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Heteroborane Ligands

Diphosphaborane and Metalladiphosphaborane: Ligands for Transition-Metal Chemistry**

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Through an impressive series of papers by Wesemann and co-workers,[1] the dianionic stannaborate [*closo*-$SnB_{11}H_{11}]^{2-}$ has been shown to be a powerful and versatile σ-donating ligand in coordination chemistry through the lone pair of electrons on the Sn atom. In marked contrast, the neutral stannacarborane 3,1,2-*closo*-$SnC_2B_9H_{11}$ and its derivatives and supra-icosahedral analogues show clear Lewis acid behavior, readily forming adducts with bases such as pyridine or 2,2′-bipyridine.[2,3] In the stannacarboranes the lone pair on Sn appears to be stereochemically active but chemically inert. The monoanionic stannacarborate [1,2-*closo*-$SnCB_{10}H_{11}]^{-}$ displays intermediate behavior, having both σ-donor and π-acceptor properties.[4]

We recently reported the structure and the first deboronation followed by metallation of the diphosphaborane 1,2-*closo*-$P_2B_{10}H_{10}$,[5] a compound originally prepared by Todd et al. in 1989.[6] Based on the above precedents it was not clear that the neutral compounds 1,2-*closo*-$P_2B_{10}H_{10}$ and 3,1,2-*closo*-MP_2B_9 (M = transition metal) would necessarily show Lewis base behavior, and certainly no examples of these species acting in this way has previously been reported. We now describe the first examples of diphosphaborane and metalladiphosphaborane as σ-bonded ligands in transition-metal chemistry.

In seeking to convert 1,2-*closo*-$P_2B_{10}H_{10}$ to a supraicosahedral species we recognized that we could not use the standard method of polyhedral expansion, that is, reduction followed by capitation,[7] since 2-electron reduction of 1,2-*closo*-$P_2B_{10}H_{10}$ leads to loss of a P vertex and formation of [7-*nido*-$PB_{10}H_{12}]^{-}$, following aqueous work-up.[8] An alternative approach to polyhedral expansion of carboranes, developed by Stone and co-workers many years ago, is that of direct insertion of a highly nucleophilic metal fragment,[9] but whilst direct insertion of a Pt^0 or Pd^0 unit is generally successful with subicosahedral carboranes, insertion into icosahedral carboranes has only been shown to work with Co^0 fragments.[10] However, whilst reaction of 1,2-*closo*-$P_2B_{10}H_{10}$ with [Co-$(PEt_3)_4]$[11] did not yield supraicosahedral products it did afford [HCo(1,2-*closo*-$P_2B_{10}H_{10})_2(PEt_3)_2$] (**1**).

Compound **1** was initially characterized spectroscopically. The $^{11}B\{^1H\}$ NMR spectrum is relatively uninformative, containing four resonances in a 1:1:6:2 pattern (high frequency to low frequency) between $\delta = +14$ and -1 ppm. The ^1H spectrum displays the usual quartet and triplet resonances associated with Et groups, but additionally an apparent septet in the hydride region (at $\delta = -14.55$ ppm) with an integral 1/12 that of the quartet resonance. In the ^{31}P NMR spectrum are three resonances of equal integral at $\delta = 49.4$ (br.), 33.0 and -13.5 ppm. From a ^1H-^{31}P correlation experiment the resonance at $\delta = 33.0$ ppm in the ^{31}P spectrum is assigned to *P*Et_3. $^1H\{^{31}P_{selective}\}$ experiments collapse the hydride resonance from an apparent septet to 1:2:1 triplets with coupling constants of 17.2 Hz (decoupling at $\delta^{31}P = 49.4$ ppm) and 33.6 Hz (decoupling at $\delta^{31}P = 33.0$ ppm). Collectively these results suggest that in **1** one of the two P atoms in 1,2-*closo*-$P_2B_{10}H_{10}$ is coordinated to a {HCo} fragment. Moreover, the two-bond J_{HP} coupling constant to the diphosphaborane P atom, 33.6 Hz, is nearly twice that to the triethylphosphine P atom, 17.2 Hz.

The structure of **1** determined crystallographically is shown in Figure 1.[12] There are four crystallographically independent molecules (**AB**, **CD**, **EF** and **GH**) in the asymmetric fraction of the unit cell. Although the precision of the determination is not high the structural identity of the species is unambiguous. Not unexpectedly the hydride ligand

