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Tungsten(VI) metallacarborane imido complexes; hydrogen bonding to a bent imido ligand in $\{W(N^tBu)_2[N(H)C(Me)NH^tBu](C_2B_9H_{11})\}$ †

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The amine elimination reaction of $W(N^tBu)_2(NH^tBu)_2$ with the di-basic carborane acid *nido*-7,8-$C_2B_9H_{13}$ generates the tungsten(VI) carborane complex, $[W(N^tBu)(NH^tBu)_2(C_2B_9H_{11})]$ **1**, in which a $C_2B_9H_{11}$ ligand has replaced one imido ligand. One of the remaining amido ligands can be substituted by acidic functions, thus 2,6-dimethylphenol yields $[W(N^tBu)(NH^tBu)(2,6\text{-}Me_2C_6H_3O)(C_2B_9H_{11})]$ **2**, and water gives the μ-oxo complex $\{[W(N^tBu)(NH^tBu)(C_2B_9H_{11})]_2(\mu\text{-}O)\}$ **3** as a mixture of racemic and meso diastereomers. Complexes **1** and **2** have been characterised by single crystal X-ray diffraction, revealing that replacing an amido ligand in **1** by a weaker π-donor phenoxide in **2** results in shorter metal–amido and metal–dicarbollide distances. Substitution of one amido ligand in **1** by a chloro ligand is achieved using Me_3SiCl giving $[W(N^tBu)(NH^tBu)Cl(C_2B_9H_{11})]$ **4**. Insertion of acetonitrile into the tungsten amido bond, followed by proton transfer gives $\{W(N^tBu)_2[N(H)C(Me)NH^tBu](C_2B_9H_{11})\}$ **5**, the *N*-*tert*-butyl acetamidine adduct of the unknown $M(1\sigma 2\pi)_3$ complex $[W(N^tBu)_2(C_2B_9H_{11})]$. A structural study by X-ray diffraction reveals that compound **5** contains one short linear (W–N 1.750(3) Å; W–N–C 173.8(3)°) and one longer bent (1.795(3) Å, 151.4(3)°) imido ligand, with a hydrogen bond between the amidine and bent imido ligand, demonstrating for the first time that a sp^2 hybridised bent imido ligand can act as a hydrogen bond acceptor.

Introduction

The coordination chemistry of the dicarbollide ligand ($C_2B_9H_{11}$) with middle and late transition metals has been established by a number of research groups,[1,2] and recently this ligand has been applied to lanthanide[3] and early transition metal chemistry in pursuit of metallocene analogues.[4] The η^5-$C_2B_9H_{11}$ and imido (NR) ligands are 4-electron LX_2 ligands[5] and both ligands share an electronic relationship with cyclopentadienyl, so that the fragment $[W(NR)(C_2B_9H_{11})]$ is isoelectronic with $[Hf(\eta\text{-}C_5H_5)_2]$. The metallacarborane chemistry of group 6 has been dominated for some time by the work of Stone and co-workers,[6] but few complexes containing W(VI) or Mo(VI) have been reported.[7] Do and co-workers synthesised both $\{[MoO_2(\eta^5\text{-}C_2B_9H_{11})]_2(\mu\text{-}O)\}^{2-}$ and $[MoO_3(\eta^1\text{-}C_2B_9H_{11})]^{2-}$ from the oxidation of the dithiolate complex $[NMe_4]_2[Mo(CO)_2(SPh)_2(C_2B_9H_{11})]$.[8] The complex $[W(NAr)(Me)(Cl)(C_2B_9H_{11})]$ (Ar = 2,6-dimethylphenyl) has been prepared from the reaction of $[C_2B_9H_{13}]$ with the tungsten alkyl complex $[W(NAr)Me_3Cl]$ and the evolution of two equivalents of methane.[9]

We have recently reported the preparation of $[M(NMe_2)_3(C_2B_9H_{11})]$ (M = Nb, Ta) by the reaction of $[M(NMe_2)_5]$ with $C_2B_9H_{13}$.[10] The amminolysis reaction of metal amido ligands with acids is well-known,[11–13] and a reaction between a M–NR_2 ligand and a Brønsted acid is thermodynamically feasible if the acid is more acidic than the eliminated HNR_2, $pK_a = 35\text{–}40$, although reactions are kinetically favoured if the "acid" is able to coordinate prior to proton transfer. Amido ligands insert into polar multiple bonds, and acetonitrile reacts with early transition metal M–NR_2 to form *N*,*N*-dialkylamidinate ligands, M–$NC(Me)NR_2$.[14,15] The group 6 homoleptic amido complexes $M(NR_2)_6$ are difficult to prepare,[16] and the readily synthesised[17] $[W(N^tBu)_2(NH^tBu)_2]$ is an alternative W(VI) starting material.[18–20] The reactions of this imido amido complex with weak Brønsted acids,[21] basic metal alkyls (LiMe,[22] $AlMe_3$[23]), and insertion chemistry with isocyanates have been investigated.[24] Whilst $[W(N^tBu)_2(NH^tBu)_2]$ is believed monomeric, the isopropyl analogue, $[W(\mu\text{-}NPr^i)(NPr^i)(NHPr^i)_2]_2$, is dimeric in the solid state.[25]

Organoimido complexes[26,27] have come under considerable scrutiny in recent years, in part due to their presumed involvement in industrial processes such as propylene ammoxidation,[28] nitrile reduction,[29] hydrodenitrogenation catalysis,[30] and application to carbodiimido metathesis[31] and imine metathesis.[32] Although traditionally considered to be inert spectator ligands capable of stabilising high oxidation state metals,[33] highly reactive $L_nM{=}NR$ species have been generated that can engage in cycloaddition chemistry,[34] function as [NR] transfer reagents[35] and C–H activate alkanes.[36]

Two alternatives have been identified for the coordination of a terminal imido ligand;[37] the vast majority of structurally characterised complexes contain linear 4-electron LX_2 ligand with M–N–C angles between 180 and 160°, but there are a number of well-characterised bent 2-electron X_2 imido ligands with M–N–C angles less than 150°[38–42] and some examples containing bent ligands as part of chelate rings.[43] Angles between 150 and 160° are frequently considered as distorted linear, since calculations reveal that there is a soft potential energy surface for bending the M–N–C unit.[44]

Here we report the synthesis and reaction chemistry of a tungsten(VI) metallacarborane complex prepared by the reaction of $[W(N^tBu)_2(NH^tBu)_2]$ with *nido*-7,8-$C_2B_9H_{13}$, demonstrating that the $C_2B_9H_{11}$ ligand is compatible with high

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams of **1**, **2** and **5** in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b100572n/

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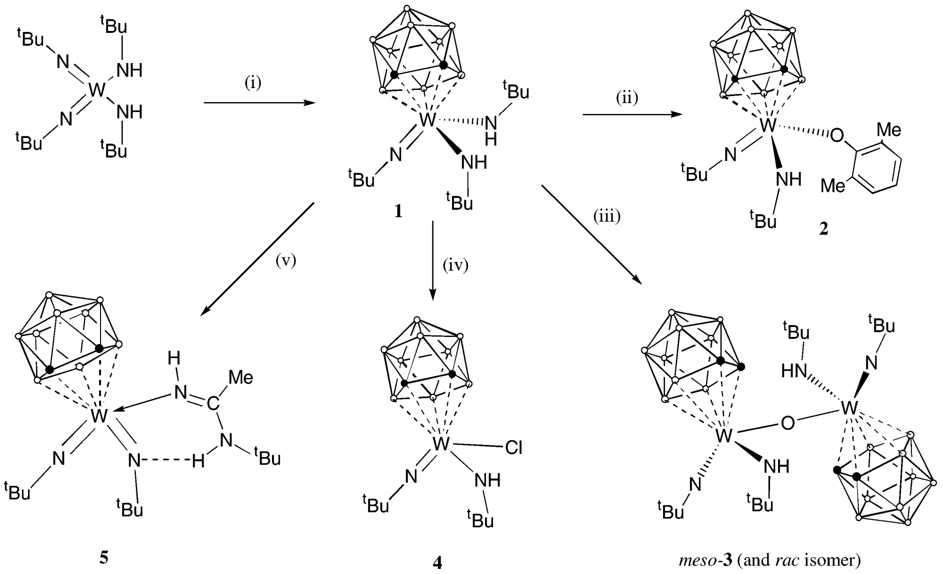


Scheme 1 The preparation and reactions of $[W(N^tBu)(NH^tBu)_2(C_2B_9H_{11})]$ **1**. Reagents: (i) $C_2B_9H_{13}$; (ii) 2,6-dimethylphenol; (iii) wet CH_2Cl_2; (iv) Me_3SiCl; (v) acetonitrile.

oxidation state tungsten. We also report the observation of a bent imido ligand acting as a hydrogen bond acceptor.

Results and discussion

The reaction of $[W(N^tBu)_2(NH^tBu)_2]$ with *nido*-7,8-$C_2B_9H_{13}$ results in the evolution of one equivalent of $^tBuNH_2$ and formation of the monomeric imido carborane complex $[W(N^tBu)(NH^tBu)_2(C_2B_9H_{11})]$ **1**. This compound is highly air- and moisture-sensitive, and on contact with either changes colour from a golden yellow to blue.

