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Transition metal dicarbollide complexes: synthesis, molecular, crystal and electronic structures of $[M(C_2B_9H_{11})(NMe_2)_3]$ (M = Nb or Ta) and their insertion reactions with CO_2 and CS_2 †

Andrei S. Batsanov, Andrei V. Churakov, Judith A. K. Howard,* Andrew K. Hughes,* Andrew L. Johnson, Andrew J. Kingsley, Ivan S. Neretin and Ken Wade

Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE

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The homoleptic amides $[M(NMe_2)_5]$ (M = Nb **1** or Ta **2**; the latter is characterised by a structural study) reacted with the carborane *nido*-$C_2B_9H_{13}$ to eliminate two equivalents of $HNMe_2$ and generate the dicarbollide half-sandwich tris(dimethylamide) complexes $[M(C_2B_9H_{11})(NMe_2)_3]$ (M = Nb **3** or Ta **4**). The crystal structures of isomorphous **3** and **4** have been determined and reveal two NMe_2 ligands in a vertical orientation and the third one in a horizontal orientation with respect to the η^5-co-ordinated face of the $C_2B_9H_{11}$ ligand. The electronic factors responsible for the amide ligand orientations in these complexes are explored using qualitative MO arguments. Complexes **3** and **4** reacted with CO_2 and CS_2 to yield the tris(carbamate) $[M(C_2B_9H_{11})(O_2CNMe_2)_3]$ (M = Nb **5** or Ta **7**) and tris(dithiocarbamate) $[M(C_2B_9H_{11})(S_2CNMe_2)_3]$ (M = Nb **6** or Ta **8**) complexes, respectively. The crystal structures of **6** and **7** show two (dithio)carbamate ligands in horizontal and one in vertical orientation, demonstrating the similarity between the σ,π-donor frontier orbitals of the ligands NMe_2 and X_2CNMe_2 in **4** and **6** or **7** respectively.

Introduction

Group 3 and 4 metallocenes provide homogenous mechanistic models for the initiation, propagation and termination steps of the polymerisation of α-olefins.[1] Catalysis requires a metal complex which formally can offer two vacant co-ordination sites and does not provide strong back bonding to an incoming olefin substrate. These requirements were initially met by the 14 electron complexes d^0 Cp_2MR^+ (M = Group 4 element) or Cp_2MR (M = Group 3 element), although it has been shown that co-ordinatively and electronically unsaturated complexes with d^n ($n \neq 0$) electron counts can provide very active polymerisation catalysts.[2,3] Many research groups are exploring the synthesis of isonumeral or isovalence-electronic species generated by replacing the $(\eta\text{-}C_5H_5)M$ unit (M = Group 4 metal) by other combinations of ligand and metal which provide the same overall electron count.[4–7] In many of these complexes the carbon atoms of the η-C_5H_5 ligand have been replaced by more- or less-electronegative atoms. Ligands designed around nitrogen are numerous, a consequence of both the well established co-ordination chemistry of nitrogen, and the ease of ligand synthesis as a result of the well established organic chemistry of nitrogen. Although such metallocene analogues are designed to be isonumeral with metallocenes, the variation in polymerisation activity in such catalysts is undoubtedly in part a function of the energies of the frontier orbitals.

The dicarbollide ligand can be isolated as neutral *nido*-$C_2B_9H_{13}$ or as salts of the $[nido\text{-}C_2B_9H_{12}]^-$ or $[nido\text{-}C_2B_9H_{11}]^{2-}$ ions, and is prepared by the base-induced removal of a BH vertex from *ortho*-carborane [1,2-dicarba-*closo*-dodecaborane(12)], *closo*-$C_2B_{10}H_{12}$. The co-ordination chemistry of this ligand with middle and late transition metals has been established by a number of research groups,[8] and recently this ligand has been applied to lanthanide[9] and early transition metal chemistry in pursuit of metallocene analogues.[10] The $C_2B_9H_{11}$ ligand is a 4 electron LX_2 ligand[11] (in the neutral ligand formalism) and thus the fragment $[Ta(C_2B_9H_{11})]$ is isonumeral with $[Hf(\eta\text{-}C_5H_5)]$. Many similar ligands derived from smaller carboranes are also known and have been used for a wide range of transition metals.[12] Jordan and co-workers[13] have described the synthesis of $[Ta(C_2B_9H_{11})Cl_3]$ and compounds derived from this by substitution of the chloride ligands. Metal amides have also found use in the synthesis of metal complexes of silaboranes.[14]

In common with many other areas of organometallic chemistry, the most extensively used method for co-ordinating $C_2B_9H_{11}$ to a transition metal has been the elimination of halide salt between a metal halide and either an alkali-metal or thallium salt of $[nido\text{-}C_2B_9H_{11}]^{2-}$. In recent years the amine elimination reaction[15] has found use as a novel method for co-ordinating ligands,[16] occasionally providing routes to otherwise inaccessible compounds[17] or thermodynamic product ratios.[18]

In this work we present the synthesis of Group 5 complexes containing the dicarbollide ligand in combination with π-donor NMe_2 ligands. The structural characterisation of the complexes reveals an unusual arrangement of NMe_2 ligands which is rationalised in terms of qualitative MO arguments. Our observations also draw attention to the metal-based π-acceptor orbital orientation preferences which can be detected in $M(NR_2)_3$ complexes, but which may be masked in complexes where the amide ligands are part of a chelate system.[19]

Results and discussion

The neutral carborane *nido*-$C_2B_9H_{13}$ is a dibasic acid, thermodynamically capable of reaction with metal amides, $M(NR_2)_n$,[20] or alkyls, MR_n,[21] to liberate amine or alkane and generate metal–dicarbollide complexes. Toluene solutions of the Group 5 homoleptic amides $[M(NMe_2)_5]$ (M = Nb **1** or Ta **2**) react with 1 equivalent of *nido*-$C_2B_9H_{13}$ to cleave two metal–amide bonds (Scheme 1) and give $[M(C_2B_9H_{11})(NMe_2)_3]$ (M = Nb **3** or Ta **4**) as yellow crystalline solids in high yields. The dicarbollide complexes **3** and **4**, characterised by X-ray diffraction studies and NMR (^1H, ^{13}C and ^{11}B) spectroscopy, are considerably less

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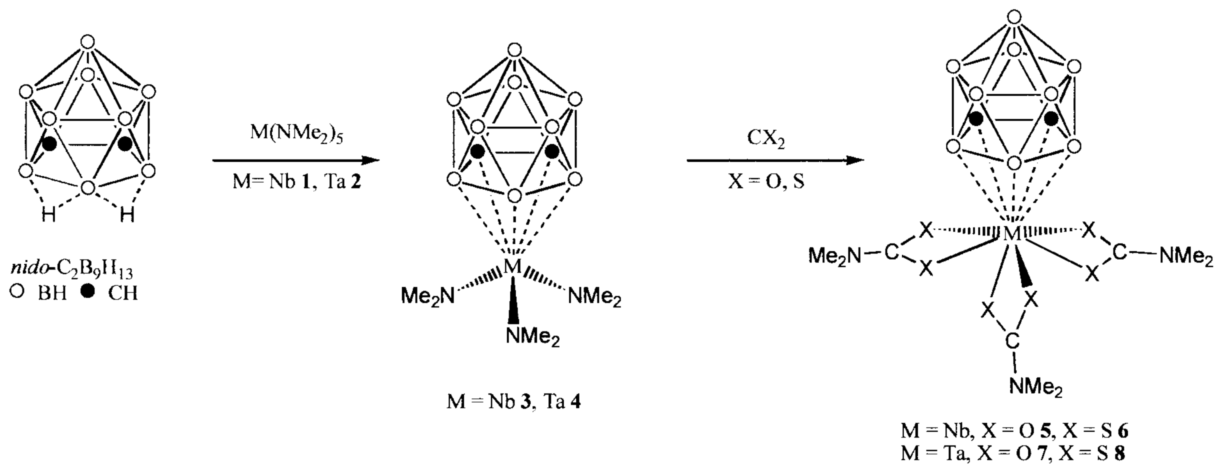
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3867/



