Vinylborane Complexes

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η^3-Vinylborane Complexes of Platinum and Nickel: Borataallyl- and Alkyl/Borataalkene-Like Coordination Modes**

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Complexes of carbon-based π ligands have occupied a central position in d- and f-block element organometallic chemistry since the remarkably early synthesis of Zeise's salt, K[PtCl$_3$-(C$_2$H$_4$)]·H$_2$O, in 1827.[1] By contrast, π-ligand complexes containing boron and carbon have only been developed in the past 50 years. Formally monoanionic boratabenzene[2] and dianionic borole ligands,[2] which are isoelectronic with arene and cyclopentadienyl ligands (Figure 1), respectively, are now prominent examples in this area.[3] However, boron analogues of acyclic π ligands are rare. For example, mononuclear η^2-borataalkene complexes (Figure 1) are limited to the tantalum complexes reported by Piers and co-workers, [Cp$_2$TaL$_x$-{CH$_2$B(C$_6$F$_5$)$_2$}] (L = CN*t*Bu and CO; $x = 0$ or 1; **III** in Figure 2),[5] and η^3-borataallyl complexes (Figure 1)[4] are limited to the palladium and zirconium complexes, [PdCl$_2${η^3-PhB(CHPPh$_3$)$_2$}] and [ZrCl$_4${η^3-PhB(CHPPh$_3$)$_2$}] (**I** and **II**, Figure 2), that were reported by the Shapiro group.[6] The PhB(CHPPh$_3$)$_2$ ligand may be viewed as a borane-bridged diylide or a zwitterionic 1,3-di-phosphonium-substituted 2-borataallyl ligand.

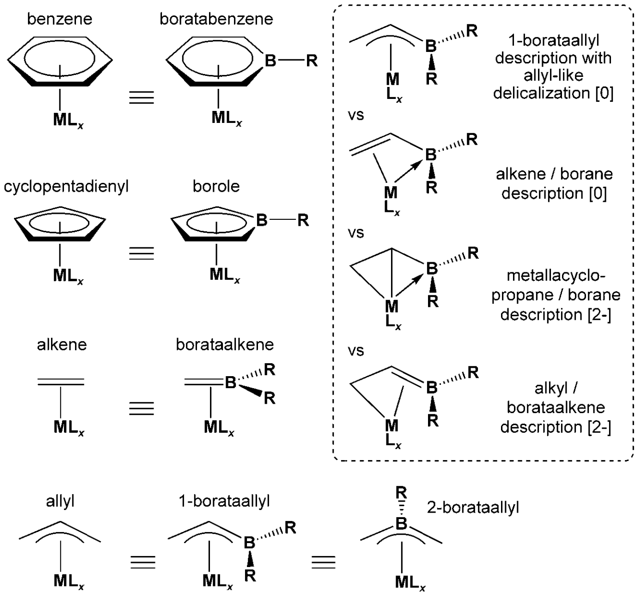

Figure 1. Structural relationships between common hydrocarbon π ligands and their boron analogues. The inset shows four possible bonding descriptions for an η^3-coordinated vinylborane; the formal charges on the ligand are shown in square brackets.[4]

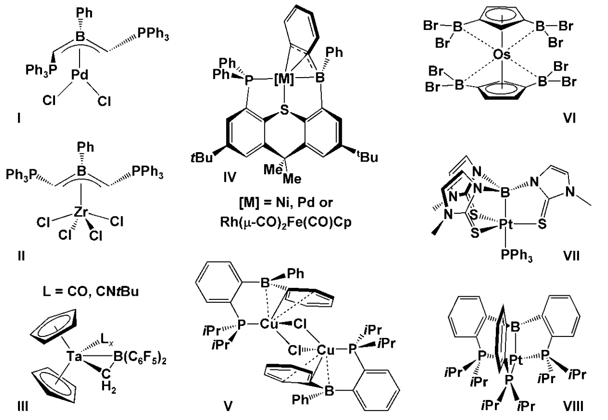

Figure 2. Selected complexes featuring M−BR$_3$ interactions. **I** and **II** are η^3-coordinated borane-bridged diylide complexes.[6] **III** is an η^2-borataalkene complex.[5] **IV** and **V** are η^3-BCC-coordinated triarylborane complexes.[8] **VI** is a metallocenylborane complex.[9] **VII** and **VIII** are platinum–η^1-borane complexes.[12–14]