The difference between the ^{13}C NMR chemical shifts of α and β carbon atoms ($\Delta\delta$) of d^0 transition metal *tert*-butylimido complexes can be used as a experimental probe of the electron density on the nitrogen atom.[45] The value observed in **1** ($\Delta\delta = 41.5$ ppm), is typical of a mono(*tert*-butylimido)-tungsten(VI) complex. In solution, the ^1H and ^{13}C NMR spectra show two different ^tBu groups in a 2 : 1 intensity ratio (amido : imido). This, along with the presence of five resonances in the $^{11}B\{^1H\}$ NMR spectrum in a 2 : 2 : 3 : 1 : 1 ratio, suggests a C_s symmetric solution state structure for **1**.

Complex **1** can be converted into other mono-dicarbollide W(VI) complexes by ligand substitution protonolysis reactions. Thus **1** reacts with one equivalent of 2,6-dimethylphenol to form $[W(N^tBu)(NH^tBu)(OC_6H_3Me_2)(C_2B_9H_{11})]$ **2** (Scheme 1). This complex has C_1 symmetry and both the ^1H and ^{13}C NMR spectra of **2** indicate the presence of an unsymmetrical carborane cage with two CH resonances in a 1 : 1 intensity ratio at δ_H 3.19 and 2.81, respectively. The ^1H NMR spectrum shows only one resonance for the methyl groups on the phenoxide ligand, as well as a simple pattern in the aromatic region, indicating free rotation of the phenoxide ligand around the O–C bond. In the ^{13}C NMR spectrum the *tert*-butyl imido group reveals a $\Delta\delta$ value of 46 ppm.

The reaction of **1** with an excess of HOAr (Ar = 2,6-dimethylphenyl) results in the exclusive formation of **2**, implying that the replacement of one of the amido ligands in **1** by an alkoxo ligand in **2** reduces the susceptibility of the complex to further electrophilic attack.

During an attempt to isolate crystals of **1**, the hydrolysis product, $[\{W(N^tBu)(NH^tBu)(C_2B_9H_{11})\}_2(\mu\text{-}O)]$ **3**, was obtained. The hydrolysis reaction was repeated quantitatively using a saturated solution of water in degassed dichloromethane. Complex **3** possesses two chiral tungsten atoms, resulting in C_2-symmetric *rac*- and C_i-symmetric *meso*-diastereomers, drawn as *rac*-**3** and *meso*-**3** in Scheme 1; the *rac* diastereomer comprises the *RR* and *SS* enantiomers, which cannot be distinguished spectroscopically. For each diastereomer, there is expected to be one set of NMR resonances for $NHCMe_3$, one set of $NCMe_3$ resonances, plus two C–H and nine B–H resonances for each diastereomer, providing that these broad resonances can be resolved; in each diastereomer the $C_2B_9H_{11}$ ligands are equivalent and have local C_s symmetry. The ^1H and ^{13}C NMR spectra do indeed show four independent CMe_3 resonances in an approximately 0.9 : 1 : 1 : 0.9 intensity ratio, indicating the presence of both diastereomers in an approximately 9 : 10 ratio. The ^1H NMR spectrum shows two N–H resonances at δ_H 8.07 and 8.10, respectively. The ^{13}C NMR spectrum shows a single broad resonance for the α-carbon atoms in the imido group, giving $\Delta\delta \sim 41$. Poor resolution and extensive overlap of resonances results in the $^{11}B\{^1H\}$ and $^1H\{^{11}B\}$ NMR spectra showing only six and nine broad resonances in a 1 : 1 : 1 : 3 : 2 : 1 and 2 : 2 : 2 : 2 : 2 : 2 : 2 : 2 : 2 intensity ratio, respectively.

The mono-chloro complex $[W(N^tBu)(NH^tBu)Cl(C_2B_9H_{11})]$ **4** is formed as the exclusive tungsten-containing product in the reaction between **1** and an excess of Me_3SiCl. Even when the reaction is carried out in neat Me_3SiCl, only one amido ligand is substituted, a consequence of replacing one of the amido ligands in **1** by a weaker π-donor resulting in a stronger, less reactive, bond to the remaining amido ligand.

The ^1H and ^{13}C NMR spectra of **4** show an unsymmetrical molecule with two CMe_3 groups in a 1 : 1 intensity ratio and two carborane CH resonances, also in a 1 : 1 intensity ratio. The $^1H\{^{11}B\}$ NMR spectrum shows the presence of eight {BH} resonances in 1 : 1 : 2 : 1 : 1 : 1 : 1 : 1 : 1 intensity ratio, however the $^{11}B\{^1H\}$ NMR spectrum shows coincidental overlapping of the boron peaks, with six broad resonances observed in a 2 : 1 : 2 : 2 : 1 : 1 intensity ratio.

Stirring **1** in acetonitrile results in an insertion reaction and quantitative conversion to the amidine complex,[46] $\{W(N^tBu)_2[N(H)C(Me)NH^tBu](C_2B_9H_{11})\}$ **5**. The ^1H and ^{13}C NMR spectra of **5** show three different *tert*-butyl environments in a 1 : 1 : 1 ratio and two carborane CH peaks. The $^1H\{^{11}B\}$ and ^{11}B NMR spectra are consistent with an unsymmetrical carborane cage, with nine resonances in both spectra. The bonding and geometry of this compound are discussed in more detail below, but the solution spectroscopic data are clearly consistent with a C_1 symmetric structure. The hypothetical complex $\{W(N^tBu)_2(C_2B_9H_{11})\}$ would represent an example of an apparently 18-electron $M(1\sigma 2\pi)_3$ complex, and as such would have insufficient metal orbitals of appropriate symmetry

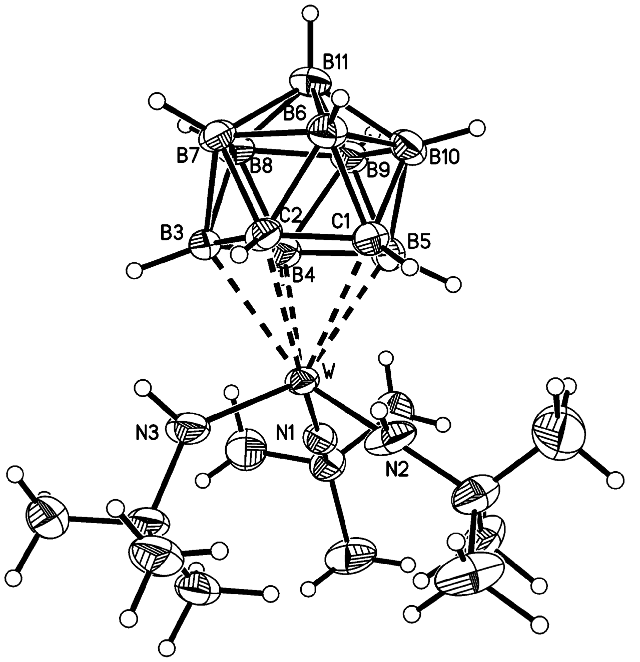


Fig. 1 The molecular structure of **1** (50% displacement ellipsoids) with hydrogen atoms drawn as arbitrary sized spheres.

Table 1 Selected bond lengths (Å) and angles (°) in [W(N^{t}Bu)(NH^{t}Bu)X(C$_2$B$_9$H$_{11}$)] complexes, X = NH^{t}Bu **1** and 2,6-Me$_2$C$_6$H$_3$O **2**

	1 Y = N(3)	**2** Y = O(1)
W–N(1)	1.721(3)	1.720(2)
W–N(2)	1.955(3)	1.926(2)
W–Y	1.949(4)	1.934(2)
N(1)–C(11)	1.472(5)	1.481(3)
N(2)–C(21)	1.427(6)	1.497(3)
Y–C(31)	1.496(5)	1.387(3)
W–C(1)	2.531(4)	2.471(3)
W–C(2)	2.572(4)	2.516(2)
W–B(3)	2.507(4)	2.491(3)
W–B(4)	2.437(4)	2.401(3)
W–B(5)	2.392(4)	2.392(3)
W–Cb	2.026(4)	1.984(3)
Cb–W–N(1)	124.5(3)	124.7(3)
Cb–W–N(2)	113.0(3)	112.9(3)
Cb–W–Y	109.7(3)	108.5(3)
W–N(1)–C(11)	165.3(3)	168.8(2)
W–N(2)–C(21)	141.6(3)	137.3(2)
W–Y–C(31)	134.8(3)	128.03(14)
N(1)–W–N(2)	101.7(2)	101.25(9)
N(1)–W–N(3)	105.6(2)	104.30(9)
N(2)–W–Y	99.2(2)	102.99(8)

Cb = centroid of the coordinated η^5-C$_2$B$_3$ ring of the C$_2$B$_9$H$_{11}$ ligand.

to accommodate π-donation from all three 1σ2π ligands.[26,47–49] All known examples of 18-electron M(1σ2π)$_3$ complexes readily coordinate a neutral[47,48,50,51] or anionic[52] donor ligand, to give formally 20-electron d^0 complexes.