Scheme 1 The syntheses of complexes **3** to **8**.

reactive towards atmospheric moisture than the parent homoleptic amides, and slowly turn white on exposure to atmospheric moisture. The ^{11}B NMR spectra of **3** and **4** show signals characteristic of a $[(C_2B_9H_{11})M]$ fragment; both the ^1H and ^{13}C NMR display only a single resonance for all the NMe_2 methyl groups and the ^1H NMR spectrum of **4** in CD_2Cl_2 at −90 °C is identical to the room temperature spectrum (apart from some small changes in chemical shift for the BH resonances). The solid-state structures of **3** and **4** (see below) show two different NMe_2 ligands which would give rise to three environments for the NMe groups and would suggest three resonances of equal intensity. Given the small chemical shift range expected for such resonances, and the likelihood that rotation about the M–N bond is facile, it seems likely that the NMe_2 resonances are in fast exchange even at −90 °C. Isoelectronic complexes containing a $M(NR_2)_3$ fragment with NR_2 ligands apparently in fast exchange include $[M(NCMe_3)(NMe_2)_3]$ (M = Nb or Ta),[22] $[Ti(\eta\text{-}C_5Me_5)(NR_2)_3]$ (R = Me or Et),[23] and $[Nb(2,6\text{-}^iPr_2C_6H_3N)(NMe_2)_3]$.[24] By contrast, the amide ligand rotation in $[M_2(NR_2)_6]$ (M = Mo or W; R = Me or Et) can be frozen out at low temperature and the barrier to rotation has been determined.[25]

The prototypical reactions of early transition metal M–NR_2 bonds are the insertion of polar multiple bonds into the M–N bond,[26] and cleavage of the M–N bond by Brønsted acids.[15] In this paper we explore the insertion reactions of $[M(C_2B_9H_{11})(NMe_2)_3]$ with CO_2 and CS_2 leading to carbamate and dithiocarbamate ligands; the reactions with acids (alcohols, phenols, thiols and nitriles) will appear elsewhere.[27]

The dicarbollide amide complexes $[M(C_2B_9H_{11})(NMe_2)_3]$ react with CO_2 and CS_2 to give carbamate $[M(C_2B_9H_{11})(O_2CNMe_2)_3]$ (M = Nb **5** or Ta **7**) and dithiocarbamate $[M(C_2B_9H_{11})(S_2CNMe_2)_3]$ (M = Nb **6** or Ta **8**) complexes respectively. All the complexes have been characterised by multinuclear NMR (^1H, ^{13}C and ^{11}B) and IR spectroscopy. The structures of **6** and **7** have been determined by single-crystal X-ray diffraction. The ^{11}B NMR spectra of complexes **5**–**8** display resonances characteristic of a $[(nido\text{-}C_2B_9H_{11})M]$ fragment. The ^{13}C spectra display two resonances for the (thio)carbamate carbon atom ($X_2\mathit{C}NMe_2$) in an approximate intensity ratio of 2:1, consistent with inequivalent ligands, and the ^1H and ^{13}C spectra each display a total of 4 closely spaced NMe resonances in a 2:2:1:1 ratio indicating four different environments for NMe_2 methyl groups, although in the spectra of some of the compounds the resonances are overlapped. These spectroscopic results are consistent with the presence of “vertical” and “horizontal” X_2CNMe_2 ligands in these complexes, as observed in the solid state structures (see below), and with rotation about the metal–(thio)carbamate axis being slow on the NMR timescale at room temperature, by contrast with the fast rotation of the NMe_2 ligands in **3** and **4**. Qualitative variable temperature ^1H NMR experiments have been performed on compound **7**. The 1:1:2:2 ratio of four closely spaced NMe resonances observed at ambient temperature becomes three peaks in a 1:1:4 ratio above 30 °C and finally a single resonance at 60 °C. These spectra are qualitatively similar to those observed for the isonumeral Group 4 cyclopentadienyl complexes $[M(\eta\text{-}C_5R_5)(X_2CNR_2)_3]$,[28] and we assume that the same mechanisms of ligand fluxionality apply.

In the course of the present work we obtained some good quality crystals of the starting homoleptic amide $[Ta(NMe_2)_5]$ **2** and studied its crystal structure for comparison, since the earlier structure determination of the niobium analogue, $[Nb(NMe_2)_5]$ **1**, had been carried out with a limited precision (using a manual diffractometer) and reported only in a preliminary communication without the atomic coordinates.[29] The gas-phase structure of $[Ta(NMe_2)_5]$ has been determined by electron diffraction.[30]

Crystal and molecular structures

The diffraction pattern of $[Ta(NMe_2)_5]$ **2** suggested unequivocally a *C*-centred orthorhombic lattice, and the structure was successfully solved in space group *Cmcm.* The molecule lies across a special position *m*2*m* (*c*), but only the Ta and N(1) atoms lie on the twofold axis. All other atoms are disordered over two positions, symmetrically related *via* mirror planes (see Fig. 1). The only combination of these positions which does not involve unrealistically short intramolecular contacts is shown in Fig. 1(a). According to the generalised topological analysis,[31] the Ta atom co-ordination shows almost equal degrees of distortion (11.2 and 10.4% respectively) from a square pyramid with the N(1) atom apical and a trigonal bipyramid with the N(2) and N(2′) axial. However, the square-pyramidal representation agrees better with the Ta–N(1) distance being considerably shorter than the rest (see Table 1).

The plane of the $N(1)Me_2$ ligand nearly bisects the N(2)–Ta–N(3) angle, while the four basal NMe_2 ligands are twisted all in the same sense, in a propeller-like fashion. The other set of positions of the disordered atoms corresponds to the enantiomer of compound **2**, with the opposite sense of the propeller twist. No such disorder was reported for the structure of **1**, solved ($R = 0.09$) in the space group *Pbcn* (no. 60) with the molecule on a twofold axis. It is noteworthy that the *primitive* unit cell of **1** has practically the same dimensions [$a = 13.84(1)$, $b = 8.19(1)$, $c = 14.48(1)$ Å at room temperature] as the *C*-centred cell of **2**, and that the diffraction experiment on **1** (using Cu-Kα radiation) gave surprisingly few observed reflections, 57% for the sphere of $2\theta_{max} = 120°$.

