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Syntheses and structures of six and seven-coordinate diene complexes of molybdenum and tungsten(II). The crystal and molecular structures of [$WBr_2(CO)_2(PMePh_2)$(norbornadiene)] and [$WBr_2(CO)(N{\equiv}CCH{=}CH_2)$(norbornadiene)]

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Abstract

Reactions of [$WI_2(CO)_3(NCMe)_2$] with norbornadiene (NBD) and 1,5-cycloctadiene (COD) give six-coordinate dicarbonyls [$WI_2(CO)_2$(NBD)] and [$WI_2(CO)_2$(COD)], respectively. The related dibromo complex [$WBr_2(CO)_2$(NBD)] reacts with tertiary phosphines L to give unstable seven-coordinate adducts [$WBr_2(CO)_2$(L)(NBD)] (L = PPh_3, $PMePh_2$, PEt_3), which in the case of L = $PMePh_2$ was shown to undergo CO loss to give the six-coordinate derivative [$WBr_2(CO)(PMePh_2)$(NBD)]. X-ray diffraction studies of [$WBr_2(CO)_2(PMePh_2)$(NBD)] reveal a seven-coordinate structure (distorted pentagonal bipyramid) with the diene C=C bonds on the pentagonal plane lying approximately parallel to the W–CO axes. Reactions of [$WBr_2(CO)_2$(NBD)] with organonitriles NCR at room temperature afford CO substitution products (R = Me, Pr^i, Ph, C_6H_4Me-4, CH=CH_2) directly with no evidence for seven-coordinate intermediates. [$WBr_2(CO)_2$(COD)] and acetonitrile similarly give [WBr_2(CO)(NCMe)(COD)]. X-ray diffraction studies of [$WBr_2(CO)(NCCH{=}CH_2)$(NBD)] confirmed a distorted octahedral structure where the carbonyl lies *trans* to the acrylonitrile ligand. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Six coordination; Seven coordination; Tungsten; Norbornadiene; Synthesis; Crystal structures

1. Introduction

An interesting feature of divalent molybdenum and tungsten chemistry is the ability of the metal to form either seven-coordinate 18-electron complexes which may be mono- or dinuclear or alternatively coordinatively unsaturated six-coordinate derivatives with a formal 16-electron configuration [1]. Although steric factors might be expected to play a significant role in determining the relative stability of six- and seven-coordinate derivatives, in some cases electronic factors may also be important. For example, formally electron deficient six-coordinate complexes could, in principle, be stabilised by π donation from certain anionic ligands, e.g. halides or oxygen donor ligands. Previously we have reported evidence for sulphur → metal π donation in thiolate complexes [$MSC_6F_5(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)$] [2], [$M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$ and [$W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]^-$ [3]. This may be responsible for the fact that pentafluorophenylthiolate norbornadiene complexes [$WBr(SC_6F_5)(CO)_2$(NBD)] and [$W(SC_6F_5)_2(CO)_2$(NBD)] [4] (NBD = norbornadiene) prefer six coordination, even when two-electron donor ligands are added. Related molybdenum and tungsten thiolate complexes have also been reported [5–7] which provide further support for this conclusion. However, substitution of one bromo ligand in [$WBr_2(CO)_2$(NBD)] (**1a**) [8] by potentially bidentate ligands L–L = O(O)CMe and O(S)CMe leads to 1:1 derivatives [$WBr(L{-}L)(CO)_2$(NBD)] [4] which, according to spectroscopic data, are probably seven coordinate. Seven coordination is also preferred in related species such as [$MoBr\{O(X)CMe\}(CO)_2(PPh_3)_2$] (X = O, S) [9].

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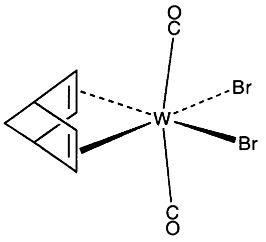


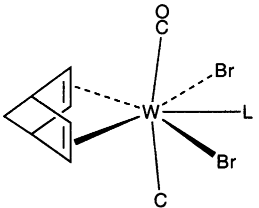
1a

It has so far proved difficult to rationalise the different structural preferences exhibited by d^4 complexes in this area of chemistry. However, there is some constraint on the structure and isomeric forms adopted by d^4 diene carbonyl derivatives such as $[WBr_2(CO)_2(NBD)]$ since, to achieve maximum π back donation to the C=C π* orbitals, the diene is constrained to lie *cis* to the carbonyl ligand(s) with the C=C axes approximately parallel to the M–C–O bonds [10]. This led us to extend our initial studies of seven-coordinate diene carbonyl complexes derived from the six-coordinate derivatives $[WBr_2(CO)_2(NBD)]$ [8] in order to assess the possible influence of diene ligands on structural preferences for six and seven coordination in W(II) derivatives.

Papers describing the reactions of $[MoX_2(CO)_2(NBD)]$ (X = I, Br) with N-donor ligands [11], the structure of the terpyridine (Terp) complex $[WBr(Terp)(CO)_2(NBD)]^+$ [12] and the tin complex $[WCl(SnCl_3)(CO)_3(NBD)]$ [13] prompt us to report some of our results in this area of chemistry.

2. Results and discussion

Previously we reported that two electron donors L (L = PMe_2Ph, $P(OMe)_3$ and $CNBu^t$) react with $[WBr_2(CO)_2(NBD)]$ (**1a**) to give related six-coordinate complexes $[WBr_2(CO)(L)(NBD)]$ (**2**) via seven-coordinate intermediates $[WBr_2(CO)_2(L)(NBD)]$ (**3**) [8]. With a view to characterising the role of seven-coordinate intermediates in CO substitution reactions of $[WBr_2(CO)_2(NBD)]$ reactions with other phosphines PPh_3, $PMePh_2$ and PEt_3 were carried out. Reactions carried out at room temperature proved to be complex although seven-coordinate species appeared to be formed initially. It subsequently proved possible to isolate the initial product in each case by slow addition of a diethylether solution of the phosphine to a diethylether solution of $[WBr_2(CO)_2(NBD)]$ at 0°C when the adducts **2a**–**c** were obtained as yellow solids.



	L
2a	PPh_3
2b	$PMePh_2$
2c	PEt_3

Elemental analysis of all three products isolated confirmed the stoichiometry $[WBr_2(CO)_2(L)(NBD)]$ (L = PPh_3 **2a**, $PMePh_2$ **2b**, and PEt_3 **2c**). Spectroscopic data are similar to those of the previously isolated adduct $[WBr_2(CO)_2(PMe_2Ph)(NBD)]$ vide infra but these did not allow unambiguous structure assignment. Consequently a single-crystal X-ray diffraction study of the $PMePh_2$ complex **2b** was carried out. Single crystals of **2b** suitable for X-ray crystallography were obtained from dichloromethane/60–80 petroleum ether solution. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1.

The tungsten atom in **2b** is seven coordinate and can be described as having a distorted pentagonal bipyramidal geometry. The two *trans* carbonyls occupy the two axial sites and the two alkene bonds, bromides and the phosphine the pentagonal plane. To a first approximation the structure is derived from $[W(CO)_2Br_2(NBD)]$ by opening out of the Br–W–Br angle from 105.86(9)° in **1a** to 146.43(4)° in **2b** thus generating a seventh coordination site which allows the phosphine to bond to tungsten. The metal therefore achieves coordinative saturation and attainment of the favoured 18-electron configuration. The effect of phosphine coordination on most of the molecular parameters is slight. Most significant are the increases in the OC–W–CO angle from 172.9(4) to 176.6(4)° and in the tungsten to bromine distances from 2.489(1) and 2.493(1) Å to 2.6452(12) and 2.6508(12) Å. The last may reflect the possibility of reduced opportunities for Br → W π bonding in the seven-coordinate complex or alternatively the effect of increased steric congestion in the pentagonal plane. We also draw attention to two intramolecular contacts between Br2 and a phenyl H atom, H22A, [2.592(12) Å] and between Br1 and another phenyl H atom, H21A, [3.036(12) Å].