The formation of complexes of η^3-coordinated R$_2$CCRBR$_2$ ligands or simple hydrocarbyl-substituted R$_2$CBRCR$_2$ ligands is of particular interest given the generally enhanced reactivity of acyclic π ligands relative to cyclic π ligands (e.g. allyl$^-$ versus C$_5$H$_5$$^-$). Metal–allyl complexes may be prepared from the reaction of a suitable metal precursor with an allyl anion or cation source. Free vinylboranes are conceptually analogous to an allyl cation; herein, we describe the reactions of (*E*)-PhHC=CH−B(C$_6$F$_5$)$_2$ (VB$^{\mathrm{Ph}}$)[7] with low-valent platinum and nickel precursors to yield η^3-BCC-coordinated vinylborane complexes. Several possible bonding descriptions for an η^3-vinylborane ligand are shown in Figure 1.

The reaction of (*E*)-PhHC=CH−B(C$_6$F$_5$)$_2$ (VB$^{\mathrm{Ph}}$)[7] with [Pt(nb)$_3$] (nb = norbornylene), followed by the addition of P*t*Bu$_3$ afforded dark red [(*t*Bu$_3$P)Pt{η^3-BCC-VB$^{\mathrm{Ph}}$}] (**1**) in 68 % yield (Scheme 1). Crystals of **1** suitable for X-ray

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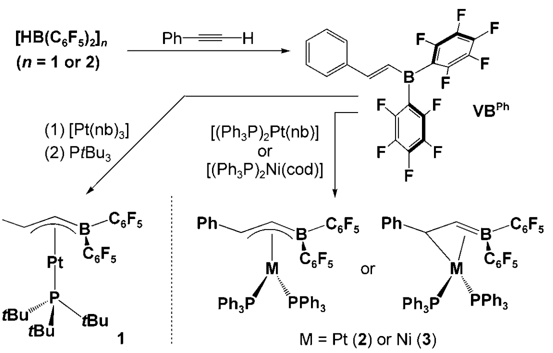

Scheme 1. Synthesis of VB^{Ph},[7] $[(tBu_3P)Pt(\eta^3\text{-BCC-VB}^{Ph})]$ (**1**), $[(Ph_3P)_2Pt(\eta^3\text{-BCC-VB}^{Ph})]$ (**2**) and $[(Ph_3P)_2Ni(\eta^3\text{-BCC-VB}^{Ph})]$ (**3**). cod = 1,5-cyclooctadiene.

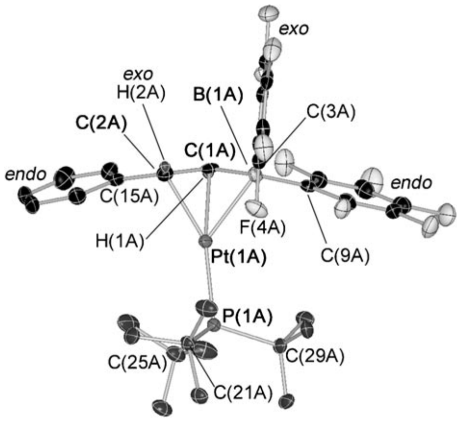

Figure 3. X-ray structure of **1** with thermal ellipsoids at 50% probability. Only molecule A (one of two independent molecules in the unit cell) is shown. Most hydrogen atoms are removed for clarity.

analysis (Figure 3), containing two independent molecules (A and B) in the unit cell, were obtained by recrystallization from hexane at −30 °C.[10] In both A and B, the VB^{Ph} ligand is η^3-BCC coordinated, with $PtBu_3$ positioned roughly *trans* to the VB^{Ph} ligand centroid. The B−C(1) distances of 1.519(7) and 1.517(6) Å in **1** are shorter than those in free vinylboranes, such as $(Mes)_2BCH{=}CHPh$ (Mes = mesityl), $[(F_5C_6)_2B]_2C{=}CHPh$, and $B[C(SiMe_3){=}CHMe]_3$ [1.54–1.57 Å], whilst the C(1)−(2) distances of 1.383(6) and 1.403(6) Å are slightly longer (cf. 1.33–1.365 Å in the vinylboranes above).[11]