The geometry reported here for compound **2** in the solid

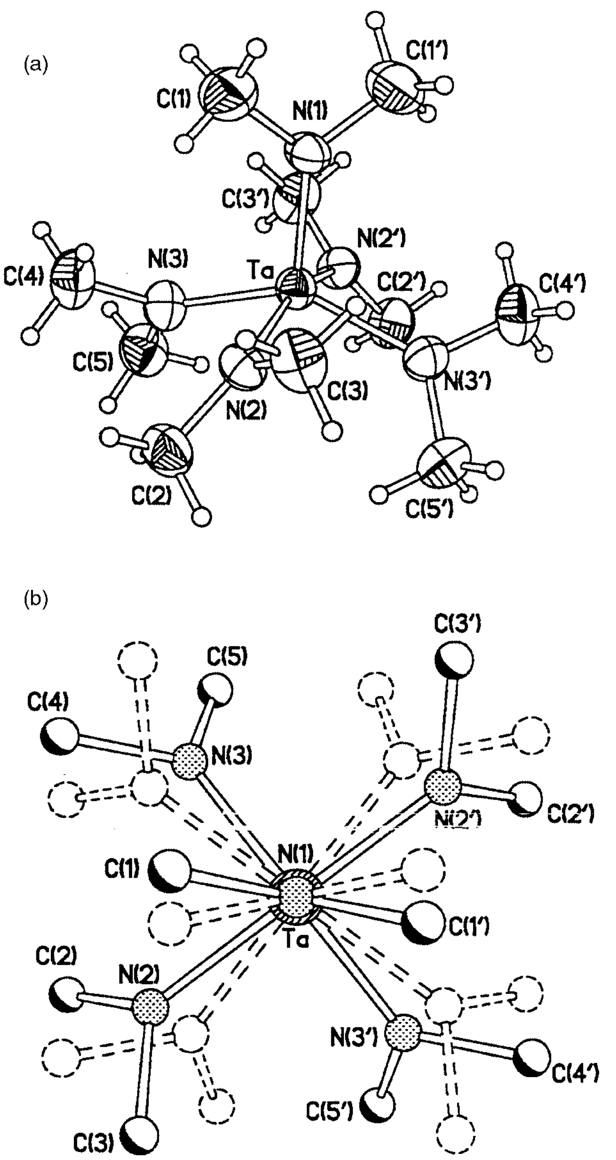


Fig. 1 Molecular structure of $[Ta(NMe_2)_5]$ **2**, showing 50% displacement ellipsoids (a) and the overlap of two enantiomers sharing the same crystallographic site (b; H atoms are omitted). Primed atoms are symmetry-related *via* a twofold axis.

state closely resembles the square pyramidal geometry reported for the gas-phase structure.[30] The gas-phase structure is necessarily constrained to have higher symmetry, and in particular places the four nitrogen atoms which define the square plane in strict co-planarity, with only one N_{apex}–Ta–N_{base} angle of 116.2(12)°. The gas-phase structure also observed one short and four longer Ta–N bonds; this observation, together with the apparent 20 electron count of the molecule, has been explained by the symmetries of the ligand σ- and π-donor orbitals and available metal orbitals.[30]

The dicarbollide amide complexes $[M(C_2B_9H_{11})(NMe_2)_3]$ (M = Nb **3** or Ta **4**) form isostructural crystals of the space group $P2_12_12_1$. The asymmetric unit comprises two molecules, A and B, with similar geometry (see Fig. 2 and Table 2). In either case, the metal atom is co-ordinated by the open C_2B_3 face of the dicarbollide ligand (in a nearly symmetrical η^5 fashion) and by three dimethylamide ligands. Here too, all the NMe_2 ligands display planar trigonal bonding of the nitrogen atoms, compatible with them acting as 3-electron LX ligands. Together with the 4-electron (or LX_2) dicarbollide ligand, this completes an 18 electron ML_4X_5 configuration of the Nb or Ta atom (see below).

A carborane cage is likely to be disordered in the solid state (with C and B positions statistically mixed), unless pinned down by substituents or by hydrogen bonds (in which C–H but not B–H groups can act as donors).[32] Although the dicarbollide ligand in **3** or **4** carries no substituents and can form no hydrogen bonds, lacking any suitable acceptor (sp^2 N atom, unlike sp^3 one, is quite inactive in this respect), it is certainly ordered. The heights of the electron density peaks, bond distances within the cage and to the hydrogen atoms all leave no doubt as to the location of the carbon atoms C(2) and C(3).

The most notable feature of both complexes is the orientation of the NMe_2 ligands with respect to the η^5-C_2B_3 face of the dicarbollide ligand. If the vector linking the centroid Cb of this face to the metal atom is coplanar with the NMe_2 ligand (*i.e.* the Cb–M–N–C torsion angle, τ, is 0 or 180°), this orientation can be described as 'vertical', and the orientation perpendicular to the latter (τ = 90°) as 'horizontal'. In **3** and **4** the

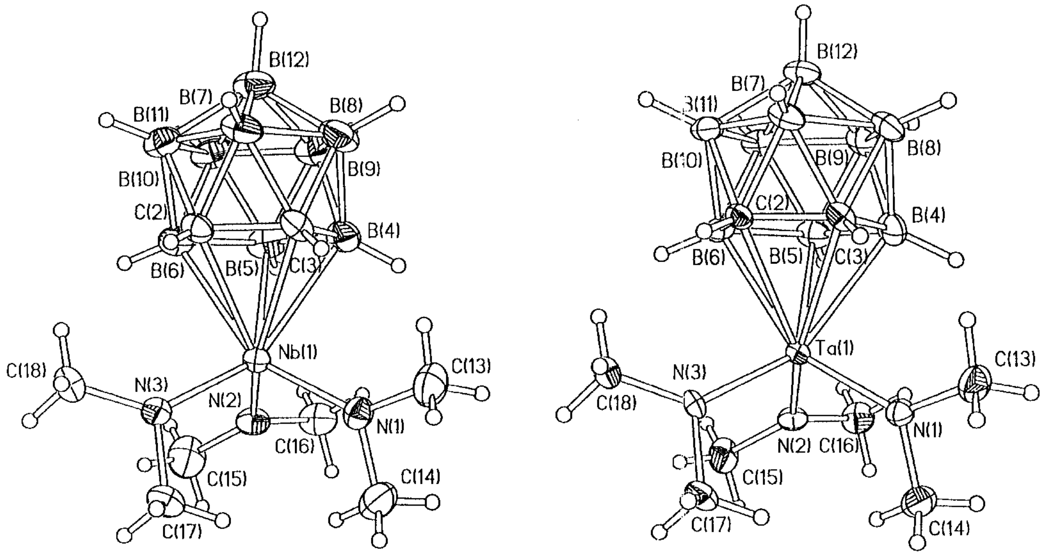
Table 1 Selected bond distances (Å), bond and torsion angles (°) in the solid state and gas-phase structures of $[M(NMe_2)_5]$

	2 (M = Ta)		
	solid (this work)	gas phase[30]	**1** (M = Nb) solid state[29]
M–N(1)	1.965(5)	1.937(25)	1.977(17)
M–N(2)	2.023(9)	2.040(6)	2.040(15)
M–N(3)	2.038(8)	2.040(6)	2.044(14)
N(1)–M–N(2)	101.1(3)	116.2(12)	101.5(4)
N(1)–M–N(3)	109.1(3)	116.2(12)	109.1(4)
N(2)–M–N(3)	85.9(3)	87.8(36)	86.1(6)
N(2)–M–N(3′)	86.9(5)	69.4(31)	87.3(6)
N(2)–M–N(2′)	157.8(5)	127.6(24)	
N(3)–M–N(3′)	141.8(5)	127.6(24)	
N(1)–M–N(2)–C(2)	142(1)	169(27)	
N(1)–M–N(3)–C(5)	139(1)	169(27)	
C(1)–N(1)–M–N(2)	−49(1)		

