$Cp^*TaCl_2B_4H_8$: synthesis, crystal structure and spectroscopic characterization of an air-stable, electronically unsaturated, chiral tantalaborane

Simon Aldridge, Hisako Hashimoto, Maoyu Shang and Thomas P. Fehlner*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, 46556, USA

Reaction between Cp^*TaCl_4 ($Cp^* = \eta^5$-C_5H_5) and BH_3·thf at 40 °C yields the pale red electronically unsaturated cluster $Cp^*TaCl_2B_4H_8$ 1 which despite having two electrons fewer than the seven pairs required for the observed square pyramidal geometry is stable in air; viewed as a cluster, 1 is the first example of an unsaturated cluster containing a single metal atom; viewed as a chiral 16-electron organometallic complex it is isoelectronic with $Cp(C_2B_9H_{11})TaCl_2$ and $Cp[(Me_3Si)_2C_2B_4H_4]TaCl_2$.

The rôle of unsaturated species in catalyzing or mediating industrially important transformations has long been acknowledged,[1] although examples of such species in transition metal cluster chemistry are rare.[2] Within the realms of metallaborane chemistry unsaturated species, that is those which are formally electron deficient with respect to the number of skeletal pairs required to sustain the observed molecular geometry, are limited to the sensitive group 6 metallaboranes $(Cp^*Cr)_2B_4H_8$[3] and $(Cp^*MoCl)_2B_3H_7$[4] both of which, having five skeletal electron pairs are formally two electrons deficient in terms of Wade's rules.[5] We now report the synthesis of the six-electron pair cluster $(Cp^*TaCl_2)B_4H_8$ **1** which has a *nido* structure formally derived from B_5H_9 by replacement of a basal BH fragment by Cp^*TaCl_2. Although **1** has two fewer electrons than the seven pairs expected for such a geometry, it is remarkably stable in air and sufficiently thermodynamically robust that it can be sublimed *in vacuo* at 230 °C.

Reaction of Cp^*TaCl_4 with 3.5 equiv. of BH_3·thf at 40 °C leads initially (4 h reaction time) to an extremely air- and moisture-sensitive deep blue intermediate thought to be a BH_3 adduct of the known dimeric tantalum hydride $(Cp^*TaCl_2H)_2$.[6] Longer reaction times lead to the isolation of the pale red air-stable cluster $Cp^*TaCl_2B_4H_8$ **1**.† **1** has been characterized by ^1H and ^{11}B NMR, IR spectroscopy and high-resolution mass spectrometry and by single crystal X-ray diffraction.‡ Consumption of BH_3·thf during the reaction is accompanied by evolution of BH_2Cl; the effective use of BH_3·thf as a dual reagent to build up a metallaborane cluster and to remove Cl as BH_2Cl has been demonstrated previously for cobalt[7] and molybdenum[4] metallaboranes. In addition, the reaction of Cp^*TaCl_4 with BH_3·thf contrasts with the analogous reaction with the more strongly reducing BH_4^-, which we find to give the known compound $(Cp^*TaB_2H_6)_2$.[8] The differing reactivities of BH_3·L and BH_4^- towards Cp^*MX_n species have been demonstrated previously for M = Cr, Mo and Co.[3,4,7]

The crystal structure of **1** is illustrated in Fig. 1 and can be interpreted as a *nido* cluster formally derived from B_5H_9 by replacement of a basal BH group by Cp^*TaCl_2. The skeletal electron count for such a molecule is six pairs, one pair short of the seven required for a square pyramidal geometry.[5] That the molecule is indeed square pyramidal, rather than trigonal bipyramidal (as would be expected for six pairs) is reflected by Ta–B(4) and B(1)–B(3) distances [3.338(12), 2.59(2) Å, respectively] which are sufficiently long to preclude any significant bonding interaction. Cluster **1** is therefore electronically unsaturated and is the first example of an unsaturated cluster containing a single metal atom.

The square pyramidal geometry of **1** is further confirmed by similarities with the only other crystallographically characterized 2-metallapentaborane, 2-$CpCoB_4H_8$.[9] The two clusters display similar B–B distances and B–B–B angles. Although the metal–apical boron distances are consistent with the differences in the covalent radii of the metals, the metal–basal boron distance for **1** is longer than expected from the structure of the cobalt compound. However, as M–B distances for hydrogen-bridged interactions exhibit large variations for the same metal, this difference is difficult to interpret.