Structural characterisation

The structures of (imido)$_2$MX$_2$ compounds (M = Cr, Mo and W) are related to those of the valence isoelectronic bent metallocene Cp$_2$MX$_2$ (M = Ti, Zr, Hf) complexes.[53,54] The relationship between the metallacarborane fragment, *closo*-3,1,2-[MC$_2$B$_9$H$_{11}$], and the cyclopentadienyl fragment, M(η-C$_5$H$_5$) has been discussed in detail elsewhere.[1] Complexes of formula (imido)(C$_2$B$_9$H$_{11}$)MX$_2$ can also be expected to adopt pseudo-metallocene structures, noting that in the dicarbollide ligand the two π-donor orbitals are non-degenerate, resulting in an orientational preference, often described as a strong *trans* influence of the dicarbollide ligand, as observed in indenyl,[55,56] pyrollyl,[57] carbonyl[58] and amido[10] complexes.

The molecular structure of [W(N^{t}Bu)(NH^{t}Bu)$_2$(C$_2$B$_9$H$_{11}$)] **1**, is shown in Fig. 1 and selected bond lengths are given in Table 1. The asymmetric unit also contains one molecule of toluene with the methyl group disordered over two adjacent sites on the ring. The imido ligand is close to linear, indicating that the nitrogen is sp-hybridised and the M–N bond (1.721(3) Å) closely approaches a triple bond. Together with the solution state Δδ value, this suggests that the imido ligand is the dominant π-donor ligand. The amido ligands in **1** are both planar (sum of angles around N(2) is 358.6°, and N(3) is 359.9°), and are orientated such that their alkyl groups are pointing away from the dicarbollide ligand, the W–N distances are in the range of other W–N amido complexes (1.87–2.03 Å).[59]

In d^0 Cp$_2$M(ER$_2$)$_2$ complexes (E = N, P), E→M π-donation is maximised when the plane of the ER$_2$ ligand lies perpendicular to the E–M–E plane with a dihedral angle between the two planes of 90°, and π-donation is zero when the two planes are parallel with a dihedral angle of 0°.[60] Experimentally, a wide range of dihedral angles (≠90°) is observed in d^0 Cp$_2$M(NR$_2$)$_2$ complexes,[61] suggesting that steric rather than electronic factors may play a role in these complexes. Complexes with a dominant π-donor ligand adopt structures with one short (double) M–E bond to a planar, sp^2-hybridized ER$_2$ group, and one long (single) M-E bond to a pyramidal, sp^3-hybridised ER$_2$ group.[62] In Cr(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(NH^{t}Bu)Cl the dihedral between the amido ligand plane and the N–Cr–Cl plane (87.9°) is reported to be consistent with the two imido ligands dominating the π-bonding,[63] but also implies maximum amido to metal π-donation. In common with the metallocene complexes, the dihedral angles between the N–W–N plane and the amido H–N–C planes in **1** are 60.7° for N(3) and 24.8° for N(2).

As noted earlier, most previously known structurally characterised *closo*-(3,1,2-WC$_2$B$_9$H$_{11}$) complexes contain 18 electron tungsten centres in low oxidation states with π-acceptor ligands, and show W–Cb (where Cb is the centroid of the C$_2$B$_3$ ring) distances between 1.744 Å[64] and 1.945 Å.[65] The complex most closely related to those in the present work is the high oxidation state molybdenum complex {[(C$_2$B$_9$H$_{11}$)MoO$_2$]$_2$(μ-O)}$^{2-}$, containing π-donor oxide ligands, with Mo–Cb of 2.064 Å.[8] The W–Cb distance in **1** is 2.026(4) Å, and the carborane ligand tilts, with the W–C bonds 5 to 7% longer than the W–B bonds. The "slippage" of a carborane ligand on an electron rich metal centre is well established in late transition metal metallacarboranes.[66] The carborane cage is orientated with the C–C centroid (C$_2$) approximately *trans* to the imido ligand (C$_2$–Cb–W–N(1) $\tau = -157.9°$).

The molecular structure of [W(N^{t}Bu)(NH^{t}Bu)(2,6-Me$_2$C$_6$H$_3$O)(C$_2$B$_9$H$_{11}$)] **2**, is shown in Fig. 2 and selected bond lengths and angles are given in Table 1. The imido ligand is close to linear, and the dicarbollide ligand is orientated with the imido ligand *trans* to the C$_2$ unit of the C$_2$B$_3$ face. The amido ligand is orientated with a dihedral angle (N–M–O/R–N–H) of 82°, which is close to optimised for π-donation to the tungsten. The phenoxide ligand also has a dihedral angle that is close to the optimum; although the W–O distance is comparable to those where the phenoxide ligand is acting as a 1-electron ligand.[67] The orientation of the phenoxide ligand may be caused by the ligand attempting to move away from the dicarbollide ligand, reducing steric interactions between the two ligands. The data in Table 1 demonstrate that replacement of one amido ligand in complex **1** by a weaker π-donor phenoxide ligand in **2** results in a significant shortening of the remaining W–amido bond and a shortening of the metal to carborane centroid distance; there is little or no tilting of the cage in **2**. The metal–imido distance is unaltered, suggesting that this is the dominant π-donor, providing maximum π-bonding in both complexes.

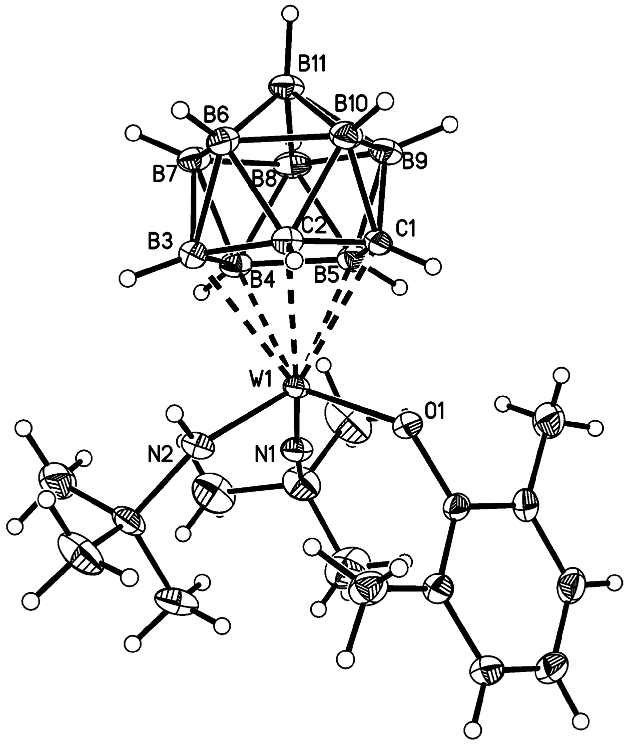


Fig. 2 The molecular structure of **2** (50% displacement ellipsoids) with hydrogen atoms drawn as arbitrary sized spheres.

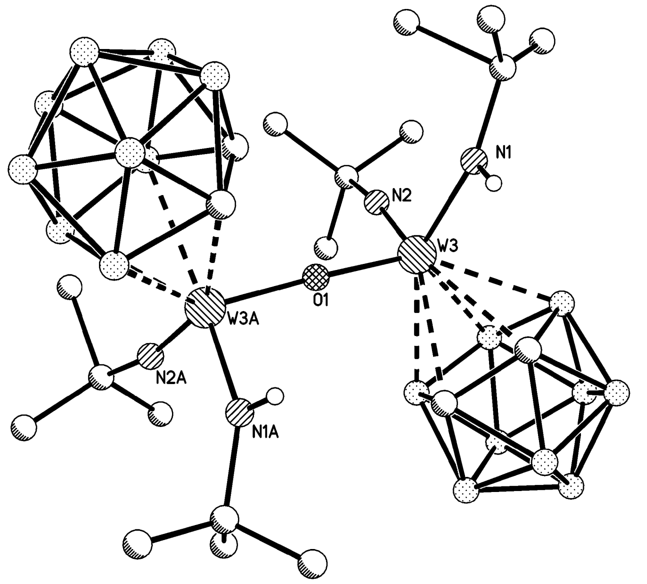


Fig. 3 The molecular structure of **3**, showing one model adopted for the disordered structure. Only the heavy atoms are shown, drawn as arbitrary sized spheres.