Table 2 Selected bond distances (Å), bond and torsion angles (°) in compounds **3** and **4**, molecules A and B

	3 (M = Nb)		**4** (M = Ta)	
	A	B	A	B
M–N(1)	2.000(3)	1.994(4)	1.987(5)	1.981(5)
M–N(2)	1.958(4)	1.955(3)	1.949(4)	1.955(4)
M–N(3)	1.980(3)	1.992(3)	1.980(4)	1.987(5)
M–C(2)	2.496(4)	2.482(4)	2.490(5)	2.480(5)
M–C(3)	2.510(4)	2.475(4)	2.501(5)	2.470(5)
M–B(4)	2.484(4)	2.465(4)	2.489(6)	2.444(6)
M–B(5)	2.485(5)	2.493(4)	2.470(7)	2.478(6)
M–B(6)	2.460(5)	2.471(4)	2.453(6)	2.475(5)
M–Cb	2.019(4)	2.029(5)	2.019(6)	2.003(6)
C(2)–C(3)	1.577(6)	1.558(6)	1.576(7)	1.570(7)
C(3)–B(4)	1.661(6)	1.692(7)	1.685(9)	1.699(9)
B(4)–B(5)	1.773(7)	1.764(6)	1.779(9)	1.769(9)
B(5)–B(6)	1.762(7)	1.756(7)	1.756(9)	1.771(8)
B(6)–C(2)	1.682(7)	1.671(6)	1.681(9)	1.686(8)
Cb–M–N(1)	115.8(2)	114.8(2)	116.4(2)	114.6(2)
Cb–M–N(2)	123.8(2)	121.4(2)	124.4(2)	122.0(2)
Cb–M–N(3)	114.6(2)	114.5(2)	114.4(2)	115.1(2)
N(1)–M–N(2)	96.6(1)	95.8(2)	96.0(2)	95.9(2)
N(2)–M–N(3)	95.6(1)	97.0(2)	95.9(2)	96.9(2)
N(1)–M–N(3)	107.3(2)	110.8(2)	106.4(2)	109.7(2)
Cb–M–N(1)–C(14)	−160.4(6)	−169.7(6)	−160.0(5)	−167.0(5)
Cb–M–N(2)–C(15)	−99.1(6)	76.1(6)	−100.0(5)	74.7(5)
Cb–M–N(2)–C(16)	68.1(6)	−81.3(6)	66.9(5)	−83.7(5)
Cb–M–N(3)–C(17)	−158.2(6)	−167.2(6)	−157.5(5)	−165.8(5)
N(2)–M–Cb–B(5)	−9.7(6)	−5.1(6)	−10.7(5)	−6.4(5)
N(2)–M–Cb–X	170.4(6)	175.2(6)	169.0(5)	173.5(5)

Cb = Centroid of the η^5-co-ordinated C_2B_3 ring; X = midpoint of the C(2)–C(3) bond.



3 **4**

Fig. 2 Molecular structures of [Nb(C$_2$B$_9$H$_{11}$)(NMe$_2$)$_3$] **3** and [Ta(C$_2$B$_9$H$_{11}$)(NMe$_2$)$_3$] **4**, showing independent molecules A in 50% displacement ellipsoids.

N(1)Me$_2$ and N(3)Me$_2$ ligands are 'vertical' while the N(2)Me$_2$ ligand is 'horizontal' (see Table 2). In each molecule the 'horizontal' ligand lies opposite to the C(2)–C(3) bond and forms a M–N bond appreciably shorter than the 'vertical' ligands, by 0.035 (10σ) in **3** and 0.032 Å (7σ) in **4**. However, both vertical and horizontal orientations are only approximate descriptions and the ligands are somewhat inclined, all in the same direction, thus adopting a chiral, propeller-like conformation.

Orientational preferences of dicarbollide ligands with respect to the other ligands are well established, often described as a strong *trans* influence of the dicarbollide ligand, and have been observed in indenyl,[33,34] pyrrolyl[35] and carbonyl[36] complexes. The origin of the orientational preference is the non-degeneracy of the π-frontier MOs of the C$_2$B$_9$H$_{11}$ ligand.[34] Other Group 5 complexes which display two "vertical" one "horizontal" arrangements of amide ligands include [Ta{(Cy-N)$_2$C(NCy)}(NMe$_2$)$_3$][37] and [Nb(2,6-^{i}Pr$_2$C$_6$H$_3$N)(NMe$_2$)$_3$].[24]

In either structure, molecule A differs from B by a small rotation around the M–Cb axis (4–5°) and the M–N bonds; they can be fitted to each other (see Fig. 3a) with an average discrepancy of 0.14 Å for all non-hydrogen atoms, or only 0.06 Å if methyl carbons are excluded. At the same time molecules A and B in the crystal are related by pseudo-symmetry, corresponding approximately to the space group *Pbca*. Thus, bringing these molecules together by symmetry transformations of this space group gives an imperfect overlap, as shown in Fig. 3b. The difference between the positions of pseudo-equivalent atoms (bearing the same numbers in both structures) averages 0.4 (**3**) or 0.5 Å (**4**) for all non-hydrogen atoms, but for the metal atoms the discrepancy is much smaller (0.15 in **3**, 0.23 Å in **4**). Note that the twisted orientation of NMe$_2$ ligands (see above) gives the molecule a conformational chirality; its sense is the *same* in molecules A and B which would be *inversion* equivalents in *Pbca*. This contradiction can be the source of the pseudo-symmetry.

This pseudo-symmetry is manifest in the X-ray diffraction data. The $\langle E^2 - 1\rangle$ averages of 0.961 (**3**) and 0.872 (**4**) are much closer to the expected value for a centrosymmetric structure (0.968) than for a non-centrosymmetric one (0.736). Reflections $hk0$, $h0l$ and $0kl$ with odd h, l and k, respectively (that would be systematically absent in *Pbca*), are weaker than the average intensity by a factor of 9 in compound **3** or 4.4 in **4**. The near-centrosymmetric positions of Nb or Ta atoms largely neutralise their anomalous scattering. Thus the Flack parameter[38] (expected to be 0 if the absolute configuration is correct and 1 if it is inverted) refined to 0.48(5) in **3** and 0.485(12) in **4**. Both structures gave Patterson maps characteristic of *Pbca* and could be solved in this space group to the correct chemical connectivity, but the refinement gave irreducible R of 0.15–0.16, high residual electron density and inconsistent anisotropic displacement parameters for most atoms.