A comparison of the molecular orbital schemes for **1** and 2-$CpCoB_4H_8$ calculated by Fenske–Hall methods[10] offers some insight into the nature of the unsaturated tantalaborane.§ For 2-$CpCoB_4H_8$ the SHOMO is an antibonding combination consisting mainly of a metal-based d orbital along with a minor contribution from a borane-based fragment orbital which is symmetric with respect to the molecular mirror plane and has a high percentage of apical boron 2p character. In the tantalum case the corresponding MO has similar character but is shifted to much higher energy (+0.41 for **1** *vs.* −12.47 eV) principally because the participating metal-based orbital is itself at much higher energy (−5.99 for **1** *vs.* −13.09 eV). In essence the significantly higher energy of the early transition metal d orbitals shifts a predominantly metal-based MO to much higher energy such that it is unoccupied, and **1** is stable despite one skeletal electron pair fewer than 2-$CpCoB_4H_8$. Although **1** is unique in being an unsaturated cluster featuring a single metal atom, the electronic factors underlying its apparent stability, the high-lying nature of the metal d orbitals and their ability to overlap well with borane-based orbitals, have much in common

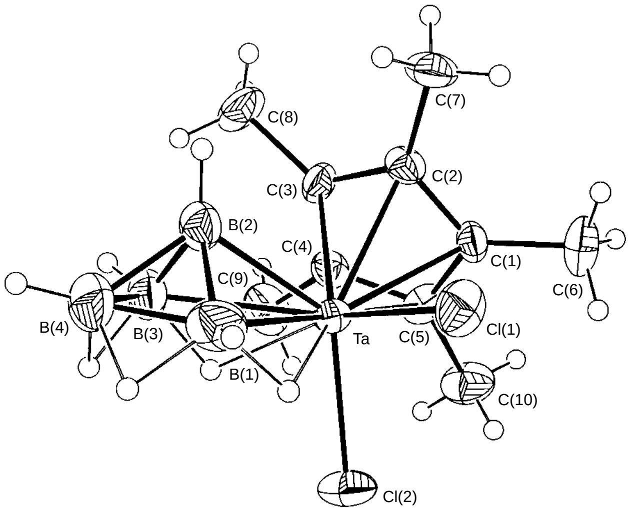

Fig. 1 The molecular structure of **1**. Relevant bond lengths (Å) and angles (°): Ta–Cl(1) 2.341(2), Ta–Cl(2) 2.370(2), Ta–Cp*(centroid) 2.123(9), Ta–B(1) 2.495(12), Ta–B(2) 2.249(12), Ta–B(3) 2.495(14), B(1)–B(2) 1.70(2), B(1)–B(4) 1.77(2), B(2)–B(4) 1.71(2), B(1)–H(11) 1.33(4), B(1)–H(12) 1.34(5), B(1)–H(13) 0.98(6), Ta–H(11) 1.88(5); Cl(1)–Ta–Cl(2) 99.20(10), H(11)–Ta–H(31) 79(3), B(1)–Ta–B(3) 62.4(5), B(1)–B(2)–B(3) 99.9(10), B(1)–B(4)–B(3) 94.0(9).

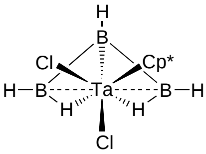

Fig. 2 Structure of **1** viewed along the Ta–B(4) axis showing the non-symmetrical distribution of ligands about the tantalum centre

with the factors stabilizing other unsaturated early transition metal metallaboranes featuring two metal centres *i.e.* (Cp*Cr)$_2$B$_4$H$_8$[3] and (Cp*MoCl)$_2$B$_3$H$_7$.[4]

Cluster **1** represents a rare example of a structurally characterized molecule containing a Ta–B bond[8,11–14] and comparison with (Cp*TaBr)$_2$B$_2$H$_6$[8] (which contains both Ta–B and Ta–H–B linkages) shows similar hydrogen-bridged Ta$\cdots$B distances [2.495 Å for **1**; 2.41 Å for (Cp*TaBr)$_2$B$_2$H$_6$][8] but a significantly shorter direct Ta–B linkage (2.249 *vs.* 2.37 Å). The Ta–B bond is also decidedly shorter than those found in η^5 bound tantalum carborane complexes (which are typically in the range 2.4–2.5 Å),[11,13,14] but of similar length to that found in both isomers of the η^1 complex Cp$_2$Ta(H)$_2$(BO$_2$C$_6$H$_4$) (2.263, 2.295 Å[12]).

An alternative view of **1** is as a 16-electron organometallic complex containing either a d^0 Ta^{V} centre coordinated to a six-electron $B_4H_8^{2-}$ ligand or a Ta^{III} centre and a four-electron neutral B$_4$H$_8$ ligand. The $B_4H_8^{2-}$ ligand is comparable to the six-electron units $C_2B_9H_{11}^{2-}$ or $(Me_3Si)_2C_2B_4H_4^{2-}$ in the analogous molecules Cp(R)TaCl$_2$ [R = C$_2$B$_9$H$_{11}$[13] or (Me$_3$Si)$_2$C$_2$B$_4$H$_4$[14]]. In contrast to these carborane complexes, however, **1** is chiral with the plane of mirror symmetry present in other 2-metallapentaboranes such as 2-CpCoB$_4$H$_8$[9] being eliminated by the non-symmetrical distribution of ligands about the tantalum centre (see Fig. 2). This results in non-equivalence of borons B(1) and B(3) which consequently give rise to two distinct ^{11}B NMR signals (at δ_B −2.9, 0.5). A similar situation arises in the osmapentaborane *nido*-[(OC)(Ph$_3$P)$_2$OsB$_4$H$_8$] which also gives rise to four distinct ^{11}B signals;[15] in the case of **1** the barrier to rotation is sufficiently high that no hint of coalescence is observed even at 90 °C.

