me_2$-

$PCH_2CH_2PMe_2)_2]$[26] and $[Mo(Me)_2(PMe_2Ph)_2(cod)]$[15] have been isolated containing no π-donor ligands, it appears that although the halogens *may* act as π donors it is not absolutely necessary for them to do so in this type of complex.

Experimental

$[\{WBr_2(CO)_4\}_2]$ was synthesised by literature methods.[10] Reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were refluxed over powdered calcium hydride and distilled under nitrogen before use. I.r. spectra were recorded as solutions on a Perkin-Elmer 580 spectrophotometer and calibrated against polystyrene. N.m.r. spectra were recorded on a Bruker WP 200 SY spectrometer at 200.13 (^1H), 188.31 (^{19}F), and 81.02 MHz (^{31}P); chemical shifts are referred to $SiMe_4$, CCl_3F, and 85% H_3PO_4 (aqueous) respectively with positive chemical shifts to high frequency. Mass spectra were obtained at 70 eV ($\approx 1.1 \times 10^{-17}$ J) on a Vacuum Generator's updated AEI MS9.

Reaction of $[\{WBr_2(CO)_4\}_2]$ *with Dienes.*—Due to the instability of $[\{WBr_2(CO)_4\}_2]$ in the solid state it was found to be more convenient to use a 'one-pot' synthesis. $[\{WBr_2(CO)_4\}_2]$ was prepared from the reaction of $[W(CO)_6]$ and bromine at -78 °C, and the excess Br_2 and unreacted $[W(CO)_6]$ removed by washing with hexane. The subsequent reaction with dienes was then carried out in the same reaction vessel. In a typical reaction *ca.* 1 g of freshly prepared $[\{WBr_2(CO)_4\}_2]$ was suspended in hexane (60 cm^3) under nitrogen and the diene (0.5 g) added. The mixture was then refluxed gently under nitrogen until no unreacted $[\{WBr_2(CO)_4\}_2]$ remained and a purple solution formed. The hot solution was filtered off and concentrated *in vacuo* when dark green-black crystals formed. Further concentrations of the mother-liquor and cooling to -15 °C gave a second batch. Recrystallisation from diethyl ether–hexane gave analytically pure samples in yields of 57%, (**1a**), 54%, (**1b**), and 65%, (**1c**).

Reactions of $[WBr_2(CO)_2(cod)]$ *with Nucleophiles* L [= $CNBu^t$, $P(OMe)_3$ *and* PMe_2Ph] (*Molar Ratio* 1:1).—In a typical reaction $[WBr_2(CO)_2(cod)]$ (300 mg) was dissolved in diethyl ether (30 cm^3). The appropriate quantity of ligand in Et_2O (5 cm^3) was added dropwise with stirring and the reaction allowed to proceed for 1 h. The reaction mixture was filtered, reduced in volume, hexane (15 cm^3) added and on cooling to -15 °C dark green crystals of product were produced. Yields: (**2a**) 55%, (**2b**) 67%, (**2c**) 41%.

In some reactions small amounts of dicarbonyl products $[WBr_2(CO)_2L_3]$ (**7**) were also produced in varying yields.

Reaction of $[WBr_2(CO)_2(cot)]$ *with* $CNBu^t$ (*Molar Ratio* 1:1).—The complex (200 mg) was reacted with $CNBu^t$ (33 mg) in Et_2O (20 cm^3) for 15 h. The solution was reduced in volume, hexane (10 cm^3) added and on cooling to -15 °C black crystals of (**3a**) were obtained in 42% yield. In some reactions trace amounts of a dark red crystalline material were also obtained which were not identified.

Reaction of $[WBr_2(CO)_2(cot)]$ *with* $P(OMe)_3$ (*Molar Ratio* 1:1).—The complex (200 mg) and $P(OMe)_3$ (50 mg) in Et_2O (30 cm^3) were stirred for 30 min. The solution was filtered, reduced in volume and hexane (10 cm^3) added. Crystallisation at -15 °C gave yellow crystals of (**7b**), yield 46%. Concentration of the mother-liquor and further cooling gave dark green crystals of (**3b**) in 26% yield.