The most significant feature of this complex is the fact that the pentagonal bipyramidal structure is preferred to the two main alternatives, the capped trigonal prism and the capped octahedron. Structural and theoretical studies suggest that the energy surface linking these three idealised seven-coordinate geometries is relatively flat [14,15]. The capped octahedron is usually preferred by halocarbonyl complexes of Mo(II) and W(II) [1b] but some examples of pentagonal bipyramidal geometry have been found e.g. $[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ and $[WI_2(CO)_3(PPh_2CH_2PPh_2)]$ [16]. Interestingly, the structure of the related seven-coordinate norbornadiene derivative $[WCl(SnCl_3)(CO)_3(NBD)]$ has been described as a distorted capped trigonal prism [13]. However, we note that the coordination geometry is almost identical to that of [$WBr_2(CO)_2$-$(PMePh_2)(NBD)$] (**2b**) which we prefer to describe as a distorted pentagonal bipyramid. To compare [WCl-$(SnCl_3)(CO)_3(NBD)$] with **2b**, the *trans* carbonyl ligands were considered axial and the pentagonal plane consisting of tungsten, the two midpoints of the NBD ligands, chloride, carbonyl and the tin ligand. The mean deviation from the pentagonal plane is 0.024 and 0.0934 Å for the former and **2b**, respectively, with the axial carbonyl carbon atoms no less than 82° from the pentagonal plane in both complexes. This similarity was confirmed by molecular modelling studies [17], which revealed a close correlation between the two structures. This apparent conflict in structure description merely illustrates that with seven-coordinate species, relating actual geometries of compounds to those of idealised polyhedra can be fraught with difficulties when distortions from idealised forms occur.

Kepert has shown that complexes of this type i.e. [$MX_2(CO)_3L{-}L$] containing a bidentate ligand L–L with a 'normalised bite' (distance between donor atoms of the chelate ring divided by the metal–ligand distance) $b < 1.11$ exhibit the pentagonal bipyramidal geometry whereas with $b > 1.11$ capped octahedral or capped trigonal prismatic structures are preferred [14]. In the case of [$WBr_2(CO)_2(PMePh_2)(NBD)$] (**2b**) a normalised bite value $b = 1.04$ was determined for the norbornadiene ligand, similarly for [$WCl(SnCl_3)$-$(CO)_3(NBD)$] [13], $b = 1.05$, consistent with the observed isomeric form. For this purpose the position of the 'donor atoms' of the diene were taken as the mid points of the C=C bonds. We note that in related complexes where the diene has a larger b value e.g. 1,5-cyclooctadiene, six rather than seven coordination is preferred e.g. in [$WBr(SC_5H_4N)(CO)(NBD)$] b ca. 1.28 [18]. Interestingly, the two equatorial halogens in pentagonal bipyramidal derivatives [$WI_2(CO)_3$-$\{P(OPh)_2\}_2NPh$] and [$WI_2(CO)_3(PPh_2CH_2PPh_2)$] [16] and the Cl and $SnCl_3$ ligands in [$WCl(SnCl_3)$-$(CO)_3(NBD)$] occupy adjacent sites, whereas the more symmetric structure in which the two equatorial halo ligands are separated by the phosphine ligand is preferred in [$WBr_2(CO)_2(PMePh_2)(NBD)$]. This difference may reflect thermodynamic preferences perhaps due to the effect of having different numbers of strong π acceptor carbonyl ligands coordinated to the metal. Alternatively, kinetic factors may be involved as a

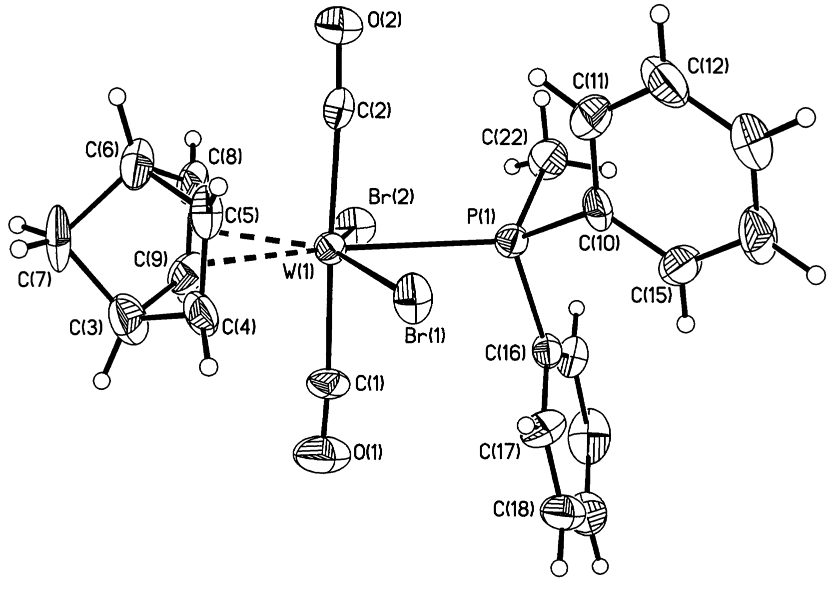


Fig. 1. Molecular structure of [$WBr_2(CO)_2(PMePh_2)(NBD)$] (**2b**).

Table 1
Selected bond lengths and angles for **2b**

Bond lengths (Å)					
W(1)–C(2)	2.013(11)	W(1)–C(1)	2.042(10)	W(1)–C(5)	2.325(11)
W(1)–C(8)	2.325(10)	W(1)–C(9)	2.333(11)	W(1)–C(4)	2.339(11)
W(1)–P(1)	2.641(3)	W(1)–Br(1)	2.6452(12)	W(1)–Br(2)	2.6508(12)
Bond angles (°)					
C(2)–W(1)–C(1)	176.6(4)	Br(1)–W(1)–Br(2)	146.43(4)	P(1)–W(1)–Br(2)	73.30(7)
P(1)–W(1)–Br(1)	74.33(6)	C(2)–W(1)–Br(2)	94.4(3)	C(1)–W(1)–Br(2)	83.0(3)

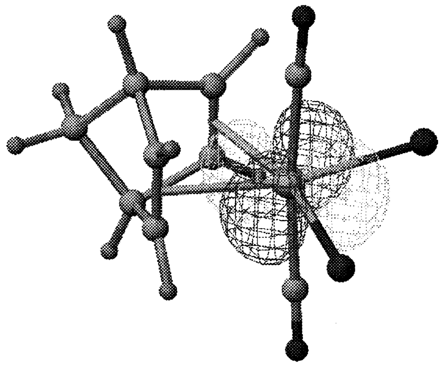


Fig. 2. The LUMO of $[WBr_2(CO)_2(NBD)]$ (**1a**) according to EHMO calculations.

consequence of the fact that the diphosphazane and tin complexes result from ligand displacement from seven-coordinate complexes, whereas $[WBr_2(CO)_2(PMePh_2)(NBD)]$ was obtained by addition of the seventh ligand, $PMePh_2$ to a six-coordinate precursor.

In this connection we note that the formal 16-electron configuration of the metal in **1a** implies the existence of a low lying metal-based orbital which could function as the site of attack by the phosphine. Consequently extended Hückel calculations [17] were carried out on the precursor $[WBr_2(CO)_2(NBD)]$ based on the geometry found in the solid state but with the NBD and CO positions adjusted to generate C_{2v} symmetry. These gave similar results to Fenske–Hall calculations on the idealised complex $[MoBr_2(CO)_2(H_2C{=}CH_2)_2]$ reported by Cotton [10] with the octahedral t_{2g} set of d_π orbitals split into a high-energy empty orbital the LUMO (primarily d_{xz} in Cotton's coordinate system) and two lower energy filled orbitals. The significant HOMO–LUMO gap, which is sufficient to produce spin pairing in the lower set of d_π orbitals, results from strong π bonding between d_{xy}, d_{yz} and the CO and diene π^* orbitals. If addition of a seventh ligand is frontier orbital controlled there are three possible directions for attack of a nucleophile such as a phosphine on the LUMO, see Fig. 2, all involving approach in the pentagonal plane. Two (equivalent) situations involve attack between a diene C=C bond and a bromide ligand. However, these are sterically less favourable than from a direction between the two bromides and *trans* to the diene. Since this would give the observed product **2b** directly it is conceivable that this reaction is indeed frontier orbital controlled.