Although reactions of monocyclopentadienylmetal halides, CpMX$_n$, with nucleophiles have been extensively investigated,[16] reactions with electrophiles have received comparatively little attention to date. Reaction of one such transition metal complex, Cp*TaCl$_4$ with the electrophile BH$_3$·thf yields the highly unusual cluster (Cp*TaCl$_2$)B$_4$H$_8$ **1**. Cluster **1** is remarkable enough in being an electronically unsaturated mono-metallated borane cluster, but its thermodynamic stability, together with its stability in air, make it unique. The synthesis and on-going investigation of the chemistry of **1** [with particular emphasis on the synthesis of chiral tantalum(v) alkyl derivatives] represents an exciting development in the little investigated area of early transition metal metallaboranes.

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Footnotes and References

* E-mail: thomas.p.fehlner.1@nd.edu

† Reaction of Cp*TaCl$_4$ (300 mg, 0.66 mmol) with 3.5 equiv. of BH$_3$·thf in toluene at 40 °C for 96 h, followed by removal of volatiles (including BH$_2$Cl) *in vacuo* and extraction with hexane gives an orange–red solution from which pale red crystals of Cp*TaCl$_2$B$_4$H$_8$ **1** can be grown by controlled cooling; **1** can also be isolated from the reaction of Cp*TaCl$_2$(CO)$_2$(thf) with a fivefold excess of BH$_3$·thf in toluene at 40–50 °C over a period of 24 h. **1** is stable to air in both solid and solution phases (toluene or hexane), is obtained in yields of up to 45% (based on boron) and can be sublimed under continuous vacuum at *ca.* 230 °C without significant decomposition. **1** has been characterized by ^{1}H and ^{11}B NMR (including selective decoupling experiments), IR, high-resolution mass spectrometry and single crystal X-ray diffraction. *Spectroscopic data* for **1**: MS (EI), M^+ = 438, 1 Ta, 4 B, 2 Cl atoms, calc. *m/z* 438.1029, obs. 438.1041. ^{11}B NMR (toluene 21 °C), [J(^{11}B–^{1}H) in parentheses] δ 6.3 [d, 1B, B(2) (150 Hz)], 4.8 [d, 1B, B(4) (160 Hz)], δ 0.5 [d, 1B, B(1) or B(3) (160 Hz)], −2.9 [d, 1B, B(1) or B(3) (140 Hz)]. ^{1}H NMR ([^{2}H$_6$]benzene, 21 °C), δ −1.24 [partially collapsed quartet (pcq), 2 H, accidental overlap of both TaHB signals (80 Hz)], −0.67 (br, 2 H, overlap of both BHB signals), 1.85 (s, 15 H, Cp*) δ 2.81 [q, 1 H, terminal H attached to B(2) (150 Hz)], 4.52 [overlapping pcq, 3 H, overlap of terminal H attached to B(1), B(3) and B(4) (*ca.* 150 Hz)]. IR (KBr, cm^{-1}) 2996w (sh), 2965m, 2912m, 2863w (sh), ν(CH); 2567s, 2544s, 2530m (sh), ν(B–H$_t$); 2076w (sh), 2057m (br), 1646m (br), ν(B–H$_b$); 1443m (br); 1378s, δ(CH$_3$); 700m, 614w, ρ(CH$_3$). (ν = stretching mode, δ = deformation mode, ρ = rocking mode).

‡ *Crystallographic data* for **1**: monoclinic, space group $P2_1/c$, a = 14.149(2), b = 8.6357(12), c = 14.328(2) Å, β = 116.981(13)°, U = 1560.1(4) Å^3, Z = 4, D_c = 1.866 g cm^{-3}. Of the 2744 reflections collected [CAD4 diffractometer, Mo-Kα radiation (λ = 0.710 73 Å, 293 K)], all were independent and 2430 were observed [$I > 2\sigma(I)$]. All non-hydrogen atoms were anisotropically refined and difference Fourier synthesis located all hydrogen atoms. Both methyl and borane hydrogens were included in the final refinement, the former as idealized riding atoms [r(C–H) = 0.96 Å, U_{iso}(H) = 1.5 U_{eq}(C)], the latter isotropically with three free-variables to restrain B–H(terminal) B–H(bridging) and Ta–H bond lengths. R_1 = 0.0433, wR_2 = 0.1118 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0494, wR_2 = 0.1199 for all 2744 unique reflections including those with negative intensities. The max., min. residual electron densities on the final difference Fourier map were 2.037 and −1.750 e Å^{-3}, respectively. The first five peaks were all within 1.4 Å of the heavy Ta atom and might have been caused by satellite diffraction and/or imperfection in the empirical absorption correction. Since no observable abnormality of the structure details was found, no further effort was made to improve the index for residual electron density. CCDC 182/705.

§ Fenske–Hall calculations were carried out on the 2-CpTaCl$_2$B$_4$H$_8$ and 2-CpCoB$_4$H$_8$ molecules, with coordinates taken from the results of single crystal X-ray diffraction studies. In the tantalum case the simplification was made that the Cp* (η^5-C$_5$Me$_5$) ligand was replaced by Cp (η^5-C$_5$H$_5$).

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