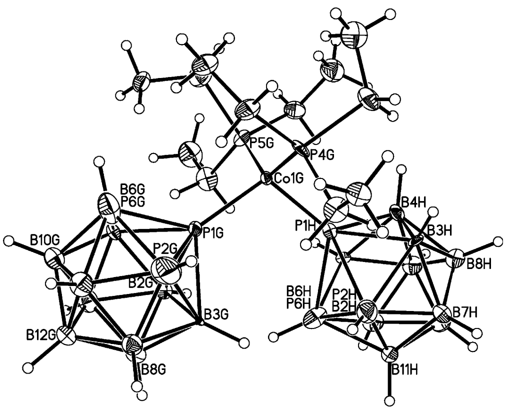

Figure 1. Perspective view of one of four crystallographically independent molecules (molecule **GH**) of [HCo(1,2-*closo*-$P_2B_{10}H_{10})_2(PEt_3)_2$] (**1**). Thermal ellipsoids drawn at 50% probability except for H atoms. There is disorder between P and B atoms in the 5-atom belts to which atoms P1 are connected. Molecule **AB**: Co1–P1A 2.051(3), Co1–P1B 2.057(3), Co1–P4 2.230(3), Co1–P5 2.179(3) Å. Molecule **CD**: Co1–P1C 2.072(3), Co1–P1D 2.096(3), Co1–P4 2.194(3), Co1–P5 2.165(3) Å. Molecule **EF**: Co1–P1E 2.044(3), Co1–P1F 2.038(3), Co1–P4 2.215(3), Co1–P5 2.205(4) Å. Molecule **GH**: Co1–P1G 2.083(3), Co1–P1H 2.087(3), Co1–P4 2.210(3), Co1–P5 2.207(3) Å.

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was not located, but we know from the NMR data that it is present.

The gross structure of **1** (excluding the hydride ligand) is distorted tetrahedral. In molecules **AB** and **EF** the six P-Co-P angles vary from 102–118° whilst in **CD** and **GH** one angle ($P_{phosphine}$-Co-$P_{phosphine}$) is much larger, ca. 135–139°, and the range of the remaining five angles correspondingly smaller, 100–109°. Distorted tetrahedral geometries for the {MP_4} cores have been found in other $HCoP_4$[13] (and more generally HMP_4)[14] structures where the P ligands are similarly unidentate, including those in which the hydride ligand has been located.[15] In **1** the Co–P_{cage} distances, 2.038(3)–2.096(3) Å, are significantly shorter than Co–$P_{phosphine}$ distances, 2.165(3)–2.230(3) Å.[16]

Compound **1** is, as far as we are aware, the first example of a neutral heteroborane cluster acting as a simple σ-bonded ligand to a transition metal.

In exploring the transition-metal chemistry of the deboronated diphosphaborane $[7,8\text{-}nido\text{-}P_2B_9H_9]^{2-}$ we recently treated this dianion with a source of the fragment $\{Ru(p\text{-cymene})\}^{2+}$ (p-cymene = η-$C_{10}H_{14}$, 1-*i*Pr,4-MeC_6H_4).[5] In addition to the anticipated species, 3-(*p*-cymene)-3,1,2-*closo*-$RuP_2B_9H_9$ (**I**), we isolated from this reaction a second product, **2**, whose NMR spectroscopic properties indicated an interesting and complex structure. Thus in the ^{31}P NMR spectrum are two singlets of equal integral but at very different chemical shifts, $\delta = 46.0$ and -35.5 ppm. The $^{11}B\{^1H\}$ spectrum is again generally uninformative; although clearly implying the presence of a *nido* heteroborane (resonance at $\delta = -32.7$ ppm)[17] the spectrum essentially contains seven very broad peaks whose relative integrals cannot be assigned with confidence. On the other hand the ^{1}H NMR spectrum clearly shows evidence for two different types of *p*-cymene ligand in a 2:1 ratio, implying a molecule containing at least three Ru atoms.

The nature of **2** was ultimately revealed by a crystallographic study.[12] As shown in Figure 2 and Figure 3 compound **2** contains both *nido*-P_2B_9 and *closo*-RuP_2B_9 cages each acting as κP:κP′ ligands bridging two {HRu(*p*-cymene)} units. Again, the hydride ligands were not located crystallographically but are clearly present from the low-frequency region of the ^{1}H NMR spectrum. In **2** the *closo*-RuP_2B_9 cage is simply the co-product (**I**) of the reaction and the *nido*-P_2B_9 cage is formally $\{7,8\text{-}nido\text{-}P_2B_9H_9\}^{2-}$ to balance charge. The central P_4Ru_2 unit is folded about the Ru···Ru axis by ca. 60.5° such that the open face of the {*nido*-P_2B_9} fragment points towards the *p*-cymene ligand on Ru3A. Ru–P_{P2B9} distances are somewhat longer than Ru–P_{RuP2B9} distances, 2.304(2) and 2.282(2) Å versus 2.254(2) and 2.252(2) Å.

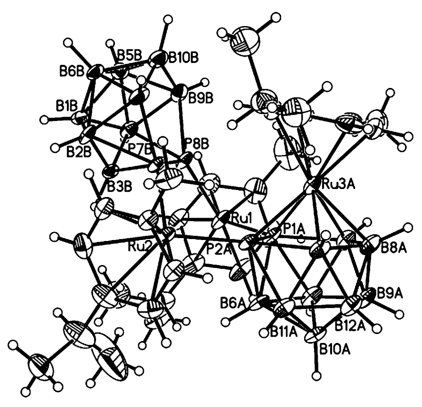

Figure 2. Perspective view of μ-[1,2-$\{HRu(p\text{-cymene})\}_2$-7′,8′-*nido*-$P_2B_9H_9$]-3-(*p*-cymene)-3,1,2-*closo*-$RuP_2B_9H_9$ (**2**). Thermal ellipsoids drawn at 50% probability except for H atoms. Ru1–P1A 2.252(2), Ru1–P8B 2.304(2), Ru2–P2A 2.252(2), Ru2–P7B 2.282(2), Ru3A–P1A 2.371(3), Ru3A-P2A 2.378(3), P1A–P2A 2.348(3), P7B–P8B 2.176(3) Å.