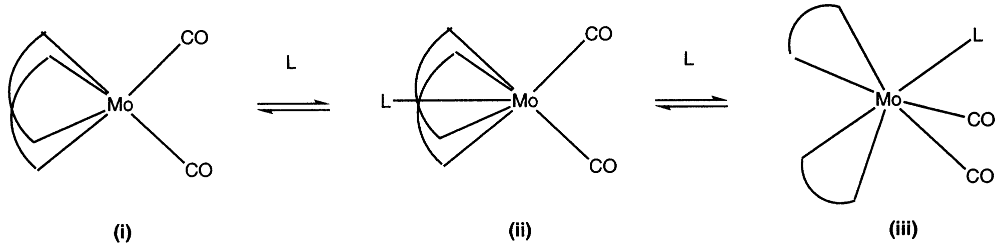
It is interesting to compare our results with those of Templeton [19] who measured equilibrium constants for a series of ligand additions to $[Mo(S_2CNR_2)_2(CO)_2]$ (R = Me, Et) including L = PPh_3 and $P(OPh)_3$ Eq. (1).

$$[Mo(S_2CNR_2)_2(CO)_2] + L \rightleftharpoons [Mo(S_2CNR_2)_2(CO)_2L] \quad (1)$$

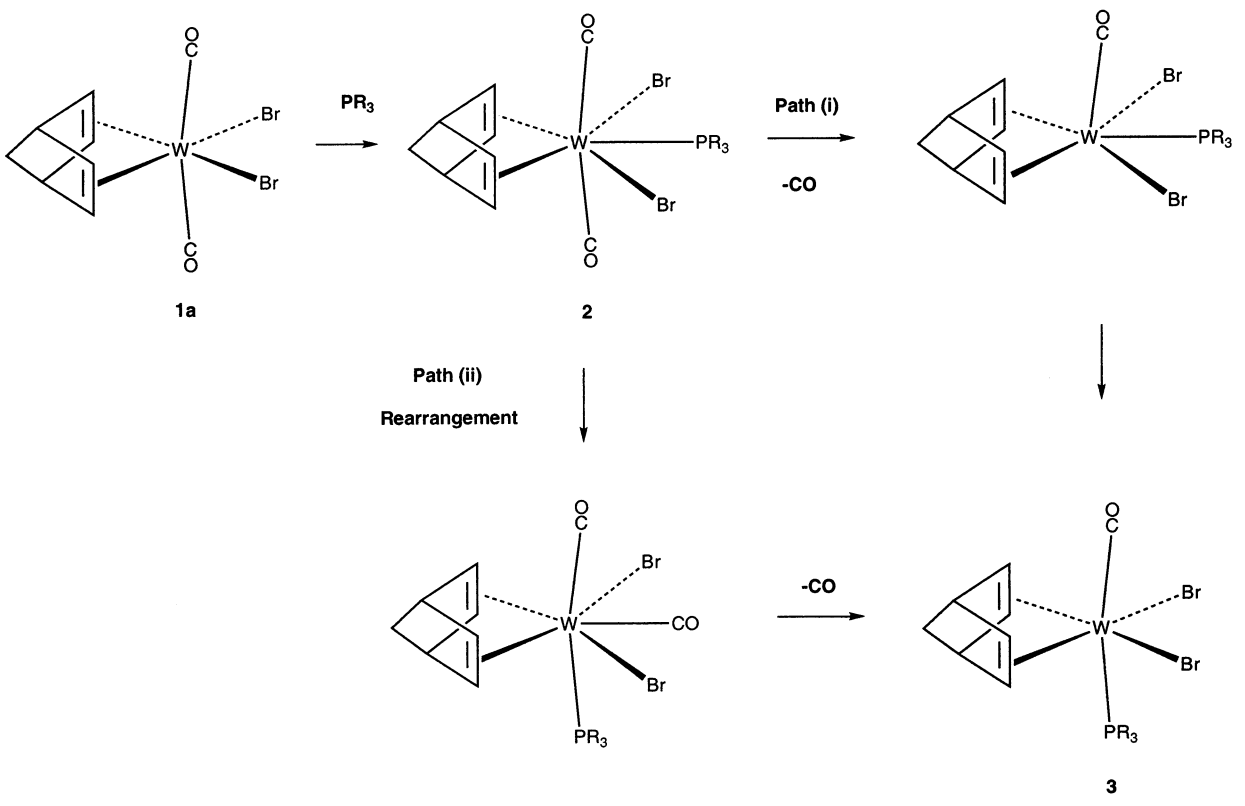
The six-coordinate derivative $[Mo(S_2CNR_2)_2(CO)_2]$ (**i**) (see Scheme 1) exhibits an unusual trigonal prismatic structure rather than the distorted octahedron found for $[WBr_2(CO)_2(NBD)]$. A frontier orbital approach to the reactivity of $[Mo(S_2CNR_2)_2(CO)_2]$ predicts ligand attack on the LUMO in the cavity defined by the dihedral angle between the two chelating ligands. Significantly, the weakly coordinating ligand tetrahydrothiophene (tht) was found to form such an adduct $[Mo(S_2CNEt_2)_2(CO)_2(tht)]$ (**ii**) whereas CO and PPh_3 form 1:1 complexes which exhibit structure (**iii**) with a mutually *cis*-$MoL(CO)_2$ fragment. However, this does not preclude frontier orbital control in the last two cases since, as mentioned previously, facile structural rearrangements are well known in seven-coordinate systems of this type. It would seem that initial attack on (**i**) occurs at the predicted site giving (**ii**) but in some cases rearrangement can occur to give the thermodynamically favoured structure (**iii**).

The spectroscopic data for $[WBr_2(CO)_2(PMePh_2)(NBD)]$ (**2b**) are in accord with the solid state structure with two ν_{CO} modes at 2037(vw) and 1944 (s) cm^{-1} reflecting the slight distortion of the OC–W–CO grouping from 180° and the consequent activation, albeit weakly, of the higher frequency asymmetric stretch. The ^1H-NMR spectrum shows phenyl and methyl group signals due to a single $PMePh_2$ and, more significantly, three norbornadiene peaks at δ 4.08 (4H), 3.68 (2H) and 1.40 (2H) with chemical shifts and intensities similar to those of the previously reported derivative $[WBr_2(CO)_2(PMe_2Ph)(NBD)]$.

Previously we observed that seven-coordinate complexes $[WBr_2(CO)_2(L)(NBD)]$ (L = PMe_2Ph, $P(OMe)_3$, $CNBu^t$), undergo CO loss at room temperature to give dark blue/black six-coordinate monocarbonyls

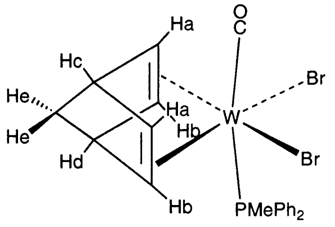


Scheme 1. Mechanism of ligand addition to $[Mo(S_2CNR_2)_2(CO)_2]$.



Scheme 2. Mechanism of CO substitution in $[WBr_2(CO)_2(NBD)]$ (**1a**).

$[WBr_2(CO)(L)(NBD)]$ (**3**). These give blue solutions similar to those observed in the formation of complexes **2**. A blue/black derivative **3a** was subsequently obtained on allowing a dichloromethane solution of $[WBr_2(CO)_2(PMePh_2)(NBD)]$ to sit at room temperature for 15 h. Analytical data suggest the stoichiometry $[WBr_2(CO)(PMePh_2)(NBD)]$ whilst the IR spectrum shows a single ν_{CO} mode at 1964 cm^{-1} in accord with this formulation. This compares with 1974 cm^{-1} for $[WBr_2(CO)(PMe_2Ph)(NBD)]$ (**3b**). The presence of a single peak in the $^{31}P\{^1H\}$-NMR spectrum at δ −4.76 with tungsten satellites $J_{P–W} = 171.5$ Hz confirms the presence of a metal-coordinated phosphine and accordingly the ^1H-NMR spectrum shows phenyl and methyl group signals due to a single $PMePh_2$. More significantly, five norbornadiene peaks are observed at δ 4.63 (2H), 3.84 (1H), 3.33 (1H), 3.22 (2H) and 0.41 (2H) with chemical shifts and intensities similar to those of $[WBr_2(CO)(PMe_2Ph)(NBD)]$ (**3b**) {δ 4.69 (2H), 3.84 (1H), 3.46 (1H), 3.23 (2H) and 0.43 (2H)}. These data suggest an octahedral structure similar to that of $[WBr_2(CO)_2(NBD)]$ but with one of the carbonyls replaced by $PMePh_2$. Direct substitution of the CO by a phosphine would give the illustrated structure which would give rise to the observed ^1H-NMR spectrum with five norbornadiene peaks. Further support for this conclusion is derived from the fact that the spectroscopic data are very similar to those of the structurally characterised nitrile derivatives $[WBr_2(CO)(NCR)(NBD)]$ reported later in this paper.



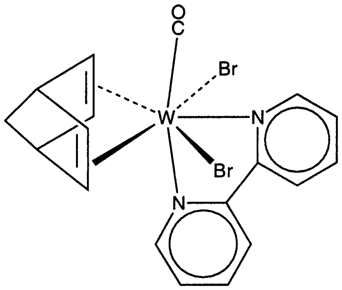
3a

These findings unequivocally establish the mechanism of CO substitution in $[WBr_2(CO)_2(NBD)]$ in reactions with phosphines. The incoming nucleophile attacks the metal *trans* to the diene in a symmetrical fashion leading to a seven-coordinate pentagonal bipyramidal derivative $[WBr_2(CO)_2(L)(NBD)]$. This is followed by slow CO expulsion and transfer of the incoming ligand to the site vacated by the leaving CO, i.e. *trans* to the remaining carbonyl. The exact mechanism by which the latter process occurs is not known but the simplest involves CO dissociation followed by non-dissociative phosphine migration to the site *trans* to CO, i.e. Scheme 2 path (i).