Table 2 Selected bond lengths (Å) and angles (°) in **5**

W(1)–N(1)	1.750(3)	N(4)–C(13)	1.504(4)
W(1)–N(2)	1.795(3)	W(1)–C(1)	2.620(4)
W(1)–N(3)	2.094(3)	W(1)–C(2)	2.573(3)
N(1)–C(3)	1.461(4)	W(1)–B(4)	2.461(4)
N(2)–C(21)	1.469(4)	W(1)–B(8)	2.469(4)
N(3)–C(11)	1.318(4)	W(1)–B(9)	2.455(4)
C(11)–N(4)	1.320(4)	W(1)–Cb	2.065(4)
C(11)–C(12)	1.496(4)		
Cb–W(1)–N(1)	114.5(4)	W(1)–N(2)–C(7)	151.4(3)
Cb–W(1)–N(2)	124.9(4)	N(1)–W(1)–N(2)	107.21(14)
Cb–W(1)–N(3)	109.3(4)	N(1)–W(1)–N(3)	95.89(12)
W(1)–N(1)–C(3)	173.8(3)	N(2)–W(1)–O(1)	99.90(13)

Cb = centroid of the coordinated η^5-C_2B_3 ring of the $C_2B_9H_{11}$ ligand.

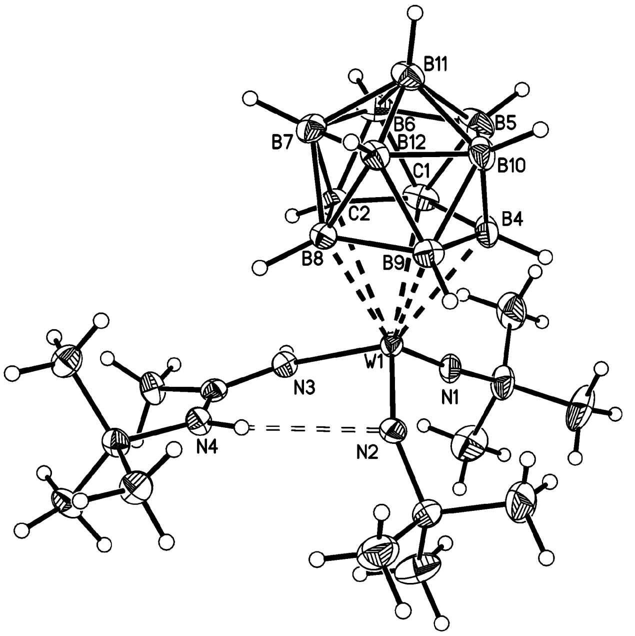


Fig. 4 The molecular structure of **5** (50% displacement ellipsoids) with hydrogen atoms drawn as arbitrary sized spheres.

Crystals of **3**, suitable for single crystal X-ray diffraction, have been grown from two different solvents, $CDCl_3$ and CH_2Cl_2. It has not proved possible to find a suitable model for the considerable disorder of the molecule of **3** and the co-crystallised solvent, but, after collecting and partially solving four datasets, we are confident that the geometry of the heavy atoms is that shown in Fig. 3. There is disorder in two of the *tert*-butyl groups attached to the same metal atom, which may arise from co-crystallisation of the *meso*- and *rac*-isomers. Solid-state inter-conversion of the diastereoisomers is potentially facile, since it only involves transfer of a proton between adjacent amido and imido ligands on the same tungsten atom. In solution there is some broadening and shift of *tert*-butyl resonances in the ^1H NMR at lower spectrometer operating frequencies (smaller peak separation in Hz), but no conclusive evidence was obtained for dynamic proton exchange. Although no confidence can be placed on the bond lengths and angles, it is clear that the molecule adopts a *transoid* configuration with the two cages as far away from each other as possible. The supplementary information (ESI) for this paper does not include .cif or .xyz files for **3**.

The molecular structure of $\{W(N^tBu)_2[N(H)C(Me)NH^tBu](C_2B_9H_{11})\}$ **5** is shown in Fig. 4, with selected bond lengths and angles in Table 2. The molecule contains a dicarbollide ligand and two imido ligands, one of which is short and linear (W–N 1.750(3) Å, W–N–C 173.8(3)°) and the second is longer and bent (1.795(3) Å, 151.4(3)°), the bond length to the linear imido is comparable to those seen in compounds **1**, **2**, and other tungsten *tert*-butyl imido ligands.[19] The coordination sphere is completed by the neutral *N*-*tert*-butyl acetamidine ligand. The long tungsten–dicarbollide centroid distance, 2.065 Å, reflects the electronic saturation in **5**. As with the dicarbollide ligand in **1** the carbon atoms in the C_2B_3 face of the ligand are moved further away from the metal atom, with W–C_{av} being 5% longer than the average W–B bond length. The dicarbollide ligand is orientated with the C_2 unit approximately *trans* to the bent imido ligand, as illustrated in Fig. 5. The amidine ligand is involved in a novel N · · · H–N hydrogen bond,[68] with the imido nitrogen as the hydrogen bond acceptor, the N(2) · · · H(4N) distance is 2.43(4) Å and N(2) · · · N(4) is 3.199(4) Å, lying within the accepted parameters for N · · · H–N hydrogen bonds.[69] Noting that atoms H(3N), N(3), C(11), C(12), N(4), H(4N) and C(13) of the amidine ligand are required to be planar due

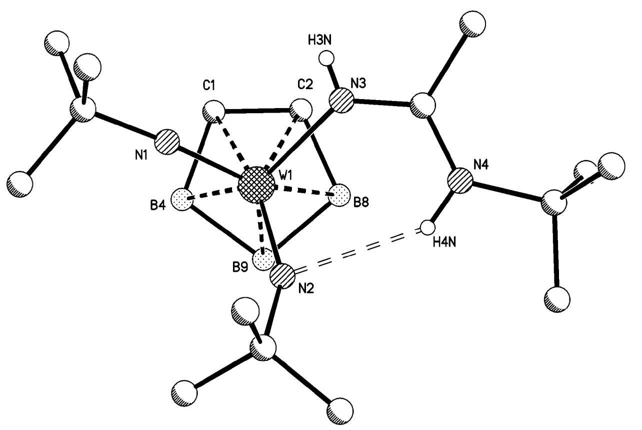
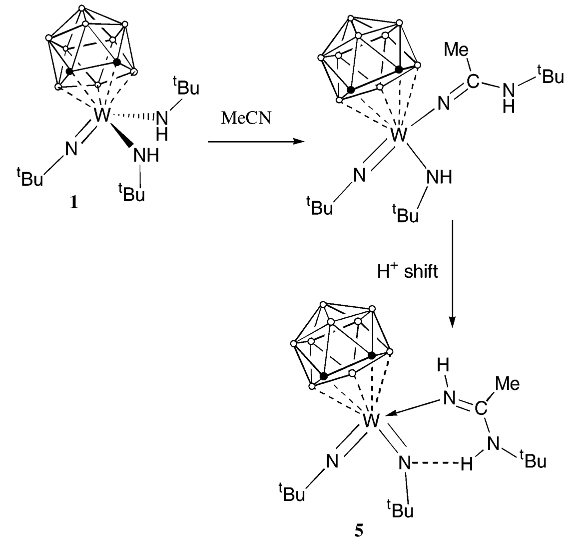


Fig. 5 A view of the molecular structure of **5** emphasising the presence of the amidine–imido hydrogen bond. Atoms are drawn as arbitrary size spheres, all cage atoms other than the η^5-C_2B_3 face are omitted as are hydrogen atoms other than N–H.

to π-conjugation, the hydrogen bond completes a very distorted six-membered ring for the atoms N(2), W(1), N(3), C(11), N(4) and H(4N). Whilst π-systems are known to act as hydrogen bond acceptors,[70] and it is possible that the hydrogen bond acceptor here is the imido M≡N bond, we propose that bending of the imido ligand containing N(2) generates a localisation of electron density (*i.e.*, a lone pair) at this atom, and it is this which acts as the hydrogen bond acceptor.

It is likely that the first stage in the formation of **5** from **1** and MeCN (Scheme 2) is the insertion of one molecule of acetonitrile into one of the W–NH^{t}Bu bonds of **1**, to form an amidinate ligand[15] which undergoes an intramolecular proton transfer from the remaining W–NH^{t}Bu ligand to the amidinate, so that the structure of **5** is {W(N^{t}Bu)$_2$[N(H)C(Me)NH^{t}Bu]-($C_2B_9H_{11}$)}, with two imido ligands and a neutral amidine donor, rather than the imido, amido, amidinate tautomer, {W(N^{t}Bu)-(NH^{t}Bu)[HNC(Me)N^{t}Bu]($C_2B_9H_{11}$)}. Such rearrangement does not occur in the case of insertion of acetonitrile into a Zr–PHR bond.[71] The observed structure of **1** in both the solution- and solid-state is [W(N^{t}Bu)(NH^{t}Bu)$_2$($C_2B_9H_{11}$)] with an imido and two amido ligands, rather than the tautomer with two imido ligands and a coordinated amine, *i.e.*, [W(N^{t}Bu)$_2$-(NH$_2$^{t}Bu)($C_2B_9H_{11}$)], analogous to that in [W(N^{t}Bu)$_2$(NH^{t}Bu)$_2$] and [W(NAr)$_2$(NHAr)$_2$].[48] These structural preferences presumably reflect the relative basicities of the ligands. More delicately balanced equilibria have been reported, where both tautomers can be observed,[20] and the α-elimination of M(NHR)$_2$ to give reactive M(NR) is well documented.[72]



Scheme 2 The formation of **5** by the insertion of acetonitrile into one of the W–NH^{t}Bu bonds of **1**, and subsequent proton transfer.