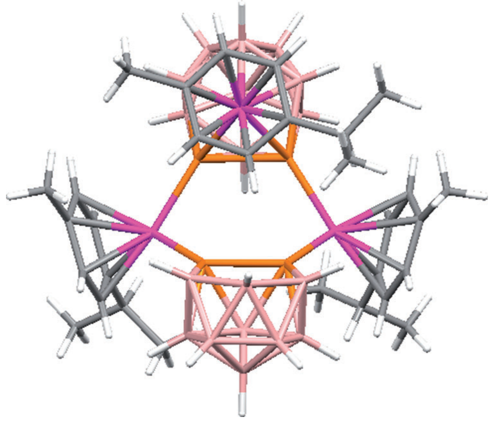

Figure 3. Alternative view of compound **2** looking perpendicular to the Ru3A···B10A axis and showing the approximate C_s symmetry of the $\{Ru_3(P_2B_9)_2\}$ core. C gray, B pink, P orange, Ru purple, H white.

Just as compound **1** represents the first example of a diphosphaborane acting as a simple σ-bonded ligand to a transition metal, so in compound **2** we have unique examples of both a metalladiphosphaborane and a diphosphaborate anion functioning as κP:κP′ ligands. We believe that compounds **1** and **2** could presage a large number of complexes in which diphosphaboranes and related species act as σ-bonded ligands in this way, and that these complexes have the potential to display interesting structures and reactivity. For example, in **2** an η-bound aromatic ligand of one cage system is held close to a formally dianionic second cage and we have recently shown that this arrangement can result in unprecedented room temperature reductive cleavage of the aromatic ring.[18] Further research in this area is currently underway in our laboratories.

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[12] Crystallography: a crystal was mounted in inert oil on a cryoloop and cooled to 100(2) K on a Bruker X8 APEX2 diffractometer using $\mathrm{Mo_{K\alpha}}$ X-radiation. Intensity data were corrected for absorption semi-empirically and structures were solved by direct and difference-Fourier methods. Refinement[19] was by full-matrix least-squares analysis on F^2. Crystal data for **1**: $\mathrm{C_{12}H_{50}B_{20}CoP_6}$, $M = 655.47$, monoclinic, $P2_1$, $a = 20.521(2)$, $b = 16.2495(15)$, $c = 23.017(2)$ Å, $\beta = 116.247(5)°$, $V = 6883.9(12)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.265$ Mg m^{-3}, $\mu = 0.787$ mm^{-1}, $F(000) = 2712$. 46640 independent reflections out of 108234 measured to $\theta_{\max} = 32.67°$, $R_{\mathrm{int}} = 0.0458$, $R_1 = 0.1814$, $wR_2 = 0.4090$, $S = 3.257$, Flack parameter = 0.19(3) for 42018 data with $I > 2\sigma(I)$, largest peak 3.83 and deepest hole -5.00 e Å^{-3}. For **2**: $\mathrm{C_{30}H_{62}B_{18}P_4Ru_3 \cdot 3\,CDCl_3}$, $M = 1405.59$, monoclinic, $P2_1/n$, $a = 11.1335(7)$, $b = 19.4976(12)$, $c = 26.8397(19)$ Å, $\beta = 100.912(4)°$, $V = 5720.9(6)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.632$ Mg m^{-3}, $\mu = 1.343$ mm^{-1}, $F(000) = 2792$, $\theta_{\max} = 25.41°$, 10443/69025 reflection, $R_{\mathrm{int}} = 0.1080$, $R_1 = 0.0707$, $wR_2 = 0.1601$, $S = 1.026$ for 6626 data with $I > 2\sigma(I)$, largest peak 3.74 and deepest hole -1.65 e Å^{-3}. CCDC 839528 (**1**) and 839529 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] A referee has suggested that, given the two forms of distorted tetrahedral structure in the four crystallographically independent molecules of **1**, what was crystallized might actually be a mixture of the 18-electron Co$^{\mathrm{I}}$ species [HCo(1,2-*closo*-$\mathrm{P_2B_{10}H_{10}})_2(\mathrm{PEt_3})_2$] and the 17-electron Co^0 species [Co(1,2-*closo*-$\mathrm{P_2B_{10}H_{10}})_2(\mathrm{PEt_3})_2$]. We thank the referee for this perceptive suggestion and are currently exploring ways to clarify the issue.

[17] For the ^{11}B NMR resonances of [7,8-*nido*-$\mathrm{P_2B_9H_{10}}]^-$ see J. L. Little, M. A. Whitesell, R. W. Chapman, J. G. Kester, J. C. Huffman, L. J. Todd, *Inorg. Chem.* **1993**, *32*, 3369–3372.

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