An alternative, path (ii), involves prior structural rearrangement in which the CO and $PMePh_2$ undergo site exchange and this is then followed by CO dissociation. This is suggested by our recent observations of fluxional behaviour in related seven-coordinate complexes [$WBr(S_2PMe_2)(CO)(PMe_2Ph)(NBD)$] and [$W(S_2PR_2)_2(CO)(NBD)$] (R = Me, OMe) containing bidentate ligands [18] in addition to which ligand site exchange in seven-coordinate compounds is a well known phenomenon, sometimes with very low energy barriers [1b].

The observation that seven-coordinate species are intermediates in CO substitution reactions of [$WBr_2(CO)_2(NBD)$] is not entirely surprising taking into account the formal 16-electron configuration of the complex. A wide range of seven-coordinate Mo(II) and W(II) carbonyl complexes is known, many of which undergo CO loss to give six-coordinate derivatives [1a,1d]. This contrasts with related six-coordinate alkyne complexes of Mo(II) and W(II) where stabilisation of the apparent 16-electron configuration has been ascribed to additional π donation from the alkyne ligands [20]. In the case of mono- and bis-alkyne complexes up to four electrons can formally be considered to be donated from the C≡C triple bond(s) to the d^4 metal center. In other cases oxo and sulphur based ligands are considered to function as π donors and thus contribute to reducing the electron deficiency at the metal. Perhaps not suprisingly, seven-coordinate intermediates have never been reported in substitution reactions of six-coordinate mono and bis alkyne d^4 complexes since this would require the alkyne(s) to revert to two-electron donation.

Previously we reported that [$WBr_2(CO)_2(NBD)$] reacts with the bidentate ligand 2,2′-bipyridyl (bipy) to give a seven-coordinate complex, the monocarbonyl [$WBr_2(CO)(bipy)(NBD)$] [8]. In view of the pentagonal bipyramidal structure established for [$WBr_2(CO)_2(PMePh_2)(NBD)$] an X-ray diffraction study of [$WBr_2(CO)(bipy)(NBD)$] was carried out [21]. This revealed a seven-coordinate structure **4** similar to that of [$WBr_2(CO)_2(PMePh_2)(NBD)$] with one nitrogen in the phosphine position in the pentagonal plane and the other *trans* to the remaining carbonyl and with a Br–W–Br angle, 144.81(4)° slightly less than that observed in the phosphine derivative **2b**, 146.43(4)°.



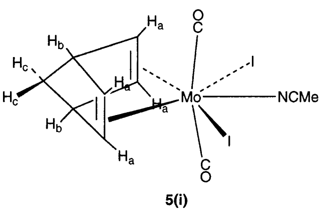
4

However, during the course of this work Nakamura reported structural studies of an almost identical complex, the molybdenum adduct [$MoBr_2(CO)(bipy)(NBD)$] [11]. The spectroscopic features of the two complexes are very similar in addition to which they are isomorphous. The crystallographic unit cell for **4** is 8.349(2), 14.277(3) and 14.615 Å, $\beta = 93.78(2)°$, $V = 1738.3(7)$ Å^3, whilst for the molybdenum species it is: 8.3808, 14.2490, 14.6530 Å, $\beta = 94.43°$, $V = 1745$. Since the structural features of the two derivatives are very similar no further details of [$WBr_2(CO)(bipy)(NBD)$] (**4**) will be reported here but crystallographic data are available from the Cambridge Crystallographic Data centre. Interestingly these reactions contrast with those of [$MoBr_2(CO)_2(NBD)$] with terpyridines (terpy) which give ionic complexes [$MoBr(CO)(terpy)(NBD)]^+$ one of which was shown to adopt an unusual structure in which the norbornadiene and Br form a triangle perpendicular to the plane of the terpyridine and CO ligands [12]. The reaction of 2,2′-bipyridyl with the related bis-alkyne derivative [WClI(CO)(NCMe)MeC≡CMe)$_2$] also yields a cationic derivative [WCl(CO)(bipy)MeC≡CMe)$_2$]I, in this case by iodine displacement [22]. Other cationic alkyne derivatives have been reported by Baker et al. in which halide displacement results from phosphine addition [23]. This again reflects the preference of alkyne derivatives for six coordination where both sets of alkyne π orbitals are involved in bonding with the metal. Diene complexes such as **1** where this is not possible, resort to seven coordination when an 18-electron configuration is required. So far we have not observed the formation of cationic derivatives in reactions of these complexes despite the fact that simple Mo(II) and W(II) ionic derivatives have been known for many years [1,24].

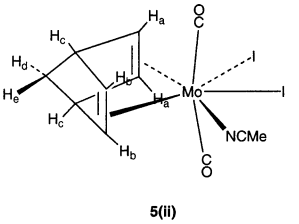
Nakamura also reported the synthesis of [$MoBr_2(CO)_2(NBD)]_{n=1}$ which exists in two forms, one a monomer ($n = 1$) structurally analogous to [$WBr_2(CO)_2(NBD)$], the other di- or polymeric, $n > 1$ [11]. This reacts with acetonitrile to give an unstable, ill defined complex formulated as the seven-coordinate derivative [$MoBr_2(CO)_2(NCMe)(NBD)$]. In principle this species should exhibit some similarities to phosphine adducts [$WBr_2(CO)_2(PR_3)(NBD)$] (**2**). Since Baker has made extensive use of the nitrile derivatives [$MI_2(CO)_3(NCMe)_2$] (M = Mo, W) in developing the chemistry of Mo(II) and W(II) [1d,25] we decided to explore the use of these reagents in the synthesis of diene complexes with the possibility in mind that carbonyl nitrile derivatives similar to that reported by Nakamura might be obtained. While this work was being carried out a report of the synthesis of the aforementioned tin derivative [$WCl(SnCl_3)(CO)_3(NBD)$] from the reaction of [$WCl(SnCl_3)(CO)_3(NCMe)_2$] with norbornadiene was published [13].

Complexes [$MI_2(CO)_3(NCMe)_2$] (M = Mo, W) were prepared as described previously by iodine oxidation of an acetonitrile solution of [$M(CO)_3(NCMe)_3$] (M = Mo,

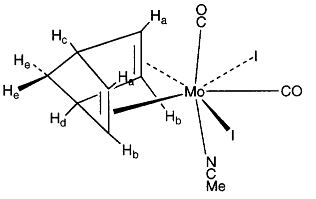
W) [26]. Although these were previously obtained in quantitative yield without the requirement for purification, in our hands this method gave impure products according to IR studies and a minor modification to the procedure was required. This involved filtration followed by two recrystallisations from CH_2Cl_2–petroleum ether to give brown (M = Mo) or red–brown (M = W) crystals of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) in good yield (M = Mo, 68%; M = W, 76%). The reaction of $[MoI_2(CO)_3(NCMe)_2]$ with norbornadiene in CH_2Cl_2 was followed by IR spectroscopy which indicated that initially the nitrile free species $[MoI_2(CO)_2(NBD)]_n$, previously reported by Nakamura [11], is formed but when the reaction was allowed to proceed further an additional broad band near 1990 cm^{-1} appeared, close to that reported for $[MoI_2(CO)_2(NCMe)(NBD)]$ (**5**). Unfortunately neither of these two species could be isolated in a pure form but ^1H-NMR data for the impure product compares well with those reported by Nakamura for the above species. We note that Nakamura suggested a seven-coordinate structure for the nitrile complex **5** but did not propose a definite structure. As illustrated seven-coordinate pentagonal bipyramidal structures based on that of the phosphine adduct **2b** and the tin complex $[WCl(SnCl_3)(CO)_3(NBD)]$ [13] would not give rise to the spectrum reported for **5** since **5(i)** has only three sets of non-equivalent protons H_a, H_b and H_c, ratio 4:2:2 and the less symmetrical **5(ii)** five sets H_a, H_b, H_c, H_d and H_e, ratio 2:2:2:1:1. A third isomeric form **5(iii)** is consistent with the NMR data but this structure with *cis* carbonyls should give rise to two strong peaks in the IR spectrum and must therefore be excluded. Interestingly however, we note that the six-coordinate form **5(iv)** should give rise to the observed NMR and IR spectra.