The hydrogen bond in **5** represents one localisation of a proton in the act of transfer between the imido and amidine ligands, and suggests that the first step in the reaction of an imido with an N–H is bending of the imido ligand to generate a hydrogen bond acceptor orbital to interact with the incoming N–H. This structure thus represents a functional model for the reaction of imido ligands with amines to give imido exchange. Indeed the seminal work on the mechanism of the imido exchange reaction notes that "It is possible that hydrogen bonding between the N–H and the imido nitrogen plays an important role".[73]

In conclusion, we have prepared and characterised the first examples of metallacarboranes of tungsten(VI), demonstrating the electronic relationships between the *tert*-butyl imido, Me$_3$CN, and dicarbollide, $C_2B_9H_{11}$, ligands. Many of the complexes are π-electron loaded, yet the metallacarborane fragment generally remains undistorted, with only modest ring slippage observed, although the M–Cb distances are typically longer than those seen in previously characterised low oxidation state tungsten metallacarborane complexes, where the tungsten carries π-acceptor ligands. An unusual example of a weak hydrogen bond between a coordinated amidine and an imido ligand has been observed, where the hydrogen bond acceptor site is generated by bending of the imido ligand.

Experimental

All manipulations of air- and moisture-sensitive compounds were performed on a conventional vacuum/nitrogen line using standard Schlenk and cannula techniques or in a nitrogen filled glove box. When required, solvents were dried by prolonged reflux over an appropriate drying agent prior to distillation and deoxygenation by freeze–thaw processes. NMR solvents were vacuum distilled from suitable drying agents and stored in ampoules under dry nitrogen. Elemental analysis was performed by the micro-analytical service of this department. Infrared spectra were run as liquid films on a Perkin-Elmer 1615 FTIR spectrometer or as solid samples on a Graseby Specac 10500 Golden Gate coupled to a Perkin-Elmer 1000 series "Paragon" spectrometer. Mass spectra were recorded on a Micromass Autospec instrument operating in EI mode; [M] denotes the molecular ion.

All NMR spectra were recorded at ambient temperature on a Varian Unity-300 (^{1}H, ^{11}B, ^{11}B{^{1}H} and ^{13}C{^{1}H}). All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent (C_6D_5H, 7.15 ppm; $CHCl_3$, 7.26 ppm; $CDHCl_2$, 5.25 ppm). ^{13}C NMR spectra were referenced to the solvent resonance (C_6D_6, 128.0 ppm; $CDCl_3$, 77.0 ppm; CD_2Cl_2, 53.5 ppm). ^{11}B NMR spectra were referenced externally to $BF_3 : Et_2O$, $\delta = 0$ ppm.

[W(N^{t}Bu)(NH^{t}Bu)$_2$($C_2B_9H_{11}$)] 1

A stirred toluene (50 cm^3) solution of W(N^{t}Bu)$_2$(NH^{t}Bu)$_2$ (4.7 g, 10 mmol) was treated dropwise at room temperature with a toluene (20 cm^3) solution of *nido*-7,8-$C_2B_9H_{13}$ (1.34 g, 10 mmol). The solution was stirred at room temperature for 12 h, during which time the solution gradually darkened. The solution was then refluxed for 12 h, after which it was cooled to room temperature and the solvent removed under reduced pressure, leaving a golden honeycomb solid, which was washed with pentane (2 × 10 cm^3) and isolated by filtration before drying *in vacuo* overnight. Crystals suitable for diffraction studies were grown by cooling a toluene solution to −30 °C. Yield 4.8 g, 91%. ^{1}H NMR (C_6D_6): δ 7.96 (br s, 2H, NH), 2.79 (br s, 2H, $C_2B_9H_{11}$), 1.46 (s, 9H, CMe_3), 1.12 (s, 18H, CMe_3). Additional peaks in ^{1}H{^{11}B} NMR (C_6D_6): δ 4.28 (1H), 3.31

(2H), 3.06 (1H), 2.87 (1H), 2.72, (2H), 1.62 (2H). $^{13}C\{^1H\}$ NMR (C_6D_6): *δ* 72.5 (1 × CMe$_3$), 58.5 (2 × *C*Me$_3$), 55.7, (br, *C*$_2$B$_9$H$_{11}$), 32.8, (2 × C*Me*$_3$), 31.0 (C*Me*$_3$). $^{11}B\{^1H\}$ NMR (C_6D_6): *δ* 2.2 (2B), −1.9 (2B), −9.4 (3B), −11.7(1B), −13.0 (1B). Calc. for $C_{14}H_{40}B_9N_3W(C_7H_8)_{0.9}$: C, 39.67; H, 7.74; N, 6.84. Found: C, 39.83; H, 7.67; N, 6.27%. MS: *m*/*z* 532 [M$^+$], 424 [M − $C_2B_9H_{11}{}^+$].

[W(N^{t}Bu)(NH^{t}Bu)(OC$_6$H$_3$Me$_2$-2,6)(C$_2$B$_9$H$_{11}$)] 2

A stirred toluene (10 cm^3) solution of **1** (0.53 g, 1 mmol) was treated dropwise with a toluene solution (10 cm^3) of $Me_2C_6H_3OH$ (0.12 g, 1 mmol). The yellow solution was refluxed for 12 h. The reaction mixture was then allowed to cool to room temperature and the solvent evaporated under reduced pressure. The yellow residue was extracted with fresh toluene (10 cm^3) and filtered. The filtrate was carefully layered with pentane (10 cm^3) and slowly cooled to −30 °C, producing yellow crystals of **2**, which were isolated by filtration. Yield 0.45 g, 78%. ^1H NMR (C_6D_6): *δ* 8.09 (br s, 1H, NH), 6.85 (d, 2H, *meta*-CH), 6.73 (t, 1H, *para*-CH), 3.19 (br s, 1H, C$_2$B$_9$H$_{11}$), 2.81 (br s, 1H, C$_2$B$_9$H$_{11}$), 2.02 (s, 6H, OC$_6$H$_3$*Me*$_2$), 1.27 (s, 9H, CMe$_3$), 1.08 (s, 9H, CMe$_3$). Additional peaks in $^1H\{^{11}B\}$ NMR (C_6D_6): *δ* 4.61 (1H), 4.19 (1H), 3.36 (1H), 3.22 (1H), 3.10 (1H), 2.92 (1H), 2.78 (1H), 2.47 (1H), 2.34 (1H). $^{13}C\{^1H\}$ NMR (C_6D_6): *δ* 160.1 (*ipso*-OC$_6$H$_3$Me$_2$), 129.2 (*meta*-*C*H), 127.1 (*ortho*-*C*Me), 122.6 (*para*-*C*H), 77.3 (*C*Me$_3$), 65.3 (br, *C*$_2$B$_9$H$_{11}$), 62.3 (*C*Me$_3$), 53.4 (br, *C*$_2$B$_9$H$_{11}$), 33.1 (C*Me*$_3$), 31.0 (C*Me*$_3$), 17.3 (OC$_6$H$_3$*Me*$_2$). $^{11}B\{^1H\}$ NMR (C_6D_6): *δ* 3.4 (3B), −4.7 (1B), −6.7 (br d, 1B), −8.9 (br d, 2B), −10.9 (br d, 1B), −12.2 (br d, 1B). Calc. for $C_{18}H_{39}B_9N_2OW$: C 37.23; H 6.77; N 4.82. Found: C 37.25, H 6.42; N 4.79%. MS: *m*/*z* 580 [M$^+$], 448 [M − $C_2B_9H_{11}{}^+$].

[{W(N^{t}Bu)(NH^{t}Bu)(C$_2$B$_9$H$_{11}$)}$_2$(μ-O)] 3

A stirred dichloromethane (10 cm^3) solution of **1** (1 g, 2 mmol) was treated dropwise with 20 cm^3 of a saturated solution of water in dichloromethane. The yellow solution was stirred for 12 h. The solvent was then evaporated under reduced pressure. The pale yellow residue was extracted with fresh dichloromethane (10 cm^3), and the resulting solution was filtered. The filtrate was carefully layered with pentane (10 cm^3) and slowly cooled to −30 °C producing yellow crystals of **3**, which were isolated by filtration. Yield 0.79 g 84%. The same procedure was followed using **4** (1 g, 2 mmol) in dichloromethane to yield 0.6 g, 64% of **3**. ^1H NMR (CD_2Cl_2): *δ* 8.10 (br s, 1H, NH), 8.07 (br s, 1H, NH), 3.20 (br s, 2H, C$_2$B$_9$H$_{11}$), 3.12 (br s, 2H, C$_2$B$_9$H$_{11}$), 1.58 (s, 9H, CMe$_3$), 1.55 (s, 9H, CMe$_3$), 1.40 (s, 9H, CMe$_3$), 1.37 (s, 9H, CMe$_3$). Additional peaks in $^1H\{^{11}B\}$ NMR (CD_2Cl_2): *δ* 3.49 (2H), 2.96 (2H), 2.78 (2H), 2.56 (2H), 2.39 (2H), 2.33 (2H), 2.18 (2H), 1.69 (2H), 1.59 (2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 72.3 (br, N*C*Me$_3$), 64.1 (br, C$_2$B$_9$H$_{11}$), 63.3 (br, C$_2$B$_9$H$_{11}$), 61.2 (N(H)*C*Me$_3$), 61.1 (N(H)*C*Me$_3$), 32.4 (C*Me*$_3$), 32.3 (C*Me*$_3$), 30.5 (C*Me*$_3$), 30.4 (C*Me*$_3$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): *δ* 3.0 (2B), 1.3 (2B), −2.4 (2B), −6.1 (2B), −8.6 (6B), −12.3 (4B). Calc. for $C_{20}H_{60}B_{18}N_4O_1W_2(CH_2Cl_2)_{0.8}$: C, 24.91; H, 6.19; N, 5.59. Found: C, 25.15; H 6.17; N 5.07%. MS: *m*/*z* 934 [M$^+$], 800 [M − $C_2B_9H_{11}{}^+$].