In molecule A, the Pt−B distance is 2.273(5) Å, Pt−C(1) is 2.130(4) Å, and Pt−C(2) is 2.155(4) Å; these distances are indicative of strong η^3 binding. In molecule B, the C_6F_5 rings lie at different angles relative to the BCC core, leading to slightly different Pt−B, Pt−C(1), and Pt−C(2) distances of 2.319(5), 2.126(4), and 2.137(4) Å, respectively. Similar M−B and M−C distances (M = Pd and Ni) were observed for **I** and **IV** (Figure 2), and the M−C distances in **1** are comparable with those in $[Pd(\eta^3\text{-}C_3H_4Me)_2]$,[12] $[(tBu_3P)PtCl(\eta^3\text{-}C_3H_5)]$[13] and $[(dmpe)Pt(\eta^3\text{-1,3-}Ph_2C_3H_3)]PF_6$[14] (2.13–2.23 Å; dmpe = 1,2-bis(dimethylphosphino)ethane). The M−B distance in **1** is also comparable with those in η^1-borane complexes, such as **VIII** [2.224(4) Å],[15] and is far shorter than those in metallocenylboranes (e.g. **VI**; Figure 2).[9] However, whereas boron is strongly pyramidalized in tightly bound η^1-borane complexes, it is only modestly pyramidalized in **1** [Σ(C−B−C) = 353 and 357°].

The η^3-coordination mode in **1** contrasts the η^2-alkene coordination mode found in the previously reported $[(CO)_4Fe\{H_2C{=}CH{-}BR(NMe_2)\}]$ (R = Br, Me)[16] and $[Cp_2Ti(ArH{=}CH{-}BCat)]$ (Ar = Ph and 4-$MeOC_6H_4$; Cat = $O_2C_6H_4$ or 4-$tBuC_6H_3O_2$),[17] presumably owing to the much higher borane Lewis acidity in **1**. The related complexes $[(CO)_3Fe\{H_2C{=}CH{-}B(R)NMe_2\}]$ (R = Br, Me, or *t*Bu)[16] and $[(CO)_4Cr\{tBuHC{=}CH{-}BH{-}N(SiMe_3)_2\}]$[18] are also known, but in both cases the vinylborane is η^4 coordinated, and acts as a four-electron donor; the former is a boron- and nitrogen-containing analogue of butadiene, whilst the latter binds through alkene and σ-borane interactions.

For molecules A and B in the unit cell of **1**, all *exo* substituents on the B−C−C core [C(3) and H(2)] are bent away from the metal, whilst the *endo* [C(9) and C(15)] and central [H(1)] substituents bend towards the metal.[23] Similar distortions were observed in $[PdCl_2\{\eta^3\text{-}PhB(CHPPh_3)_2\}]$,[6] and are typical of late-transition-metal–allyl complexes.[19] These results highlight striking similarities between the VB^{Ph} ligand in **1** and π-allyl ligands.

The ^{11}B NMR spectrum shows a single broad signal at δ = 15.6 ppm; far upfield of the corresponding signal for the free VB^{Ph} (δ = 58.3 ppm),[7] and significantly upfield of **I**, **IV** (Pd and Ni), and **VIII** (δ = 35–18 ppm). Furthermore, ^{195}Pt satellites were observed for the BC*H*C*H*Ph atoms ($^1J_{^{13}C,^{195}Pt}$ = 196 Hz; $^2J_{^1H,^{195}Pt}$ = 47 and 80 Hz) in the ^1H and ^{13}C NMR spectra of **1**. These data are consistent with the tight η^3-BCC coordination of VB^{Ph}.