Reaction of $[WBr_2(CO)_2(cot)]$ *with* PMe_2Ph (*Molar Ratio* 1:1).—The complex (200 mg) was reacted with PMe_2Ph (55 mg) in Et_2O (30 cm^3) for 6 h. The solution was filtered, reduced in volume, and hexane (15 cm^3) added. Cooling to -15 °C gave a mixture of yellow crystals (**7c**) and black crystals (**3c**) which were separated by hand. Recrystallisation from Et_2O–hexane gave (**3c**) in 35% yield and (**7c**) in 19% yield.

Reactions of $[WBr_2(CO)_2(nbd)]$ *with Nucleophiles* L [= $CNBu^t$, $P(OMe)_3$, *and* PMe_2Ph] (*Molar Ratio* 1:1).—In a typical reaction, the complex (250 mg) was dissolved in Et_2O (20 cm^3) and a solution of ligand L in Et_2O (5 cm^3) added slowly with stirring. A yellow solution formed and the crystalline product was obtained on addition of hexane and cooling to -15 °C. A second recrystallisation from Et_2O–hexane gave analytically pure samples of $[WBr_2(CO)_2L(nbd)]$ (**5**) in yields of 65%, (**5a**), 32%, (**5b**), and 47%, (**5c**). The above reactions were repeated but on addition of ligand L the mixture was stirred for several hours until the solution turned dark blue [L = $P(OMe)_3$ or PMe_2Ph]. Recrystallisation of the product from Et_2O–hexane gave dark green crystals of $[WBr_2(CO)L(nbd)]$ (**4**) in yields of 46%, (**4b**), and 41%, (**4c**). No reaction was observed with L = $CNBu^t$. In some cases small amounts of the 1:3 adducts (**6a**) and (**6b**) were isolated in these reactions.

Decarbonylation of $[WBr_2(CO)_2(CNBu^t)(nbd)]$ (**5a**).—Complex (**5a**) (100 mg) was refluxed gently in hexane (30 cm^3) under nitrogen for 1 h when the solution turned dark blue. The hot solution was filtered quickly and on cooling to -15 °C gave dark blue-green crystals. Subsequent recrystallisation from diethyl ether–hexane gave $[WBr_2(CO)(CNBu^t)(nbd)]$ (**4a**) in 43% yield.

Decarbonylation of $[WBr_2(CO)_2(PMe_2Ph)(nbd)]$.—The complex (40 mg) was dissolved in Et_2O (30 cm^3) and allowed to sit under nitrogen for 16 h, when a deep blue solution was obtained. This was filtered, reduced in volume and on addition of hexane (10 cm^3) and cooling to -15 °C dark green crystals of (**4c**) were obtained in 34% yield.

Reaction of $[WBr_2(CO)_2(nbd)]$ *with* $P(OMe)_3$ (*Molar Ratio* 1:3).—The complex (200 mg) in Et_2O (30 cm^3) was reacted with $P(OMe)_3$ (150 mg) for 2 h, when a yellow-orange solution was obtained. This was filtered, reduced in volume, and hexane added. Cooling to -15 °C gave orange crystals of (**6a**), yield 34%. A similar reaction of $[WBr_2(CO)_2(nbd)]$ with PMe_2Ph gave orange crystals of (**6b**) in 29% yield.

Reaction of $[WBr_2(CO)_2(nbd)]$ *with 2,2′-Bipyridyl.*—The complex (200 mg) in Et_2O (50 cm^3) was treated with bipy (65 mg) and the mixture stirred for 14 h. The resulting dark brown product was filtered off and washed with small quantities of Et_2O. The crude material was then recrystallised from dichloromethane–hexane to give red-brown crystals of (**6c**) in 65% yield.

Reaction of $[WBr_2(CO)_2(cot)]$ *with* $CNBu^t$ (*Molar Ratio* 1:2.5).—The complex (200 mg) and $CNBu^t$ (83 mg) in Et_2O (30 cm^3) were reacted for 18 h. The solution was filtered, reduced in volume, hexane (15 cm^3) added and on cooling to -15 °C dark yellow crystals obtained. Recrystallisation from Et_2O–hexane gave (**7a**) in 37% yield.

Reaction of $[WBr_2(CO)_2(cot)]$ *with* $P(OMe)_3$ (*Molar Ratio* 1:4).—The complex (250 mg) and $P(OMe)_3$ (250 mg) were reacted in Et_2O (30 cm^3) for 1.5 h to give a yellow solution. This was filtered, volatiles removed and the product recrystallised twice from Et_2O–hexane to give yellow crystals of (**7b**) in 65% yield.