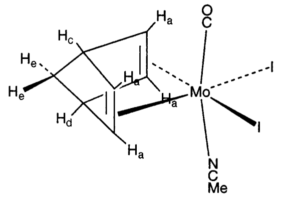
5(i)



5(ii)



5(iii)



5(iv)

In view of this anomaly we attempted synthesis of an analogous complex by reacting $[MoI_2(CO)_3(NCMe)_2]$ with 1,5-cyclooctadiene in CH_2Cl_2, THF or Et_2O and also by refluxing in petroleum ether. However, all of these attempts were unsuccessful. The tungsten complex $[WBr_2(CO)_2(COD)]$ has been obtained previously [8] by the same route which affords the norbornadiene compound i.e. refluxing a solution of the diene and $[WBr_2(CO)_4]_2$ in 60–80 petroleum ether. In contrast to the reactions involving the molybdenum derivative, refluxing a suspension of $[WI_2(CO)_3(NCMe)_2]$ and norbornadiene in 60–80 petroleum ether for 3 h gave a red-wine coloured solution which, on work up gave dark-green crystals of the dicarbonyl derivative $[WI_2(CO)_2(NBD)]$ (**1b**) (42% yield) analogous to $[WBr_2(CO)_2(NBD)]$ (**1a**). This formulation is based on elemental analysis and mass spectrometry which shows a molecular ion at $m/z = 584$ $[M]^+$. The IR spectrum contains two bands at 2058 (w) and 1992 (s) cm^{-1} indicating *trans* carbonyls but no trace of the $\nu_{C\equiv N}$ mode of coordinated acetonitrile. This, and the fact that all other data are similar to that of the analogous bromide complex **1a**, indicates that $[WI_2(CO)_2(NBD)]$ has a distorted octahedral structure where the OC–W–CO angle is slightly less than 180° as revealed in $[WBr_2(CO)_2(NBD)]$ by single-crystal X-ray diffraction studies. Two norbornadiene resonances are observed in the ^1H-NMR spectrum at δ 4.56 (4H) and 3.99 ppm. This, and a simple triplet for the two methylene protons, underlines the high symmetry of the norbornadiene ligand as found in the free hydrocarbon.

Subsequently, the corresponding cyclooctadiene complex $[WI_2(CO)_2COD]$ (**1c**) was obtained as dark-green crystals in 31% yield using the synthetic methodology employed for the norbornadiene complex **1b**. The IR and NMR spectra are almost identical to those of the previously reported bromo complex $[WBr_2(CO)_2COD]$ [8] suggesting a similar structure. These findings contrast with the fact that the aforementioned seven-coordinate tricarbonyl $[WCl(SnCl_3)(CO)_3(NBD)]$ was obtained from the reaction of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ with norbornadiene [13]. It would therefore appear that, as with complexes **2** and **3**, the stability of the seven-coordinate species with respect to CO loss to give a six-coordinate derivative depends on a subtle combination of donor and acceptor properties of the various ligands.

In view of these findings, reactions of $[WBr_2(CO)_2(NBD)]$ (**1a**) with nitriles RC≡N (R = Me, Pr^i, Ph, C_6H_4Me-4, $CH{=}CH_2$) were carried out and followed by IR spectroscopy. In each case little change in colour was observed over several hours but IR spectroscopy indicated the formation of a new carbonyl containing species. Work up from dichloromethane–light petroleum gave, in each case, a dark blue/black crystalline complex which analysed as the carbonyl substitution product $[WBr_2(CO)(NCR)(NBD)]$ **6**. The complexes are reasonably stable in the solid state for lengthy periods if kept at low (−15°C) temperature

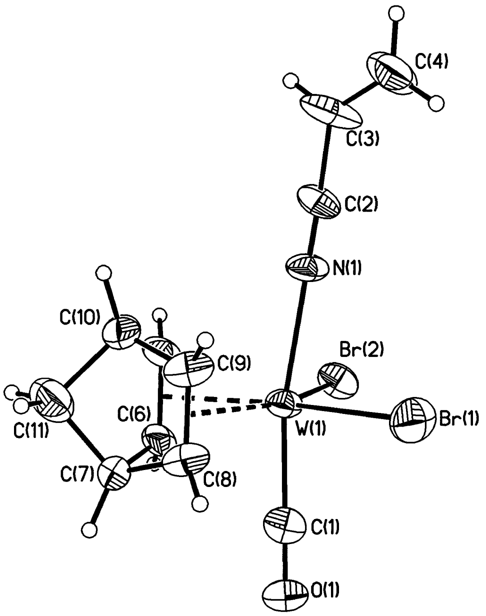
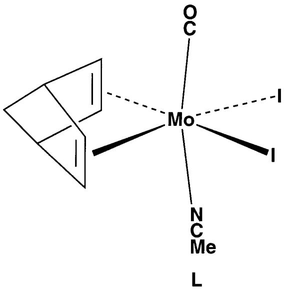


Fig. 3. Molecular structure of [$WBr_2(CO)(NCCH{=}CH_2)(NBD)$] (**6e**).

under nitrogen. However, they become unstable in solution at room temperature but addition of free nitrile significantly inhibits the decomposition process. This may suggest that initial nitrile dissociation is occurring. In view of the contrast with Nakamura's report that [$MoI_2(CO)_2(NBD)$]$_n$ and acetonitrile reversibly give a seven-coordinate 1:1 dicarbonyl adduct **5** a single-crystal X-ray diffraction study of the acrylonitrile complex [$WBr_2(CO)(NCCH{=}CH_2)(NBD)$] (**6e**) was carried out. Single crystals of **6e** were obtained from a dichloromethane–light petrolium mixture at −15°C. The molecular structure is shown in Fig. 3 and selected bond lengths and angles are given in Table 2.

The structure of [$WBr_2(CO)(NCCH{=}CH_2)(NBD)$] (**6e**) is based on distorted octahedral coordination about the metal centre and is therefore closely related to that of the precursor [$WBr_2(CO)_2(NBD)$] (**1a**). The nitrile lies *trans* to the remaining CO whilst the NBD ligand is *cis* to the CO and in the same plane as the two Br ligands. Direct substitution of one of the carbonyl ligands in **1a** by the nitrile ligand appears to have little overall effect on the geometry of the molecule. For example the largest distortion from octahedral geometry, Br(1)–W(1)–Br(2), is 107.15(9)°, which compares with 105.86(5)° in the parent dicarbonyl **1a**. The OC–W–CO angle in the latter, 172.9(4)° is similarly close to the equivalent N–W–C angle of 169.9(7)° in **6e.**



6a NCMe
6b NCPr^i
6c NCPh
6d NCC$_6$H$_4$Me-4
6e NCCH=CH$_2$

Interestingly the replacement of a π acceptor, carbon monoxide, by a σ donor nitrile also has little effect on the bond distances. For example the remaining CO has a C–W distance of 1.98(2) Å, which compares with an average of 2.04 (1) Å in the precursor **1a**, probably reflecting the expected increase in π back donation to the remaining carbonyl. However, the tungsten to carbon distances of the diene ligand W(1)–C(5) 2.26(2), W(1)–C(6) 2.31(2), W(1)–C(8) 2.27(2) and W(1)–C(9) 2.26(2) are very similar to those of the precursor, i.e. 2.29 (1), 2.30 (1), 2.26 (1) and 2.26 (1) Å implying that tungsten–alkene bonding is little affected by CO substitution. This is a little unexpected since with this structure the diene π* orbitals effectively interact with the same metal d$_\pi$ orbitals as the CO ligands. The only other features of note are the short C=C bond in the nitrile ligand, 1.21(3) Å, which may simply be a consequence of libration and the intermolecular contact between Br(2) and a NBD H atom, H8A, of 2.88(2) Å.

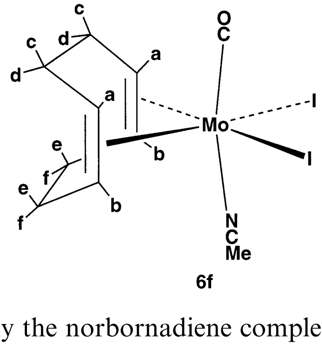
The structure of [$WBr_2(CO)(NCCH{=}CH_2)(NBD)$] (**6e**) can also be compared with that of bis alkyne complexes [$WI_2(CO)(NCR)(R'C{\equiv}CR')_2$] (W, R = Me, Bu^t, R = Me, R = Me, R′ = Ph) reported by Baker et al [27,28]. The structure of [$WI_2(CO)(NCMe)(MeC{\equiv}CMe)_2$] is similar to that of **6e** but with two *cis* alkynes occupying the donor sites in place of the norbornadiene. The W–CO distance 1.937(14) Å is somewhat shorter and the W–N distance, 2.132(14) Å, slightly longer than those of **6e.** However the most

Table 2
Selected bond lengths and angles for **6e**

Bond lengths (Å)					
W(1)–C(1)	1.98(2)	W(1)–N(1)	2.228(13)	C(3)–C(4)	1.21(3)
W(1)–Br(1)	2.512(2)	W(1)–Br(2)	2.516(2)	N(1)–C(2)	1.07(2)
Bond angles (°)					
C(1)–W(1)–N(1)	169.9(7)	Br(1)–W(1)–Br(2)	107.15(9)	N(1)–W(1)–C(9)	78.6(6)

significant differences lie in the distortion from octahedral geometry, which is much more significant in the alkyne complex. This is exemplified by the I–W–I bond angle, which at 83.51(4) is much more acute {cf. **6e**, Br–W–Br, 107.15(9)°}, as is the N–W–CO angle of 163.3(6)°, cf. 169.9(7)° in **6e**. This may reflect: (a) the steric effects of the bulky iodine ligands; (b) the effect of the geometrically constrained diene with limited chelate bite; and (c) the presence of $\pi_{\perp}$ orbitals on the alkynes which enables additional electron donation (a total of six electrons from the two alkynes) giving, in effect, a coordinatively saturated 18-electron complex.