The molecules of [Nb(C$_2$B$_9$H$_{11}$)(S$_2$CNMe$_2$)$_3$] **6** and [Ta(C$_2$B$_9$H$_{11}$)(O$_2$CNMe$_2$)$_3$] **7** are isostructural (Fig. 4, Table 3) and bear significant similarities to those of **3** and **4** and to the isonumeral M(η-C$_5$H$_5$) complexes [M(η-C$_5$H$_5$)(S$_2$CNMe$_2$)$_3$] (M = Ti[39] or Zr[40]) and [(4-MeC$_6$H$_4$N)Nb(S$_2$CNEt$_2$)$_3$].[41] Each (thio)carbamate ligand is essentially planar and co-ordinated in a slightly asymmetric bidentate fashion, the asymmetry of M–X distances being stronger in **7** than in **6** (average 0.08 *vs.* 0.03 Å). Here, too, the carbon atom positions in the dicarbollide cage are clearly identified. The (thio)carbamate ligand containing N(1) adopts a vertical orientation ($\tau \approx 180°$) and those containing N(2) and N(3) are close to horizontal ($\tau \approx 90°$). The vertical (thio)carbamate ligand lies in a position exactly *trans* to C(3). Thus the molecule has a local mirror symmetry, violated only by the non-equivalence of C(2) and B(4). Alternatively the molecule can be described as having a pentagonal bipyramid geometry, with five of the (thio)carbamate chalcogen atoms defining the plane and the axial positions occupied by the sixth chalcogen atom and the dicarbollide centroid. The M–X bonds to the vertical (thio)carbamate ligand are shorter than to the horizontal ones (on average, by 0.03 Å in **6** and 0.04 Å in **7**), notwithstanding the more sterically hindered position of the former (evident from the angular distortions). The dicarbollide ligand in **6** lies *ca.* 0.04 Å closer to the metal atom than in **7** (*cf.* in **3** the dicarbollide ligand lies 0.01 Å further away from the metal than in **4**); this effect is explicable by the smaller size and higher electronegativity of the oxygen compared to sulfur atoms.

π Bonding in [M(C$_2$B$_9$H$_{11}$)(NMe$_2$)$_3$] complexes

In the MLXZ nomenclature of Green,[11] the dicarbollide ligand (C$_2$B$_9$H$_{11}$) is a 4 electron LX$_2$ ligand, and the NMe$_2$ ligand is a 3 electron LX ligand, so that the apparent electron count for [M(C$_2$B$_9$H$_{11}$)(NMe$_2$)$_3$] (M = Nb or Ta) is 18, ML$_4$X$_5$. It is well established[42] that the C$_2$B$_9$H$_{11}$ ligand has three frontier orbitals, one of σ and two of π symmetry with respect to ligand–metal bonding, and is thus classified by Gibson[43] as a Π$_2$ ligand; other

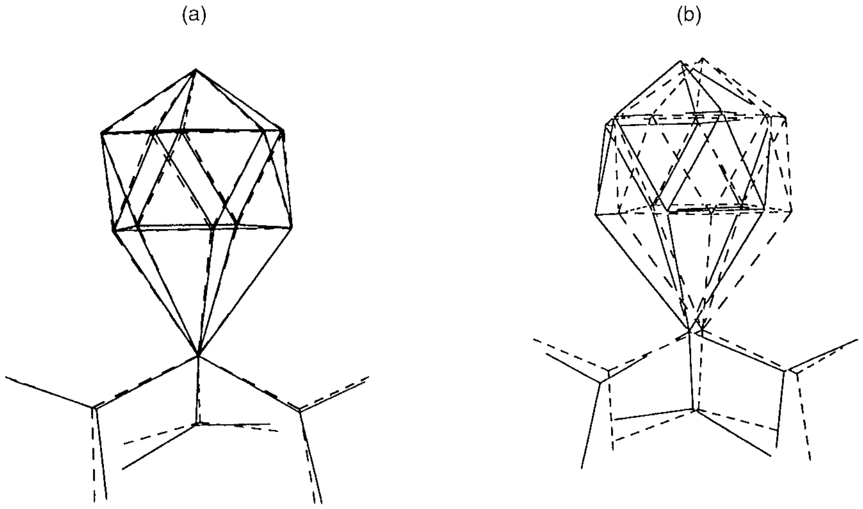
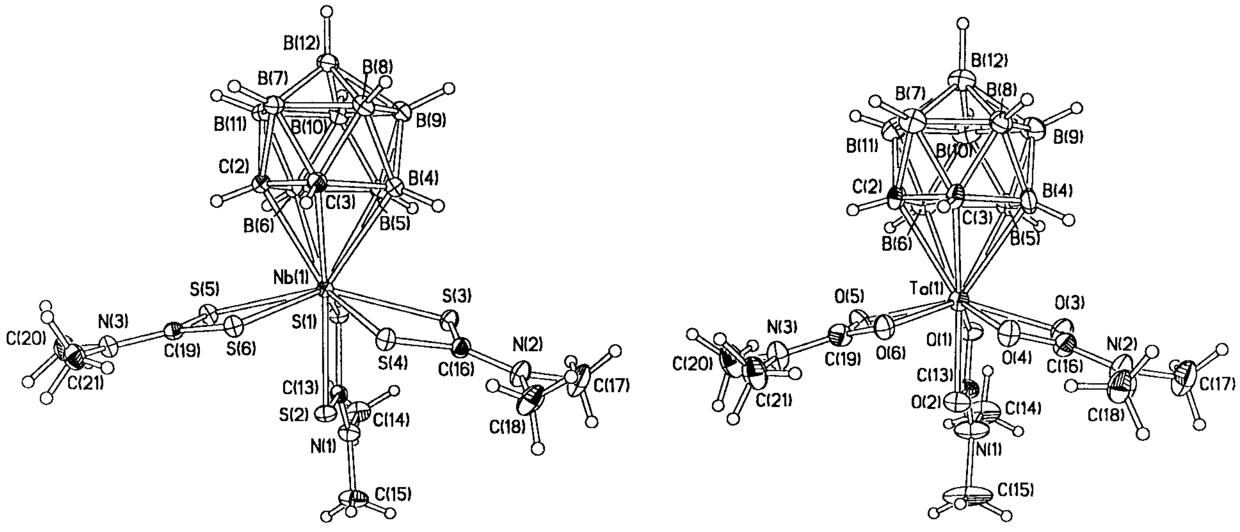


Fig. 3 Comparison of molecules A (solid) and B (dashed) in the structure of compound **4**: (a) best fit between molecular geometries, (b) molecules brought together by the pseudo-symmetry operation $x + \frac{1}{2}, 1 - y, z$.



6

7

Fig. 4 Molecular structures of $[Nb(C_2B_9H_{11})(S_2CNMe_2)_3]$ **6** and $[Ta(C_2B_9H_{11})(O_2CNMe_2)_3]$ **7**.