[W(N^{t}Bu)(NH^{t}Bu)Cl(C$_2$B$_9$H$_{11}$)] 4

A stirred toluene (20 cm^3) solution of **1** (0.53 g, 1 mmol) was treated dropwise with neat Me$_3$SiCl (0.54 g, 5 mmol) at room temperature. After stirring at room temperature for 12 h, the solution was refluxed for 1 h, and then allowed to cool to room temperature. Solvent and residual Me$_3$SiCl were removed under reduced pressure. The residue was washed with hexanes (2 × 10 cm^3) and then extracted with dichloromethane and the resulting solution was filtered. The dichloromethane solution was layered with pentane (10 cm^3) and cooled to −30 °C giving yellow microcrystalline product, which was isolated by filtration and washed with a small volume of pentane. Yield 0.3 g, 61%. ^1H NMR ($CDCl_3$): *δ* 9.78 (br s, 1H, NH), 3.85 (br s, 1H, C$_2$B$_9$H$_{11}$), 3.37 (br s, 1H, C$_2$B$_9$H$_{11}$), 1.72 (s, 9H, CMe$_3$), 1.58 (s, 9H, CMe$_3$). Additional peaks in $^1H\{^{11}B\}$ NMR ($CDCl_3$): *δ* 3.89 (1H), 3.36 (1H), 3.24 (1H), 2.83 (1H), 2.71 (1H), 2.63 (1H), 2.48 (2H), 2.03 (1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 74.0 (N*C*Me$_3$), 64.1 (N(H)*C*Me$_3$), 62.3 (br, *C*$_2$B$_9$H$_{11}$), 54.3 (br, *C*$_2$B$_9$H$_{11}$), 32.7 (N(H)C*Me*$_3$), 30.3 (NC*Me*$_3$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): *δ* 3.1 (2B), −5.0 (1B), −7.5 (2B), −8.9 (2B), −11.5 (1B), −13.6 (1B). Calc. for $C_{10}H_{30}B_9Cl_1N_2W$: C, 24.27; H, 6.11; N, 5.66. Found: C, 25.19; H, 6.22; N, 5.72%.

Table 3 Crystallographic data

	1·C$_7$H$_8$	**2**	**5**
Empirical formula	$C_{21}H_{48}B_9N_3W$	$C_{18}H_{39}B_9N_2OW$	$C_{16}H_{43}B_9N_4W$
Formula weight	623.76	580.65	572.68
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Temperature/K	150(2)	150(2)	120(2)
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a/Å	11.404(1)	11.053(2)	17.825(3)
b/Å	11.501(1)	11.859(2)	10.920(2)
c/Å	22.696(1)	20.074(4)	13.523(3)
$β$/°		90.016(4)	95.333(4)
U/Å^3	2976.7(4)	2631.3(8)	2620.7(8)
Z	4	4	4
$μ$(Mo-Kα)/mm^{-1}	3.895	4.403	4.418
Reflections collected	25039	29490	21485
Independent reflections	8084	6033	7346
R_{int}	0.0306	0.0306	0.0526
Reflections with $I \geq 2σ(I)$	7682	5314	5273
R [$I \geq 2σ(I)$]	0.0237	0.0184	0.0311
$wR(F^2)$, all data	0.0603	0.0397	0.0560

{W(N^{t}Bu)$_2$[N(H)C(Me)NH^{t}Bu](C$_2$B$_9$H$_{11}$)} 5

Complex **1** (1 g, 2 mmol) was dissolved in 20 cm^3 of dry degassed acetonitrile and stirred until the entire solid had dissolved. The solution was then filtered and the volume of solvent was reduced to 10 cm^3. Slow recrystallisation over 48 h at −20 °C gave yellow crystals, which were isolated by filtration and washed with a small volume of pentane. Yield 0.95 g, 83%. ^1H NMR (C_6D_6): *δ* 6.44 (br s, 1H, NH), 5.27 (br s, 1H, NH), 3.42 (br s, 1H, C$_2$B$_9$H$_{11}$), 2.81 (br s, 1H, C$_2$B$_9$H$_{11}$), 1.53 (s, 3H, C*H*$_3$), 1.46 (s, 9H, CMe$_3$), 1.35 (s, 9H, CMe$_3$), 1.32 (s, 9H, CMe$_3$). Additional peaks in $^1H\{^{11}B\}$ NMR (C_6D_6): *δ* 4.54 (1H), 4.06 (1H), 3.82 (1H), 3.64 (1H), 3.40 (1H), 3.19 (1H), 2.93 (1H), 2.38 (1H), 1.38 (1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 168.9 (N=*C*(Me)–N), 71.6 (*C*Me$_3$), 69.1 (*C*Me$_3$), 58.2 (*C*Me$_3$), 56.5 (C$_2$B$_9$H$_{11}$), 49.6 (C$_2$B$_9$H$_{11}$), 34.0 (C*Me*$_3$), 32.5 (C*Me*$_3$), 31.5 (C*Me*$_3$), 30.9 (CH$_3$). $^{11}B\{^1H\}$ NMR (C_6D_6): *δ* 2.2 (1B), 0.8 (1B), −0.1 (1B), −4.8 (1B), −8.9 (1B), −10.6 (1B), −12.9 (1B), −14.2 (1B), −18.4 (1B). Calc. for $C_{16}H_{43}B_9N_4W_1$: C, 33.56; H, 7.57; N, 9.78. Found: C, 33.76; H, 7.58; N, 9.67%.

X-Ray crystallography

Single-crystal diffraction experiments were carried out with a SMART 1K CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The reflection intensities were corrected for absorption by numerical integration based on measurements of the crystal and face-indexing (for **1** and **5**, using SHELXTL software[74]) or by a semi-empirical method based on multiple scans of identical reflections and Laue equivalents using SHELXTL software for **2**. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs.[74] Crystal data and experimental details are listed in Table 3. For **2** the monoclinic angle β is nearly 90°; possible orthorhombic, *i.e.*, *mmm* Laue symmetry was examined as follows. Merging 26857 reflections assuming *mmm* Laue symmetry gives $R_{int} = 0.412$ (41.2%), while for the monoclinic case (Laue symmetry 2/*m*) merging 23946 reflections gives $R_{int} = 0.031$ (3.1%). For this reason, no attempt was made to solve the structure in an orthorhombic space group. At the end of the refinement, the results were tested using the ADDSYMM program,[75] and no extra crystallographic symmetry was found.

CCDC reference number 156702–156704.

See http://www.rsc.org/suppdata/dt/b1/b100572n/ for crystallographic data of **1**, **2** and **5** in CIF or other electronic format.

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References

1 R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol 1, ch. 9; M. F. Hawthorne, *Acc. Chem. Res.*, 1968, **1**, 281; A. K. Saxena and N. S. Hosmane, *Chem. Rev.*, 1993, **93**, 1081.

2 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, K. Nestor, M. Thornton-Pett, S. Heřmánek, T. Jelínek and B. Štíbr, *J. Chem. Soc., Dalton Trans.*, 1990, 681.

3 M. J. Manning, C. B. Knobler, R. Khattar and M. F. Hawthorne, *Inorg. Chem.*, 1991, **30**, 2009.

4 Z. Xie, S. Wang, Z.-Y. Zhou, F. Xue and T. C. W. Mak, *Organometallics*, 1998, **17**, 489; E. Hong, Y. Kim and Y. Do, *Organometallics*, 1998, **17**, 2933; D. Rabinovich, C. M. Haswell, B. L. Scott, R. L. Miller, J. B. Nielsen and K. D. Abney, *Inorg. Chem.*, 1996, **35**, 1425; R. Uhrhammer, Y. X. Su, D. C. Swenson and R. F. Jordan, *Inorg. Chem.*, 1994, **33**, 4398; C. Kreuder, R. F. Jordan and H. Zhang, *Organometallics*, 1995, **14**, 2993.