The spectroscopic features of the nitrile derivatives **6** are in full accord with the solid-state structure of **6e** with one weak $\nu_{C\equiv N}$ and a strong ν_{CO} band in the IR spectra. The spectra were recorded in KBr to minimise decomposition which was occasionally significant in solution. In all cases peaks due to the precursor [$WBr_2(CO)_2$(NBD)] (**1a**) were observed. Even in the solid state additional weak peaks were observed and these increased in intensity with time. The decomposition process was also followed by ^{1}H-NMR spectroscopy which confirmed the formation of **1a.** For this reason ^{1}H-NMR spectra were recorded at low temperatures, ca. − 20°C. The ^{1}H-NMR spectra of the majority of the complexes are initially confusing since only three non-methylene norbornadiene proton signals are observed, with an integrated ratio of 2:2:2, suggesting a higher symmetry structure. However, the NCC_6H_4Me-4 derivative **6d** shows the expected five signals ratio 2:1:1:2 suggesting accidental degeneracy of two of the peaks in the spectra of the other nitrile derivatives. Further support for this conclusion was provided by synthesis of the cyclooctadiene derivative [WBr_2(CO)(NCMe)(COD)] (**6f**) from the reaction of MeCN and [$WBr_2(CO)_2$(COD)] (**1c**). The green crystalline product has the expected single ν_{CO} mode at 1927 cm^{-1} but, more significantly, six well resolved equal intensity cyclooctadiene multiplets (a–f) between δ 2.7 and 5.7 consistent with the illustrated six-coordinate structure.



6f

Interestingly the norbornadiene complexes **6a–e** have very similar spectroscopic features to the purported seven-coordinate derivative [$MoI_2(CO)_2$(NCMe)(NBD)] (**5**) which has five norbornadiene peaks in the ratio 2:2:1:1:2 in the ^{1}H-NMR spectrum. The possibility therefore exists that Nakamura's complex is a six-coordinate derivative [MoI_2(CO)(NCMe)(NBD)] with structure **5(iv)** similar to complexes **6**. Although this is not consistent with Nakamura's observation that prolonged drying of the complex in vacuo regenerates the dicarbonyl [$MoI_2(CO)_2$(NBD)] we note that all of the tungsten complexes [WBr_2(CO)(NCR)(NBD)] reported herein undergo decomposition in solution generating peaks in the IR and NMR spectra due to [$WBr_2(CO)_2$(NBD)]. This presumably results from nitrile dissociation and intermolecular CO transfer. The process appears to be inhibited by addition of excess organonitrile suggesting that decomposition proceeds via nitrile dissociation. This may raise some doubts as to the exact composition of the molybdenum derivative **5** or alternatively that the structure is totally unrelated to that exhibited by the phosphine adducts **2**.

3. Experimental

NMR spectra were recorded on Bruker AM 400 and WP 200SY spectrometers at 400 and 200.13 MHz (^{1}H, ^{13}C) and 80.13 MHz (^{31}P). Coupling constants are in Hertz and chemical shifts are referenced to Me_4Si (^{1}H, ^{13}C) and H_3PO_4 (^{31}P), ($\delta = 0$ ppm). IR spectra were recorded on a Nicolet Impact 400 FT–IR machine and mass spectra (FAB, EI) on an Vacuum Generators updated A.E.I. MS 11. Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over P_2O_5 (CH_2Cl_2), sodium/benzophenone (petroleum ether (60–80), Et_2O, THF, MeCN) and distilled just before use. [$WBr_2(CO)_2$(NBD)] was synthesised as described previously [8] as were [$MI_2(CO)_3(NCMe)_2$, (M = Mo, W) [26] although some modifications to the published procedure were employed as described in Section 2.

3.1. *Reaction of [$WI_2(CO)_3(NCMe)_2$] with norbornadiene*

Norbornadiene (0.25 ml, 2.46 mmol) was added to a suspension of [$WI_2(CO)_3(NCMe)_2$] (1.24 g, 2.05 mmol) in petroleum ether (100 ml) and the solution was refluxed gently for 3 h until an intense red-wine coloured solution was obtained. The hot solution was filtered, concentrated in vacuo and crystallised from petroleum ether. The crystalline solid was recrystallised from CH_2Cl_2/petroleum ether to give dark-green crystals of [$WI_2(CO)_2$(NBD)] (**1b**) (0.51 g, 42%). (Found: C, 17.7; H, 1.0. $C_9H_8I_2O_2W$ requires: C, 18.44; H, 1.38%). (m/z) = 584 [M]$^+$). IR (CH_2Cl_2): $\nu_{(CO)}$ 2058(w), 1992(s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.56 (m, 4H), 3.99 (m, 2H), 0.52 (t, 2H).

3.2. Reaction of [$WI_2(CO)_3(NCMe)_2$] with 1,5-cyclooctadiene

Cyclooctadiene (0.13 ml, 1.03 mmol) was added to a suspension of [$WI_2(CO)_3(NCMe)_2$] (0.52 g, 0.86 mmol) in petroleum ether (80 ml) and the solution gently refluxed for 3 h until an intense dark-green solution was obtained. The hot solution was filtered and worked up as for complex **1b** to give dark-green crystals of [$WI_2(CO)_2COD$] (**1c**) (0.16 g, 31%). (Found: C, 20.1; H, 1.7. $C_{10}H_{12}I_2O_2W$ requires: C, 19.96; H, 2.01%). MS: $(m/z)=601$ $[M]^+$). IR(CH_2Cl_2): $\nu_{(CO)}$ 2056(w), 1992(s) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 4.52 (m, 4H), 3.73 (m, 4H), 3.05 (m, 4H).

3.3. Reaction of [$WBr_2(CO)_2(NBD)$] with PPh_3

A total of 300 mg (0.61 mmol) of [$WBr_2(CO)_2(NBD)$] were dissolved in 20 cm^3 diethylether and cooled to 0°C. A solution of 159 mg (0.61 mmol) PPh_3 was added slowly to the stirred mixture upon which a yellow precipitate immediately formed. The solid was allowed to settle and the remaining blue solution syringed off. The yellow precipitate was washed with 20 ml petroleum ether and dried in vacuo to give [$WBr_2(CO)_2(PPh_3)(NBD)$] (**2a**) (410 mg, 90%). (Found: C, 42.5; H, 2.99. $C_{27}H_{23}Br_2O_2PW$ requires: C, 43.00; H 3.07%). IR (KBr): ν_{CO} 2039(w), 1934(s), 1926(s) cm^{-1}. ^1H-NMR ($CDCl_3$, −40°C): δ 7.3–7.7 (m, 15H), 4.12 (m, 4H), 3.70 (br s, 2H), 1.40 (br s, 2H).

3.4. Reaction of [$WBr_2(CO)_2(NBD)$] with $PMePh_2$ at 0°C

A total of 150 mg (0.31 mmol) of [$WBr_2(CO)_2(NBD)$] were dissolved in 10 ml ether, stirred and cooled down to 0°C. A solution of ten drops PPh_2Me in 20 ml ether was added very slowly until the formation of a yellow precipitate was complete. The blue solution was syringed off and the precipitate washed with 10 ml petroleum ether and dried in vacuo to give yellow crystals of [$WBr_2(CO)_2(PMePh_2)(NBD)$] (**2b**) (178 mg, 86%). (Found: C, 38.5; H, 3.0. $C_{23}H_{21}Br_2OPW$ requires: C, 39.24; H 3.01%). IR (CH_2Cl_2): ν_{CO} 2037(w), 1944(s) cm^{-1}. ^1H-NMR ($CDCl_3$, −55°C): δ 7.4–7.7 (m, 10H), 4.08 (br s, 4H), 3.68 (br s, 2H), 2.55 (d, 3H P**Me**Ph_2), 1.40 (br s, 2H).