Reaction of $[\mathrm{WBr_2(CO)_2(cot)}]$ *with* $\mathrm{PMe_2Ph}$ (*Molar Ratio* 1:4).—The complex (250 mg) and $\mathrm{PMe_2Ph}$ (275 mg) were reacted in $\mathrm{Et_2O}$ (30 $\mathrm{cm^3}$) for 1.5 h. The yellow solution was filtered and volatiles removed. Recrystallisation from $\mathrm{Et_2O}$–hexane gave (**7c**) in 49% yield.

Reaction of $[\mathrm{WBr_2(CO)_2(cot)}]$ *with* $\mathrm{CNBu^t}$ (*Molar Ratio* 1:4).—The complex (200 mg) in $\mathrm{Et_2O}$ (30 $\mathrm{cm^3}$) was reacted with $\mathrm{CNBu^t}$ (130 mg) for 15 h. The yellow solution was filtered, reduced in volume, hexane (10 $\mathrm{cm^3}$) added and cooled to −15 °C to give yellow crystals. Recrystallisation from $\mathrm{Et_2O}$–hexane a second time gave analytically pure samples of (**8**) in 21% yield.

Acknowledgements

We thank the S.E.R.C., the C.N.R., and the British Council for financial support of this work. We also thank Professor F. A. Cotton for access to unpublished data.

References

1 (*a*) J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1983, 1667; (*b*) J. J. Davidson and G. Vasapollo, *Polyhedron*, 1983, **2**, 305; (*c*) J. L. Davidson, W. F. Wilson, Lj. Manojlović-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1983, **254**, C6; (*d*) L. Carlton, J. L. Davidson, J. C. Miller, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1984, 12.
2 G. J. Kubas, *J. Chem. Soc., Chem. Commun.*, 1980, 61.
3 R. Colton, *Coord. Chem. Rev.*, 1971, **6**, 269.
4 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 6568 and refs. therein; J. L. Templeton, P. B. Winston, and B. C. Ward, *J. Am. Chem. Soc.*, 1981, **103**, 7713.
5 M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida, and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 5772.
6 P. Kubáček and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 4320.
7 R. Colton and G. R. Scollary, *Aust. J. Chem.*, 1968, **21**, 1427.
8 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1981, **103**, 3743 and refs. therein; D. L. Kepert, *Prog. Inorg. Chem.*, 1979, **25**, 42; M. G. B. Drew, *ibid.*, 1976, **23**, 67.
9 J. L. Davidson and G. Vasapollo, *J. Organomet. Chem.*, 1983, **241**, C24.
10 J. A. Bowden and R. Colton, *Aust. J. Chem.*, 1968, **21**, 2657.
11 F. A. Cotton and J. H. Meadows, unpublished work.
12 M. G. B. Drew, I. B. Tomkins, and R. Colton, *Aust. J. Chem.*, 1970, **23**, 2517.
13 (*a*) M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *J. Am. Chem. Soc.*, 1979, **101**, 7615; (*b*) M. H. Chisholm, J. C. Huffman, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1981, **103**, 4945.
14 R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.
15 E. Carmano-Guzman and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 1139.
16 W. R. Cullen and L. M. Mihichuk, *Can. J. Chem.*, 1976, **54**, 2548.
17 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.
18 'N.M.R. Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin, 1979, vol. 16.
19 C. M. Giandomenico, L. H. Hanau, and S. J. Lippard, *Organometallics*, 1982, **1**, 142 and refs. therein.
20 J. C. Dewan, M. M. Roberts, and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 1529.
21 J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 1970, 595.
22 (*a*) P. Umland and H. Vahrenkamp, *Chem. Ber.*, 1982, **115**, 3565; (*b*) E. Carmona, K. Doppert, J. M. Marin, M. L. Poveda, L. Sanchez, and R. Sanchez-Delgado, *Inorg. Chem.*, 1984, **23**, 530.
23 A. Mawby and G. E. Pringle, *J. Inorg. Nucl. Chem.*, 1972, **34**, 517.
24 M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1977, 557.
25 J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, 1976, **98**, 3160; D. Lichtenberger and T. L. Brown, *ibid.*, 1978, **100**, 366.
26 G. S. Girolami, J. E. Scott, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 5954.

Received 14*th November* 1984; *Paper* 4/1936