5 M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127.

6 F. G. A. Stone, *Adv. Organomet. Chem.*, 1990, **31**, 53; S. A. Brew and F. G. A. Stone, *Adv. Organomet. Chem.*, 1993, **35**, 135; F. G. A. Stone, *Pure and Appl. Chem.*, 1986, **58**, 529.

7 J.-H. Kim, M. Lamrani, J.-W. Hwang and Y. Do, *Inorg. Chim. Acta*, 1998, **283**, 145.

8 J.-H. Kim, E. Hong, J. Kim and Y. Do, *Inorg. Chem.*, 1996, **35**, 5112.

9 D. J. Crowther, R. A. Fisher, J. A. M. Canich, G. G. Hlatky and H. W. Turner, *US Pat.* 5,502,124. Exxon Chemical Patents Inc., 1996.

10 A. S. Batsanov, A. V. Churakov, J. A. K. Howard, A. K. Hughes, A. L. Johnson, A. J. Kingsley, I. S. Neretin and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1999, 3867; C. K. Broder, A. E. Goeta, J. A. K. Howard, A. K. Hughes, A. L. Johnson, J. M. Malget and K. Wade, *J. Chem. Soc., Dalton Trans.*, 2000, 3526.

11 G. Chandra and M. F. Lappert, *J. Chem. Soc., A*, 1968, 1940; M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood Publishers, Chichester, 1980; M. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, Volume 2, ch. 13.4.

12 A. K. Hughes, A. Meetsma and J. H. Teuben, *Organometallics*, 1993, **12**, 1936; W. A. Herrmann and W. Baratta, *J. Organomet. Chem.*, 1996, **506**, 357; Y. Mu, W. E. Piers, M. A. MacDonald and M. J. Zaworotko, *Can. J. Chem.*, 1995, **73**, 2233; Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko and V. G. Young, *Organometallics*, 1996, **15**, 2720; Z. Ziniuk, I. Goldberg and M. Kol, *J. Organomet. Chem.*, 1997, **546**, 441.

13 I. A. Guzei, A. G. Baboul, G. P. A. Yap, A. L. Rheingold, H. B. Schlegel and C. H. Winter, *J. Am. Chem. Soc.*, 1997, **119**, 3387; I. A. Guzei, G. P. A. Yap and C. H. Winter, *Inorg. Chem.*, 1997, **36**, 1738; Y. Mu, W. E. Piers, L. R. MacGillivray and M. J. Zaworotko, *Polyhedron*, 1995, **14**, 1.

14 G. Chandra, A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *J. Chem. Soc. A*, 1970, 2550.

15 A. S. Batsanov, P. A. Eva, M. A. Fox, J. A. K. Howard, A. K. Hughes, A. L. Johnson, A. M. Martin and K. Wade, *J. Chem. Soc., Dalton Trans.*, 2000, 3519.

16 M. H. Chisholm, F. A. Cotton, M. Extine and B. R. Stults, *J. Am. Chem. Soc.*, 1976, **98**, 4477.

17 W. A. Nugent, *Inorg. Chem.*, 1983, **22**, 965; W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777.

18 A. K. Hughes and A. J. Kingsley, *J. Chem. Soc., Dalton Trans.*, 1997, 4139; U. Radius and J. Attner, *Eur. J. Inorg. Chem.*, 1999, 2221.

19 L. King, M. Motevalli and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1999, 3225.

20 D. M.-T. Chan, W. C. Fultz, W. A. Nugent, D. C. Roe and T. H. Tulip, *J. Am. Chem. Soc.*, 1985, **107**, 251.

21 J. Takacs and R. G. Cavell, *Inorg. Chem.*, 1994, **33**, 2635.

22 A. A. Danopoulos, G. Wilkinson, B. Hussain and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1989, 896.

23 A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 2753.

24 H. W. Lam, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1993, 781.

25 H.-T. Chiu, S.-H. Chuang, G.-H. Lee and S.-M. Peng, *Polyhedron*, 1994, **13**, 2443.

26 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.

27 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*; John Wiley and Sons, New York, 1988; W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; P. R. Sharp, *Comments Inorg. Chem.*, 1999, **21**, 85.

28 E. A. Maatta, Y. Du and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1990, 756; E. A. Maatta and Y. Du, *J. Am. Chem. Soc.*, 1988, **110**, 8249; D. M.-T. Chan, W. C. Fultz, W. A. Nugent, D. C. Roe and T. H. Tulip, *J. Am. Chem. Soc.*, 1985, **107**, 251.

29 M. Bakir, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1988, **27**, 2016; S. H. Han, G. L. Geoffroy, *Polyhedron*, 1988, **7**, 2331.

30 S. D. Gray, D. P. Smith, M. A. Bruck and D. E. Wigley, *J. Am. Chem. Soc.*, 1992, **114**, 5462; G. Perot, *Catal. Today*, 1991, **10**, 447.

31 I. Meisel, G. Hertel and K. Weiss, *J. Mol. Catal.*, 1986, **36**, 159; K. R. Birdwhistell, T. Boucher, M. Ensminger, S. Harris, M. Johnson and S. Toporek, *Organometallics*, 1993, **12**, 1023; K. R. Birdwhistell, J. Lanza and J. Pasos, *J. Organomet. Chem.*, 1999, **584**, 200.

32 K. E. Mayer, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1994, **116**, 2669; G. K. Cantrell and T. Y. Mayer, *Organometallics*, 1997, **16**, 5381; S.-H. Kim, N. Bowden and R. H. Grubbs, *J. Am. Chem. Soc.*, 1994, **116**, 10801; R. L. Zuckerman, S. W. Krska and R. G. Bergman, *J. Am. Chem. Soc.*, 2000, **122**, 751.

33 J. S. Murdzek and R. R. Schrock, *Organometallics*, 1987, **6**, 1373; R. R. Schrock, S. A. Krouse, K. Knoll, J. Feldman, J. S. Murdzek and D. C. Yang, *J. Mol. Catal.*, 1988, **46**, 243; C. C. Cummins, S. M. Baxter and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731; V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 2371.

34 P. L. McGrane, M. Jensen and T. Livinghouse, *J. Am. Chem. Soc.*, 1992, **114**, 5459; P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705; J. L. Bennett and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1994, **116**, 2179.

35 E. W. Harlan and R. H. Holm, *J. Am. Chem. Soc.*, 1990, **112**, 186; P. J. Walsh, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 1708.

36 P. J. Walsh, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8729; C. C. Cummins, S. M. Baxter and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731; C. C. Cummins, G. D. Van Duyne, C. P. Schaller and P. T. Wolczanski, *Organometallics*, 1991, **10**, 164; C. P. Schaller and P. T. Wolczanski, *Inorg. Chem.*, 1993, **32**, 131; P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705; J. de With and A. D. Horton, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 903; C. P. Schaller, J. B. Bonanno and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1994, **116**, 4133; R. E. Blake, D. M. Antonelli, L. M. Henling, W. P. Schaefer, K. I. Hardcastle and J. E. Bercaw, *Organometallics*, 1998, **17**, 718.

37 P. Barrie, T. A. Coffey, G. D. Forster and G. Hogarth, *J. Chem. Soc., Dalton Trans.*, 1999, 4519.

38 For M = Cr; ref. 19; M. C. W. Chan, F.-W. Lee, K.-K. Cheung and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1999, 3197.

39 For M = Mn; A. A. Danopoulos, G. Wilkinson, T. Sweet and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1993, 495; A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1994, 1037; A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1995, 205; A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1995, 937.

40 For M = Re; A. A. Danopoulos, G. Wilkinson and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 181; C. J. Longley, P. D. Savage, G. Wilkinson, B. Hussain and M. B. Hursthouse, *Polyhedron*, 1988, **7**, 1079; A. A. Danopoulos, G. Wilkinson, B. Hussain and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1989, 896; A. Gutierrez, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1990, **9**, 2081; V. Saboonchian, A. A. Danopoulos, A. Gutierrez, G. Wilkinson and D. J. Williams,

Polyhedron, 1991, **10**, 2241; H.-W. Lam, G. Wilkinson and D. J. Williams, *Polyhedron*, 1991, **10**, 2647.

41 For M = Os; W. A. Nugent, R. L. Harlow and R. J. McKinney, *J. Am. Chem. Soc.*, 1979, **101**, 7265; D. W. H. Rankin, H. E. Robertson, A. A. Danopoulos, P. D. Lyne, D. M. P. Mingos and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1563; J. A. Smieja, K. M. Omberg and G. L. Breneman, *Inorg. Chem.*, 1994, **33**, 614.

42 For M = Mo; ref. 37; B. L. Haymore, E. A. Maatta and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 1979, **101**, 2063; V. C. Gibson, E. L. Marshall, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4197; J. Sundermeyer, K. Weber, H. Werner, N. Mahr, G. Bringmann and O. Schupp, *J. Organomet. Chem.*, 1993, **444**, C37.