3.5. Reaction of [$WBr_2(CO)_2(NBD)$] with PEt_3

A total of 150 mg (0.31 mmol) of [$WBr_2(CO)_2(NBD)$] were dissolved in 10 ml ether, stirred and cooled down to 0°C. A solution of 0.22 ml PEt_3 in 20 ml diethylether was added slowly over a period of about 1 min to give a yellow solution. The solution was filtered off, 10 ml petroleum ether added and the solution reduced in vacuo to ca. 4 ml when yellow crystals formed. The remaining solvent was removed by syringe and the crystals washed with petroleum ether and dried in vacuo to give [$WBr_2(CO)_2(PEt_3)(NBD)$] (**2c**) (75 mg, 41%). (Found: C, 29.52; H, 3.76. $C_{15}H_{23}Br_2O_2PW$ requires: C, 29.54; H 3.80%). IR (Nujol/pet. ether) ν_{CO} 2035(w), 1950(s) cm^{-1}. NMR ($CDCl_3$): ^1H δ 4.08 (m, 4H), 3.68 (m, 2H), 2.35 (m, 6H, $\mathbf{CH_2}CH_3$), 1.45 (m, 2H), 1.22 (m, 9H, $CH_2\mathbf{CH_3}$).

3.6. Synthesis of [$WBr_2(CO)(PMePh_2)(NBD)$]

[$WBr_2(CO)_2(PMePh_2)(NBD)$] (**2b**) (0.200 g, mmol) was dissolved in 20 ml CH_2Cl_2 at room temperature to give a yellow solution. Within 1 h the solution turned blue, and after 15 h the reaction reached completion according to IR studies. The resulting blue solution was reduced in volume and petroleum ether was added to give a green powder. This was recrystallised from Et_2O–petroleum ether at −15°C to give green crystals of [$WBr_2(CO)(PMePh_2)(NBD)$] (**3a**) (33 mg, 17%) (Found: C, 37.64; H, 3.01. $C_{21}H_{21}Br_2OPW$ requires: C, 37.98; H, 3.19%). IR (CH_2Cl_2): $\nu_{(CO)}$ 1964(s) cm^{-1}. ^1H-NMR ($CDCl_3$, 25°C): δ 7.78–7.35 (m, 10H, Ph), 4.63 (m, 2H, NBD), 3.84 (M, 1H, NBD), 3.33 (m, 1H, NBD), 3.22 (m, 2 H, NBD), 2.26 (d, 3H, Me), 0.41 (br s, 2H, NBD). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 25°C) δ −4.76 (t, $J_{P-W}=171.5$ Hz).

3.7. Reaction of [$WBr_2(CO)_2(NBD)$] with NCMe

The complex [$WBr_2(CO)_2(NBD)$] (0.133 g, 0.27 mmol) was dissolved in 20 ml Et_2O and cooled down to 0°C. A solution of NCMe (0.016 ml, 0.28 mmol) was slowly added to the previous purple solution. The solution was allowed to warm up to room temperature to react for 5 h. At this stage of the reaction another mole equivalent of the ligand was added to the mixture and 1 h at room temperature was required to complete the reaction. The resulting blue solution was concentrated in vacuo and a layer of petroleum ether added. Slow recrystallisation at −15°C afforded green crystals of [$WBr_2(CO)(NCMe)(NBD)$] (**6a**) (0.058g, 43%). (Found C, 23.62; H, 2.10; N, 2.65. $C_{10}H_{11}Br_2NOW$ requires: C, 23.79, H, 2.20; N, 2.77%). IR (KBr): $\nu_{(C\equiv N)}$ 2311(w), 2284(w), $\nu_{(CO)}$ 2028(w), 1929(s) cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$, −20°C): δ 5.29 (tm, 2H, NBD), 3.99 (m, 2H, NBD), 3.78 (tm, 2H, NBD), 2.86 (s, 3H, NC**Me**), 0.77 (s, 2H, NBD).

3.8. Reaction of [$WBr_2(CO)_2(NBD)$]with $NCPr^i$

The complex [$WBr_2(CO)_2(NBD)$] (0.179 g, 0.36 mmol) was dissolved in 20 ml Et_2O and a solution of $NCPr^i$ (0.033 ml, 0.37 mmol) was slowly added. The reaction was allowed to proceed at room temperature for 14 h with addition of a mole equivalent of $NCCH(CH_3)_2$ after ca. 6 h. The resulting blue solution was slightly concentrated before addition of a petroleum ether layer. Slow recrystallisation at -15°C afforded dark-green crystals of $[WBr_2(CO)(NCPr^i)(NBD)]$ (**6b**) (0.121 g, 63%). (Found C, 26.72; H, 2.70; N, 2.57. $C_{12}H_{15}Br_2ONW$ requires: C, 27.05; H, 2.84; N, 2.63%). IR (KBr): $\nu_{(C\equiv N)}$ 2282(w), $\nu_{(CO)}$ 2029(w), 1934(s) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, -20°C): δ 5.28 (t, 2H, NBD), 3.93 (m, 2H, NBD), 3.72 (t, 2H, NBD), 3.41 (sept, 1H, **CH**$(CH_3)_2$), 1.63 (d, 6H, CH(**CH**$_3)_2$), 0.76 (br s, 2H, NBD).

3.9. *Reaction of $[WBr_2(CO)_2(NBD)]$ with NCPh*

The complex $[WBr_2(CO)_2(NBD)]$ (0.143 g, 0.29 mmol) was dissolved in 20 ml Et_2O and cooled down to 0°C. A solution of NCPh (0.030 ml, 0.30 mmol) was slowly added to the previous purple solution. The solution was allowed to warm up to room temperature to react for 4 h. At the stage of the reaction another mole equivalent of the ligand was added to mixture and left to react for 7 h. Half of a mole equivalent was finally added and another 7 h were allowed to complete the reaction. The resulting blue solution was slightly concentrated before addition of a petroleum ether layer. Slow recrystallisation at -15°C afforded dark-green crystals of $[WBr_2(CO)(NCPh)(NBD)]$ (**6c**) (0.093 g, 57%). (Found: C, 31.46; H, 2.16; N, 2.38. $C_{15}H_{13}Br_2ONW$ requires: C, 31.78; H, 2.31; N, 2.47%). IR (KBr): ν(C≡N) 2266(w), ν(CO) 1992(w), 1929(s) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, -20°C): δ 7.98 (m, 2H, Ph), 7.79 (tt, 1H, Ph), 7.67 (m, 2H, Ph), 5.33 (t, 2H, NBD), 4.06 (m, 1H, NBD), 4.00 (m, 1H, NBD), 3.89 (t, 2H NBD), 0.79 (br s, 2H, NBD).

3.10. *Reaction of $[WBr_2(CO)_2(NBD)]$ with NCC_6H_4Me-4*

The complex $[WBr_2(CO)_2(NBD)]$ (0.197 g, 0.40 mmol) was dissolved in 20 ml Et_2O and a solution of NCC_6H_4Me-4 (0.027 ml, 0.41 mmol) was slowly added. The mixture was allowed to react at room temperature for 20 h with addition of another two mole equivalents of the ligand during the course of the reaction. The resulting blue solution was concentrated to 10 ml and a layer of petroleum ether was added. Slow recrystallisation at -15°C over several days afforded dark-green crystals of $[WBr_2(CO)(NCC_6H_4Me\text{-}4)(NBD)]$ (**6d**) (0.139 g, 60%). (Found: C, 32.92; H, 2.38; N, 2.38. $C_{16}H_{15}Br_2ONW$ requires: C, 33.08; H, 2.60; N, 2.41%). IR (KBr): $\nu_{(C\equiv N)}$ 2255(m), $\nu_{(CO)}$ 2045(w), 1951(s) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, -20°C): δ 7.5–7.3 (m, 5H, Ph), 5.25 (tm, 2H, NBD), 4.00 (br m, 2H, NBD), 3.84 (tm, 2H, NBD), 2.81 (s, 3H, CH_3).

3.11. *Reaction of $[WBr_2(CO)_2(NBD)]$with $NCCH{=}CH_2$*

The complex $[WBr_2(CO)_2(NBD)]$ (0.197 g, 0.40 mmol) was dissolved in 20 ml Et_2O and a solution of $NCCH{=}CH_2$ (0.027 ml, 0.41 mmol) was slowly added. Another two mole equivalents were added every 3 h and the reaction was allowed to completion for an extra 6 h after the last addition. The resulting blue solution was concentrated to 10 ml and a layer of petroleum ether was added. Slow recrystallisation at -15°C afforded green crystals of $[WBr_2(CO)(NCCH{=}CH_2)(NBD)]$ (**6e**) (0.128 g, 62%). (Found C, 25.32; H, 1.88; N, 2.59. $C_{11}H_{11}Br_2ONW$ requires: C, 25.56; H, 2.15; N, 2.71%). IR (KBr): $\nu_{(C\equiv N)}$ 2258(w); $\nu_{(CO)}$ 2033(w), 1992(w), 1942(s). ^{1}H-NMR (400 MHz, $CDCl_3$, -20°C): δ 6.70 (d, 1H, CH=**CH**$_2$), 6.49 (d, 2H, CH=**CH**$_2$), 6.34 (dd, 1H, **CH**=CH$_2$), 5.30 (t, 2H, NBD), 4.00 (m, 2H, NBD), 3.83 (t, 2H, NBD), 0.78 (br s, 2H, NBD).