Table 3 Selected bond lengths (Å), bond and torsion angles (°) in compounds **6** and **7**

	6	7		6	7
M–X(1)	2.573(1)	2.091(3)	X(1)–C(13)	1.723(2)	1.292(6)
M–X(2)	2.609(1)	2.156(4)	X(2)–C(13)	1.713(2)	1.294(6)
M–X(3)	2.629(1)	2.205(3)	X(3)–C(16)	1.704(2)	1.280(6)
M–X(4)	2.612(1)	2.106(3)	X(4)–C(16)	1.724(2)	1.292(6)
M–X(5)	2.642(1)	2.208(3)	X(5)–C(19)	1.709(2)	1.282(6)
M–X(6)	2.615(1)	2.121(3)	X(6)–C(19)	1.724(2)	1.296(6)
M–C(2)	2.484(2)	2.462(5)	C(2)–C(3)	1.584(2)	1.590(6)
M–C(3)	2.514(2)	2.486(5)	C(3)–B(4)	1.674(2)	1.676(7)
M–B(4)	2.544(2)	2.519(6)	B(4)–B(5)	1.784(2)	1.780(9)
M–B(5)	2.567(2)	2.508(6)	B(5)–B(6)	1.777(2)	1.768(8)
M–B(6)	2.506(2)	2.464(6)	B(6)–C(2)	1.685(2)	1.657(7)
M–Cb	2.067(2)	2.028(6)			
Cb–M···C(13)	137.1(1)	140.2(4)	C(13)···M···C(16)	86.5(1)	88.9(2)
Cb–M···C(16)	108.7(1)	108.0(4)	C(13)···M···C(19)	91.7(1)	89.3(2)
Cb–M···C(19)	107.4(1)	107.7(4)	C(16)···M···C(19)	127.9(1)	125.0(2)
Cb–M···C(13)–X(3)	178.5	−179.6	C(3)–Cb–M···C(13)	−179.3	−177.8
Cb–M···C(16)–X(2)	−83.1	−88.2	Cb–M···C(19)–X(5)	89.0	86.7

For **6**, M = Nb(1), X = S; for **7**, M = Ta(1), X = O; Cb = centroid of the η^5-co-ordinated C_2B_3 ring.

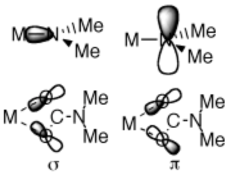


Fig. 5 The frontier orbitals of the NMe_2 and O_2CNMe_2 ligands, emphasising the orientation of the σ and π donor orbitals.

familiar examples of this class of ligand are the five electron L_2X cyclopentadienyl (η-C_5H_5), 4 electron LX_2 imido, RN, ligands, and 3 electron X_3 ligands such as nitride (N). Since the dicarbollide and imido ligands are both LX_2 ligands, the complexes $[M(C_2B_9H_{11})(NMe_2)_3]$ are isonumeral with the imido complexes $[Nb(2,6\text{-}{}^iPr_2C_6H_3N)(NMe_2)_3]$[24] and $[Ta(NCMe_3)(NMe_2)_3]$.[22] The arylimido complex has the same structural features as the dicarbollide complex, with two vertical and one horizontal NMe_2 ligands; by contrast the alkylimido complex has a crystallographically imposed threefold propeller geometry, with three almost vertical NMe_2 ligands.

Since the most significant feature of $[M(C_2B_9H_{11})(NMe_2)_3]$ is the presence of an amide ligand with $\tau \approx 90°$ we have carried out extended Hückel molecular orbital calculations to explore the significance of this in the context of the π bonding of this, and other, $[M(\Pi_2)(NMe_2)_3]$ molecules. The full details of the calculations will be presented elsewhere,[44] but we conclude that the non-degeneracy of the π-donor orbitals of $C_2B_9H_{11}$ and the aryl imide $2,6\text{-}{}^iPr_2C_6H_3N$ is responsible for the observed structures of $[M(C_2B_9H_{11})(NMe_2)_3]$ and $[Nb(2,6\text{-}{}^iPr_2C_6H_3N)(NMe_2)_3]$.

The dimethylamide (NMe_2) and carbamate or dithiocarbamate (X_2CNMe_2) ligands each offer a metal atom one frontier orbital that has metal–ligand σ symmetry and one which has metal–ligand π symmetry, Fig. 5. The frontier orbitals of the (dithio)carbamate are based on the in-plane oxygen or sulfur p orbitals, the out-of-plane orbitals will be used in X_2CN π bonding. The orientational preferences of the two ligands can be expected to be similar, taking account of the fact that the π orbital of the NMe_2 ligand is perpendicular to the NC_2 plane, whilst for the (dithio)carbamate ligand the π orbital is contained within the plane of the planar ligand. The geometries of $[M(C_2B_9H_{11})(NMe_2)_3]$ and $[M(C_2B_9H_{11})(X_2CNMe_2)_3]$ are thus related, each having two ligand π orbitals perpendicular to the carborane centroid–metal axis, and one π orbital collinear with the centroid–metal axis.

In conclusion, we have demonstrated that the acidic carborane *nido*-$C_2B_9H_{13}$ reacts with the niobium and tantalum homoleptic dimethylamides to liberate two equivalents of dimethylamine and generate the three-legged piano-stool complexes $[M(C_2B_9H_{11})(NMe_2)_3]$. The dicarbollides in these complexes play the role of spectator ligands, such that familiar insertion reactions with CO_2 and CS_2 can be performed with the remaining three dimethylamide ligands, generating di(thio)carbamate ligands. Structural studies on a selection of these compounds indicate a marked orientational preference in the dicarbollide and dimethylamide ligands, with the C_2 unit of the dicarbollide *trans* to the unique NMe_2 or X_2CNMe_2 ligand, which can be accounted for by the non-equivalence of the frontier orbitals of the $C_2B_9H_{11}$ ligand. In subsequent publications we will report on the reaction of compounds **3** and **4** with alcohols, thiols and amines, and the synthesis of complexes containing metal–carbon σ bonds.

Experimental

Air sensitive compounds were manipulated under a nitrogen atmosphere using standard Schlenk and glove-box techniques. The NMR spectra were recorded on Varian Mercury-200 (^1H and ^{13}C) and Varian Unity-300 (^1H, ^{13}C and ^{11}B) instruments, all chemical shifts being reported in δ (ppm) with ^{11}B referenced externally to $BF_3 \cdot Et_2O$ (δ 0.0). Variable temperature ^1H NMR spectra were recorded on a Varian VX-400 spectrometer. Infrared spectra were run as hexachlorobutadiene mulls on a Perkin-Elmer 1615 FTIR spectrometer. Mass spectroscopy was undertaken on a VG Micromass 7070E instrument operating in EI mode; all samples display characteristic carborane isotopic patterns, and only the most abundant peak in each envelope is listed. Solvents were pre-dried and distilled from appropriate drying agents. Unless indicated otherwise all reagents were used as received. Literature methods were used for the preparation of *nido*-$C_2B_9H_{13}$,[45] $[Ta(NMe_2)_5]$[46] and $[Nb(NMe_2)_5]$.[47] Extended Hückel molecular orbital[48] calculations were performed using the packages EH and CACAO.[49] Bond lengths and angles were taken from the molecular structures determined by X-ray diffraction, and, where appropriate, idealised to provide the highest possible symmetry.