43 O. D. Sloan and P. Thornton, *Polyhedron*, 1988, **7**, 329; M. Minelli, M. R. Carson, D. W. Whisenhunt, W. Imhof and G. Huttner, *Inorg. Chem.*, 1990, **29**, 4801; W. A. Herrmann, D. W. Marz and E. Herdtweck, *Z. Naturforsch.*, *Teil B*, 1991, **46**, 747; M. Minelli, R. L. Kuhlman, S. J. Schaffer and M. Y. Chiang, *Inorg. Chem.*, 1992, **31**, 3891; S. D. Gray, D. P. Smith, M. A. Bruck and D. E. Wigley, *J. Am. Chem. Soc.*, 1992, **114**, 5462; M. T. Ahmet, B. Coutinho, J. R. Dilworth, J. R. Miller, S. J. Parrott, Y. Zheng, M. Harman, M. B. Hursthouse and A. Malik, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3041; F. Refosco, F. Tisato, A. Moresco and G. Bandoli, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3475; R. R. Schrock, S. W. Seidel, N. C. Moesch-Zanetti, D. A. Dobbs, K.-Y. Shih and W. M. Davis, *Organometallics*, 1997, **16**, 5195; T. I. Gountchev and T. D. Tilley, *J. Am. Chem. Soc.*, 1997, **119**, 12831.

44 E. W. Jandciu, P. Legzdins, W. S. McNeil, B. O. Patrick and K. M. Smith, *Chem. Commun.*, 2000, 1809.

45 W. A. Nugent, R. J. McKinney, R. V. Kasowski and F. A. Van-Catledge, *Inorg. Chim. Acta*, 1982, **65**, L91.

46 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.

47 D. L. Morrison and D. E. Wigley, *Inorg. Chem.*, 1995, **34**, 2610.

48 D. L. Morrison, P. M. Rodgers, Y.-W. Chao, M. A. Bruck, C. Grittini, T. L. Tajima, S. J. Alexander, A. L. Rheingold and D. E. Wigley, *Organometallics*, 1995, **14**, 2435.

49 Z. Lin and M. B. Hall, *Coord. Chem. Rev.*, 1993, **123**, 149; M. T. Benson, J. C. Bryan, A. K. Burrell and T. R. Cundari, *Inorg. Chem.*, 1995, **34**, 2348; K. A. Jørgensen, *Inorg. Chem.*, 1993, **32**, 1521.

50 P. Mountford, *Chem. Commun.*, 1997, 2127; S. C. Dunn, P. Mountford and D. A. Robson, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 293.

51 Y. W. Chao, P. M. Rodgers, D. E. Wigley, S. J. Alexander and A. L. Rheingold, *J. Am. Chem. Soc.*, 1991, **113**, 6326; D. L. Morrison and D. E. Wigley, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 79.

52 W. A. Herrmann, G. Weichselbaumer, R. A. Paciello, R. A. Fischer, E. Herdtweck, J. Okuda and D. W. Marz, *Organometallics*, 1990, **9**, 489; A. Gutierrez, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1990, **9**, 2081; A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1037.

53 J. Sundermeyer and D. Runge, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1255.

54 V. C. Gibson, C. Redshaw, W. Clegg, M. R. J. Elsegood, U. Siemeling and T. Türk, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4513.

55 Z. G. Lewis, D. Reed and A. J. Welch, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 731; U. Grädler, A. S. Weller, A. J. Welch and D. Reed, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 335.

56 D. E. Smith and A. J. Welch, *Organometallics*, 1986, **5**, 760.

57 F. Teixidor, S. Gómez, M. Lamrani, C. Viñas, R. Sillanpää and R. Kivekäs, *Organometallics*, 1997, **16**, 1278; S. Gómez, C. Viñas. M. Lamrani, F. Teixidor, R. Kivekäs and R. Sillanpää, *Inorg. Chem.*, 1997, **36**, 3565; M. Lamrani, S. Gómez, C. Viñas, F. Teixidor, R. Sillanpää and R. Kivekäs, *New J. Chem.*, 1996, **20**, 909.

58 J. Cowie, E. J. M. Hamilton, J. C. V. Laurie and A. J. Welch, *J. Organomet. Chem.*, 1990, **394**, 1.

59 H. Schulz, K. Folting, J. C. Huffman, W. E. Streib and M. H. Chisholm, *Inorg. Chem.*, 1993, **32**, 6056; M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar and B. R. Stults, *Inorg. Chem.*, 1977, **16**, 320; Z. Gebeyehu, F. Weller, B. Neumuller and K. Dehnick, *Z. Anorg. Allg. Chem.*, 1991, **593**, 99; K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas and M. B. Hursthouse, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 2088; R. H. Cayton, M. H. Chisholm, M. J. Hampden-Smith, J. C. Huffman and K. G. Moodley, *Polyhedron*, 1992, **11**, 3197; M. H. Chisholm, M. J. Hampden-Smith, J. C. Huffman, J. D. Martin, K. A. Stahl and K. G. Moodley, *Polyhedron*, 1988, **7**, 1991; R. L. Huff, S. Y. S. Wang, K. A. Abboud and J. M. Boncella, *Organometallics*, 1997, **16**, 1779; P. Legzdins, K. J. Ross, S. F. Sayers and S. J. Rettig, *Organometallics*, 1997, **16**, 190; M. H. Chisholm, J. C. Huffmann and R. L. Kelly, *Inorg. Chem.*, 1979, **18**, 3554; R. H. Cayton, S. T. Chacon, M. H. Chisholm, K. Folting and K. G. Moodley, *Organometallics*, 1996, **15**, 992; D. M. Berg and P. R. Sharp, *Inorg. Chem.*, 1987, **26**, 2959; M. H. Chisholm, I. P. Parkin, W. E. Streib and K. S. Folting, *Polyhedron*, 1991, **10**, 2309; S. W. Seidel, R. R. Schrock and W. M. Davis, *Organometallics*, 1998, **17**, 1058.

60 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

61 R. Vann Bynum, W. E. Hunter, R. D. Rogers and J. L. Atwood, *Inorg. Chem.*, 1980, **19**, 2368; G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4030; J. N. Christopher, G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4038; G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4045; G. M. Diamond, R. F. Jordan and J. L. Petersen, *J. Am. Chem. Soc.*, 1996, **118**, 8024; W. A. Herrmann, M. J. A. Morawietz and T. Priermeier, *J. Organomet. Chem.*, 1996, **506**, 351; A. Vogel, T. Priermeier and W. A. Herrmann, *J. Organomet. Chem.*, 1997, **527**, 297; J. N. Christopher, R. F. Jordan, J. L. Petersen and V. G. Young, *Organometallics*, 1997, **16**, 3044.

62 R. T. Baker, J. F. Whitney and S. S. Wreford, *Organometallics*, 1983, **2**, 1049; L. Weber, G. Meine, R. Boese and N. Augart, *Organometallics*, 1987, **6**, 2484; E. Hey-Hawkins and F. Lindenberg, *Organometallics*, 1994, **13**, 4643; T. L. Breen and D. W. Stephan, *Organometallics*, 1996, **15**, 4223.

63 M. P. Coles, C. I. Dalby, V. C. Gibson, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1995, **14**, 2455.

64 F.-E. Baumann, J. A. K. Howard, O. Johnson and F. G. A. Stone, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 2917.

65 S. A. Brew, D. D. Devore, P. D. Jenkins, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 393.

66 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 619.

67 J. I. Davies, J. F. Gibson, A. C. Skapski, G. Wilkinson and W.-K. Wong, *Polyhedron*, 1982, **1**, 641; A. Lehtonen and R. Sillanpää, *Polyhedron*, 1999, **18**, 175; V. M. Visciglio, P. E. Fanwick and I. P. Rothwell, *Inorg. Chim. Acta*, 1993, **211**, 203.

68 (*a*) A search of the October 2000 release of the Cambridge Structural Database reveals no examples of N–H···imido or O–H···imido hydrogen bonds; there are many examples of short C–H···imido contacts, reflecting the widespread use of imido ligands with bulky organic substituents; (*b*) F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 1; F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.

69 T. Steiner, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1331; G. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; S. N. Vinogradov and R. H. Linnell, *The Hydrogen Bond*, Van Nostrand Reinhold, New York, 1971, p. 177; G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, London, 1960, p. 289; A. L. Llamas Saiz and C. Foces-Foces, *J. Mol. Struct.*, 1990, **238**, 367.

70 F. H. Allen, J. A. K. Howard, V. J. Hoy, G. R. Desiraju, D. S. Reddy and C. K. Wilson, *J. Am. Chem. Soc.*, 1996, **118**, 4081; D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81.

71 U. Segerer, S. Blaurock, J. Sieler and E. Hey-Hawkins, *Organometallics*, 1999, **18**, 2838.

72 P. J. Walsh, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 1708; T. Straub, W. Frank, G. J. Reiss and M. S. Eisen, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2541.

73 R. I. Michelman, R. G. Bergman and R. A. Andersen, *Organometallics*, 1993, **12**, 2741.

74 SHELXTL-NT, Version 5.1, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.

75 Y. Le Page, *J. Appl. Crystallogr.*, 1987, **20**, 264; Y. Le Page, *J. Appl. Crystallogr.*, 1988, **21**, 983.