3.12. *Reaction of $[WBr_2(CO)_2(COD)]$with NCMe*

The complex $WBr_2(CO)_2COD$ (0.098 g, 0.19 mmol) was dissolved in 20 ml CH_2Cl_2 at room temperature. NCMe (0.030 ml, 0.58 mmol) was added to the green solution. After 3 h an extra three mole equivalents of NCMe were added to the solution and 26 h at room temperature were required to complete the reaction. The resulting blue solution was concentrated to ca. 10 ml and a layer of petroleum ether was added. Slow recrystallisation at -15°C afforded dark-green crystals of $[WBr_2(CO)(NCMe)(COD)]$ (**6f**) (0.057 g, 58%) (Found C, 24.69; H, 2.72; N, 2.59. $C_{11}H_{15}Br_2NOW$ requires: C, 25.36; H, 2.90; N, 2.69%). IR (KBr): $\nu_{(C\equiv N)}$ 2318(w), 2291(w), $\nu_{(CO)}$ 1927(s) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, -19°C): δ 5.65 (m, 2H, COD), 4.06 (m, 2H, COD), 3.83 (m, 2H, COD), 3.54 (m, 2H, COD), 3.02 (m, 2H, COD), 2.95 (s, 3H, NCMe), 2.80 (m, 2H, COD).

4. Crystallographic studies

Crystals of **6e** and **2b** were both grown by solvent diffusion from CH_2Cl_2/60–80 petroleum ether in an N_2 atmosphere. Intensity measurements on **6e** and **2b** were carried out at room temperature on a Siemens P4 diffractometer [29] with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å) using ω scans. Table 3 lists details of unit cell data, intensity data collection and structure refinement. Data were corrected for absorption by psi scans (for **2b**) and integration via indexing of crystal faces for **6e**. Both structures were solved by direct and difference Fourier methods and refined [30] by full-matrix least squares against F^2. All H atom positions were calculated and treated as riding models.

Table 3
Crystallographic data for complexes **2b** and **6e**

	2b	**6e**
Crystal colour, habit	Yellow needle	Green block
Crystal size (mm)	$0.5\times0.3\times0.2$	$0.58\times0.25\times0.21$
Formula	$C_{22}H_{21}Br_2O_2PW$	$C_{11}H_{11}Br_2NOW$
M	692.03	516.88
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.7487(8)	8.2867(9)
b (Å)	15.6411(15)	12.1208(12)
c (Å)	16.043(2)	13.315(2)
β (°)	96.174(12)	91.103(12)
U (Å^3)	2182.5(4)	1337.1(3)
Z	4	4
μ(Mo–K$_\alpha$) mm^{-1}	9.043	14.60
$\theta_{\text{data collection}}$ (°)	1.82–25.0	2.27–25.00
Completeness (%, $\theta=25$)	99.3	100
Data measured (% decay)	5004(10)	3174(3.4)
Unique data	3832	2359
R, wR_2 (all data)	0.0738, 0.1059	0.0990, 0.1570
R_{int}	0.0812	0.0379
Observed data [$I>2\sigma(I)$]	2768	1626
R, wR_2 (observed data)	0.0429, 0.0876	0.0599, 0.1343
S	1.022	1.047
Variables	253	145
$E_{\max}$, $E_{\min}$ (e Å^{-3})	1.54, -0.976	2.44, -2.88, near W

Phenyl, norbornadiene, nitrile ligand and methyl H atom displacement parameters were treated as riding models with U_{ij} 1.2, 1.2, 1.2, and 1.5 times the bound carbon atom U_{ij}, respectively.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data centre, CCDC No's CCDC 127758 for **2b**, CCDC 133547 for **4** and CCDC 127759 for **6e**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) R. Colton, Coord. Chem. Rev. 6 (1971) 269. (b) M.G.B. Drew, Prog. Inorg. Chem. 23 (1977) 67. (c) M. Melnick, P. Sharrock, Coord. Chem. Rev. 64 (1985) 49. (d) P.K. Baker, Adv. Organomet. Chem. 40 (1996) 45.
[2] J.L. Davidson, J. Chem. Soc. Dalton Trans. (1986) 2423.
[3] W.A. Wan Abu Bakar, J.L. Davidson, W.E. Lindsell, K.J. MacCullough, J. Chem. Soc. Dalton Trans. (1990) 61.
[4] L. Carlton, J.L. Davidson, G. Vasapollo, G. Douglas, K.W. Muir, J. Chem. Soc. Dalton Trans. (1993) 3341.
[5] (a) T.E. Burrow, A.J. Lough, R.H. Morris, A. Hills, D.L. Hughes, J.D. Lane, R.L. Richards, J. Chem. Soc. Dalton Trans. (1991) 2519. (b) M.C. Guedes da Silva, P.B. Hitchcock, D.L. Hughes, K. Marjani, A.J.L. Pombeiro, R.L. Richards, J. Chem. Soc. Dalton Trans. (1997) 3725.
[6] M. Kamata, K. Hirotsu, T. Higuchi, M. Kido, K. Tatsumi, T. Yoshida, S. Otsuka, Inorg. Chem. 22 (1983) 2416.
[7] J.A. Connor, E.J. James, J. Organomet. Chem. 316 (1986) 79.
[8] J.L. Davidson, G. Vasapollo, J. Chem. Soc. Dalton Trans. (1985) 2231.
[9] V. Riera, F.J. Arnaiz, G.G. Herbosa, J. Organomet. Chem. 315 (1986) 51.
[10] F.A. Cotton, J.H. Meadows, Inorg. Chem. 23 (1984) 4688.
[11] T. Daniel, H. Nagao, K. Tanaka, A. Nakamura, Chem. Ber. 128 (1995) 1007.
[12] T. Daniel, H. Nagao, H. Nakajima, K. Tanaka, A. Nakamura, J. Organomet. Chem. 509 (1996) 225.
[13] T. Szymanska-Buzar, T. Glowiak, Polyhedron 16 (1997) 1599.
[14] D.L. Kepert, Prog. Inorg. Chem. 25 (1979) 41.
[15] R. Hoffmann, B.F. Beier, E.L. Muetterties, A.R. Rossi, Inorg. Chem. 16 (1977) 511.
[16] (a) M.S. Balakrishna, S.S. Krishnamurthy, H. Manohar, Organometallics 10 (1991) 2522. (b) D.L. Kepert, unpublished work.
[17] CAChe 4.02, Oxford Molecular, Oxford, 1998.
[18] J.L. Davidson, unpublished work.
[19] J.L. Templeton, S.J. Neiter-Burgmayer, Organometallics 1 (1982) 1007.
[20] (a) R.S. Herrick, S.J. Nieter-Burgmayer, J.L. Templeton, J. Am. Chem. Soc. 105 (1983) 2599. (b) J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1.
[21] J.L. Davidson, G. Rosair, B.J.S. Thiebaut, unpublished work.
[22] P.K. Baker, M.G.B. Drew, M.M. Meehan, H.K. Patel, A. White, J. Chem. Res. 329 (1998) 1461.
[23] P.K. Baker, M.G.B. Drew, M.M. Meehan, J. Chem. Soc. Dalton Trans. (1999) 765.
[24] (a) S.W. Warner, S.J. Lippard, Organometallics 5 (1986) 1716. (b) J.A. Bowden, R. Colton, Aust. J. Chem. (1968) 2657. (c) J.R. Mossand B.L. Shaw, J. Chem. Soc. (A) (1970) 595.
[25] (a) P.K. Baker, S.J. Coles, D.E. Hibbs, M. Meehan, J. Chem. Soc. Dalton Trans. (1996) 3995. (b) P.K. Baker, A.I. Clark, S.J. Coles, M.G.B. Drew, M.C. Durrant, M.B. Hursthouse, R.L. Richards, J. Chem. Soc. Dalton Trans. (1998) 1281.
[26] P.K. Baker, S.G. Fraser, E.M. Keys, J. Organomet. Chem. 309 (1986) 319.
[27] E.M. Armstrong, P.K. Baker, M.G.B. Drew, Organometallics 7 (1988) 319.
[28] P.K. Baker, M.E. Harman, M.B. Hursthouse, A.J. Lavery, K.M.A. Malik, D.J. Muldoon, A. Shawcross, J. Organomet. Chem. 484 (1994) 169.
[29] XSCANS, X-ray Single Crystal Analysis System, Version 2.2, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1994.
[30] G.M. Sheldrick, SHELXTL/PC, Siemens Analytical X-ray Instruments, Madison, WI, 1994.