Preparations

$[Nb(C_2B_9H_{11})(NMe_2)_3]$ 3. A stirred toluene (50 cm^3) solution of $Nb(NMe_2)_5$ (0.94 g, 3 mmol) was treated dropwise at room temperature with a toluene (10 cm^3) solution of *nido*-$C_2B_9H_{13}$ (0.43 g, 3 mmol). The solution was stirred at room temperature for 12 h and slowly lightened from brown to orange. It was concentrated to 10 cm^3 under reduced pressure, leaving a yellow solid, which was isolated by filtration and washed with 10 cm^3 of pentane before drying under reduced pressure. Yield 0.93 g, 87%. ^1H NMR ($CDCl_3$): δ 3.54 (s, 18 H, 3 × NMe_2), 2.73 (br s, 2 H, carborane C–H). Additional resonances in $^1H\text{-}\{^{11}B\}$: δ 2.37 (1 H), 2.25 (3 H), 2.11 (2 H), 2.06 (1 H) and 1.90 (2 H). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 53.0 (carborane C) and 51.2 (NMe_2). ^{11}B NMR ($CDCl_3$): δ 3.3 (d, 1 B, $J_{B\text{-}H}$ 121), −2.9 (d, 2 B, $J_{B\text{-}H}$ 149), −5.1 (d, 2 B, $J_{B\text{-}H}$ 146), −13.2 (d, 3 B, $J_{B\text{-}H}$ 147) and −14.4 (d, 1 B, $J_{B\text{-}H}$ 112 Hz). Calc. for $C_8H_{29}B_9N_3Nb$: C, 26.88; H, 8.18; N, 11.75. Found: C, 27.4; H, 8.16; N, 10.90%. MS: *m/z* 358 $[M^+]$, 343 $[M - CH_3^+]$ and 225 $[M - C_2B_9H_{11}^+]$. IR: 2516s, 1444w, 1414w, 1230s, 1135w and 1032s cm^{-1}.

$[Ta(C_2B_9H_{11})(NMe_2)_3]$ 4. A stirred toluene (100 cm^3) solution of $Ta(NMe_2)_5$ (8.026 g, 20 mmol) was treated dropwise at room temperature with a toluene (50 cm^3) solution of *nido*-$C_2B_9H_{13}$ (2.68 g, 20 mmol). The solution was stirred at room temperature for 15 h and slowly changed from yellow to orange. It was concentrated to 20 cm^3 under reduced pressure, leaving a pale yellow solid, which was isolated by filtration and washed with 10 cm^3 of pentane before drying under reduced pressure. Yield 7.9 g, 89%. ^1H NMR ($CDCl_3$): δ 3.62 (s, 18 H, 3 × NMe_2) and 2.73 (br s, 2 H, carborane C–H). Additional resonances in $^1H\text{-}\{^{11}B\}$: δ 3.02 (1 H), 2.37 (1 H), 2.29 (2 H), 2.18 (2 H) and 1.62 (3 H). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 52.1 (carborane C) and 49.1 (NMe_2). ^{11}B NMR ($CDCl_3$): δ 1.7 (d, 1 B, $J_{B\text{-}H}$ 124), −3.4 (d, 2 B, $J_{B\text{-}H}$ 144), −5.7 (d, 2 B, $J_{B\text{-}H}$ 138), −13.8 (d, 3 B, $J_{B\text{-}H}$ 158) and −16.2 (d, 1 B, $J_{B\text{-}H}$ 158 Hz). Calc. for $C_8H_{29}B_9N_3Ta$: C, 21.56; H, 6.56; N, 9.43. Found: C, 21.14; H, 6.55; N, 8.71%. MS: *m/z* 446 $[M^+]$, 431 $[M - CH_3^+]$ and 313 $[M - C_2B_9H_{11}^+]$. IR: 2552vs, 1446s, 1420w, 1238s, 1124w and 1035s cm^{-1}.

$[Nb(C_2B_9H_{11})(O_2CNMe_2)_3]$ 5. A stream of CO_2 was passed through a toluene (20 cm^3) solution of compound **3** (0.357 g, 1 mmol) at room temperature. The yellow solution rapidly changed to pale green over a small amount of flocculent white precipitate; the gas flow was stopped when no further colour change was apparent. After stirring at room temperature for 2 h, the solution was filtered and the filtrate layered with pentane (10 cm^3) and allowed to stand at room temperature. After 2 d pale green micro crystals were isolated by filtration and washed with a small volume of pentane. Yield 0.19 g, 49%. ^1H NMR (C_6D_6): δ 3.7 (s, 2 H, carborane C–H), 2.01 (s, 3 H, NMe), 1.98 (s, 3 H, NMe) and 1.94 (s, 12H, NMe_2). Additional

Table 4 Crystal data for compounds **2**–**4**, **6** and **7**

	2	**3**	**4**	**6**	**7**
Formula	$C_{10}H_{30}N_5Ta$	$C_8H_{29}B_9N_3Nb$	$C_8H_{29}B_9N_3Ta$	$C_{11}H_{29}B_9N_3NbS_6{\cdot}CD_2Cl_2$	$C_{11}H_{29}B_9N_3O_6Ta{\cdot}\frac{1}{2}C_7H_8$
M	401.34	357.54	445.58	672.87	623.68
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	*Cmcm* (no. 63)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	13.845(3)	13.456(1)	13.484(1)	9.879(3)	12.297(2)
b/Å	7.900(2)	15.623(1)	15.472(1)	11.637(3)	17.424(3)
c/Å	14.544(3)	16.932(1)	17.042(1)	13.957(4)	13.308(3)
α/°				98.77(1)	
β/°				97.42(1)	111.34(5)
γ/°				113.04(1)	
U/Å^3	1590.8(6)	3559.6(4)	3555.4(4)	1427.5(7)	2656(1)
Z	4	8	8	2	4
μ(Mo-Kα)/cm^{-1}	69.0	6.7	61.7	10.6	41.7
Reflections measured	5601	28 901	29 543	17 790	17 271
Unique reflections	985	9689	9744	7477	6082
R_{int} [a]	0.132, 0.024	0.086, 0.035	0.115, 0.043	0.040, 0.029	0.122, 0.044
Reflections with $I \ge 2\sigma(I)$	979	7929	8789	6548	4715
$R\ [F^2 \ge 2\sigma(F^2)]$	0.027	0.036	0.028	0.022	0.033
$wR(F^2)$, all data	0.066	0.076	0.069	0.053	0.098

[a] Before and after the absorption correction.

peaks in ^{1}H-{^{11}B}: δ 4.12 (s, 1 H), 3.40 (s, 2 H), 3.21 (s, 2 H), 3.11 (s, 1 H), 2.87 (s, 2 H) and 2.80 (s, 1 H). ^{13}C-{^{1}H} NMR (C_6D_6): δ 171.2 (1 × O_2CN), 167.7 (2 × O_2CN), 73.1 (carborane C), 34.6, 34.2, 34.1, 34.0 (NMe). ^{11}B-{^{1}H} NMR (C_6D_6): δ 23.0 (1 B), 6.9 (2 B), 3.1 (3 B), −4.0 (1 B) and −7.4 (2 B). Calc. for $C_{11}H_{29}B_9N_3NbO_6{\cdot}0.45C_7H_8$: C, 32.00; H, 6.19. Found: C, 31.95; H, 6.50%. MS: *m*/*z* 446 [M$^+$ − NMe$_2$], 402 [M − O$_2$CNMe$_2$$^+$] and 357 [M − C$_2B_9H_{11}$$^+$]. IR: 2566s, 1632s, 1459s, 1416s, 1260w and 1093vw cm^{-1}.

[Nb($C_2B_9H_{11}$)(S_2CNMe_2)$_3$] 6. A stirred toluene (20 cm^3) solution of compound **3** (0.357 g, 1 mmol) was cooled to −78 °C and treated dropwise with CS$_2$ (0.228 g, 3 mmol). The yellow solution was allowed to warm to room temperature, giving an orange solution over a small amount of yellow precipitate. After stirring at room temperature for 16 h the solution was filtered and the volatiles were removed from the filtrate under reduced pressure. The residue was extracted with dichloromethane (15 cm^3) and the extract layered with toluene (10 cm^3) and cooled to −20 °C giving yellow crystals, which were isolated by filtration and washed with a small volume of toluene. Yield 0.307 g, 71%. ^{1}H NMR (CH_2Cl_2): δ 3.61 (s, 2 H, carborane C–H), 3.34 (s, 3 H, NMe), 3.25 (s, 3 H, NMe), 3.20 (s, 6 H, NMe$_2$) and 3.12 (s, 6 H, NMe$_2$). Additional peaks in ^{1}H-{^{11}B}: δ 2.83 (1 H), 2.35 (1 H), 2.21 (s, 2 H), 2.10 (s, 3 H) and 1.88 (s, 2 H). ^{13}C-{^{1}H} NMR (CH_2Cl_2): δ 207.5 (1 × NCS$_2$), 204.5 (2 × NCS$_2$), 66.6 (carborane C), 39.7, 39.0, 38.6, 36.9 (NMe). ^{11}B-{^{1}H} NMR (CH_2Cl_2): δ 16.2 (1 B), 0.9 (2 B), −3.1 (3 B), −12.4 (2 B) and −16.4 (1 B). Calc. for $C_{11}H_{29}B_9N_3NbS_6{\cdot}0.85C_7H_8$: C, 30.65; H, 5.43. Found: C, 30.65; H, 5.51%. MS: *m*/*z* 586 [M$^+$], 466 [M − S$_2$CMe$_2$$^+$] and 453 [M − C$_2B_9H_{11}$$^+$]. IR: 2533s, 1510vs, 1450s, 1392vs, 1257s, 1166s, 1096w and 1016vw cm^{-1}.

[Ta($C_2B_9H_{11}$)(O_2CNMe_2)$_3$] 7. A stream of CO$_2$ was passed through a toluene (20 cm^3) solution of compound **4** (0.445 g, 1 mmol) at room temperature. The yellow solution rapidly changed to a pale yellow solution over a small amount of flocculent white precipitate; the gas flow was stopped when no further colour change was apparent. After stirring at room temperature for 2 h the solution was filtered and the filtrate layered with pentane (10 cm^3) and allowed to stand at room temperature. After 3 d colourless crystals were isolated by filtration and washed with a small volume of pentane. Yield 0.3 g, 52%. ^{1}H NMR (C_6D_6): δ 3.73 (s, 2 H, carborane C–H), 2.28 (s, 3 H, NMe), 2.23 (s, 3 H, NMe), 2.19 (s, 6 H, NMe$_2$) and 2.17 (s, 6 H, NMe$_2$). Additional peaks in ^{1}H-{^{11}B}: δ 4.18 (1 H), 3.92 (2 H), 3.72 (s, 1 H), 3.30 (s, 2 H) and 3.17 (s, 3 H). ^{13}C-{^{1}H} NMR (C_6D_6): δ 170.0 (1 × NCO$_2$), 166.9 (2 × NCO$_2$), 68.3 (carborane C), 34.3, 34.1, 33.9, 33.8 (NMe). ^{11}B-{^{1}H} NMR (C_6D_6): δ 16.4 (1 B), 3.4 (2 B), 1.2 (3 B), −8.6 (1 B) and −9.5 (2 B). Calc. for $C_{11}H_{29}B_9N_3O_6Ta{\cdot}0.25C_7H_8$: C, 25.50; H, 5.20. Found: C, 25.44; H, 5.15%). MS: *m*/*z* 475 [M − CH$_3$$^+$] and 490 [M − O$_2$CNMe$_2$$^+$]. IR: 2559s, 1641s, 1471m, 1451m, 1269s and 1022vw cm^{-1}.

[Ta($C_2B_9H_{11}$)(S_2CNMe_2)$_3$] 8. A stirred toluene (20 cm^3) solution of compound **4** (0.445 g, 1 mmol) was cooled to −78 °C and treated dropwise with CS$_2$ (0.228 g, 3 mmol). The yellow solution was allowed to warm to room temperature, giving an orange solution over a yellow precipitate. After stirring at room temperature for 12 h the solution was filtered and the volatiles were removed from the filtrate under reduced pressure. The residue was extracted with dichloromethane (10 cm^3) and the extract layered with toluene (10 cm^3) and cooled to −20 °C giving yellow crystals of [Ta($C_2B_9H_{11}$)(S_2CNMe_2)$_3$], which were isolated by filtration and washed with a small volume of toluene. Yield 0.411 g, 61%. ^{1}H NMR ($CDCl_3$): δ 3.59 (s, 2 H, carborane C–H), 3.30 (s, 3 H, NMe), 3.25 (s, 6 H, NMe$_2$), 3.21 (s, 6 H, NMe$_2$) and 3.19 (s, 3 H, NMe). Additional peaks in ^{1}H-{^{11}B}: δ 3.36 (1 H), 2.75 (3 H), 2.54 (s, 1 H), 2.42 (s, 2 H) and 2.20 (s, 2 H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 207.9 (1 × NCO$_2$), 204.6 (2 × NCO$_2$), 66.9 (carborane CH), 40.3, 39.8, 39.6, 38.9 (NMe). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 13.0 (1 B), −0.5 (2 B), −3.6 (2 B), −5.8 (1 B), −13.6 (2 B) and −17.2 (1 B). Calc. for $C_{11}H_{29}B_9N_3NbS_6{\cdot}C_7H_8$: C, 28.22; H, 4.87. Found: C, 28.15; H, 4.87%. MS: *m*/*z* 674 [M$^+$], 629 [M − 2CH$_3$$^+$], 541 [M − C$_2B_9H_{11}$$^+$] and 554 [M − S$_2$CNMe$_2$$^+$]. IR: 2535s, 1528s, 1442m, 1393vs, 1258s, 1166s, 1098w and 1019w cm^{-1}.

X-Ray crystallography

Single-crystal diffraction experiments were carried out with a SMART 1K CCD area detector, using graphite-monochromated Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å). The reflection intensities were corrected for absorption by numerical integration based on measurements of the crystal and face indexing (for **6**, using SHELXTL software[50]) or by a semi-empirical method based on multiple scans of identical reflections and Laue equivalents (using SHELXTL software for **2** and the SADABS program[51] for **3**, **4** and **7**). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs.[50] In **7** the entire toluene molecule of crystallisation was treated as a rigid body. Crystal data and experimental details are listed in Table 4.

The CD_2Cl_2 molecule of crystallisation is enclosed in an intermolecular cavity in the crystal of compound **6**. Both its chlorine atoms are disordered over two positions, A and B, with occupancies of 93.0(7) and 7.0(7)% respectively. The structure of **7** contains infinite open channels parallel to the *z* axis, occupied by disordered toluene molecules of crystallisation. The preferential position of the toluene molecule (its principal axis at 15° with the *z* direction) was located from the electron density map and refined with 50% occupancy. Full occupancy at this site would lead to unrealistically short toluene–toluene contacts. High (up to 1.2 e Å^{-3}) and diffuse residual electron density along the channel suggests incommensurate distribution of toluene therein, which could give (in the closest packing) a maximum of 1.5 molecules per *c* translation, *i.e.* the $\mathbf{5}\cdot\frac{3}{4}C_6H_5Me$ stoichiometry.

CCDC reference number 186/1657.

See http://www.rsc.org/suppdata/dt/1999/3867/ for crystallographic files in .cif format.

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