To examine the generality of the η^3-BCC bonding mode for vinylborane ligands, and the extent to which M−B and M−C bond distances are sensitive to changes in the central metal and the phosphine coligands, $[(Ph_3P)_2Pt\{\eta^3\text{-BCC-VB}^{Ph}\}]$ (**2**) and $[(Ph_3P)_2Ni\{\eta^3\text{-BCC-VB}^{Ph}\}]$ (**3**), were prepared as shown in Scheme 1.[24] Significant $^1J_{^{13}C,^{195}Pt}$ (171 Hz), $^2J_{^1H,^{195}Pt}$ (40 and 49 Hz), and $^2J_{^{13}C,^{13}P}$ (30 and 16 Hz) couplings for the BC*H*C*H*Ph atoms are indicative of strong metal−carbon interactions in **2** and **3**. However, the ^{11}B NMR signals for **2** and **3** (δ = 25 and 34 ppm, respectively) were shifted to a higher frequency than that for complex **1**. ^{31}P NMR spectroscopy showed that the VB^{Ph} ligand in complexes **2** and **3** exhibited hindered rotation around the metal–ligand axis. Substantial barriers to acyclic π-ligand rotation are also encountered in 16-electron allyl complexes, such as $[(Ph_3P)ClPt(\eta^3\text{-}C_3H_5)]$,[20] and in a broad range of late-transition-metal–alkene complexes.[21]

Crystals of **3** suitable for X-ray analysis were obtained from a benzene/hexane mixture at −30 °C (Figure 4).[10] Key differences in the structure of **3** relative to **1** are: 1) a longer M−B distance of 2.660(3) Å; 2) shorter M−C(1) and M−C(2) distances of 2.025(2) and 2.032(2) Å, respectively; 3) a shorter B(1)−C(1) bond of 1.483(4) Å (see below); 4) a somewhat longer C(1)−C(2) distance of 1.431(3) Å; 5) less pronounced distortions of the *exo* H, *exo* C_6F_5, *endo* C_6F_5, and the central H substituents on the η^3-coordinated core of **3**; and 6) distortion of the *endo* Ph substituent away from the metal, rather than towards it in **1**.[22]

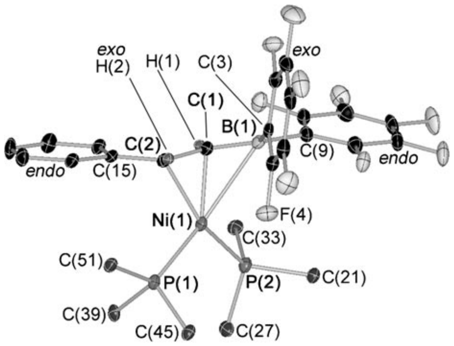

Figure 4. X-ray structure of **3** with thermal ellipsoids at 50% probability. Most hydrogen atoms are removed for clarity.

Returning to point (3) above, the B–C distance in **3** is in fact more similar to that found in free $R_2B{=}CR_2^-$ or $R_2B{=}C{=}BR_2^{2-}$ anions (1.39–1.51 Å)[23] than in vinylboranes (see below), and is also shorter than those in the tantalum borataalkene complexes reported by Piers and co-workers (1.51–1.53 Å).[5] These data, and the distortion away from the metal of both substituents on the C(2) atom, are indicative of a more alkyl/borataalkene-like coordination (see inset, Figure 1). A range of η^3-coordination modes have also been reported for azaallyl complexes, with more single C–N and double C=C bond character in some cases.[24]

DFT calculations (ADF 2008.01, TZ2P, VWN, PW91, ZORA) were carried out to further probe the nature of the bonding in $H_2C{=}CH\text{-}BH_2$, VB^{Ph}, **1**, and **3**. All of the geometries were fully optimized, and those of **1** and **3** matched the solid-state structures, including a shortening of the B–C(1) bond in **3** by 0.035 Å relative to that in **1**. However, metal–boron distances were over-estimated by 3% in **1** and 9% in **3**, although this is not expected to significantly alter the overall analysis. The bonding in **1** and **3** was then investigated by using a fragment approach that considered the interaction of an uncharged $\{(tBu_3P)Pt\}$ or $\{(Ph_3P)_2Ni\}$ fragment with the neutral VB^{Ph} ligand (all fragments were generated from the geometry optimized structures of **1** and **3**).

In free $H_2C{=}CH\text{-}BH_2$, the HOMO is fully bonding across the BCC unit, and is analogous to the HOMO of an allyl cation. The LUMO + 1 is also analogous to that of an allyl cation, with nodes between B and C(1), and C(1) and C(2). However, the vinylborane LUMO is bonding in character between B and C(1), and antibonding in character between C(1) and C(2) owing to the lower electronegativity of boron relative to carbon. Analogous MOs were observed for VB^{Ph} (free and in **1** and **3**), although in this case several lower lying orbitals also exhibit π-bonding character within the BCC core.

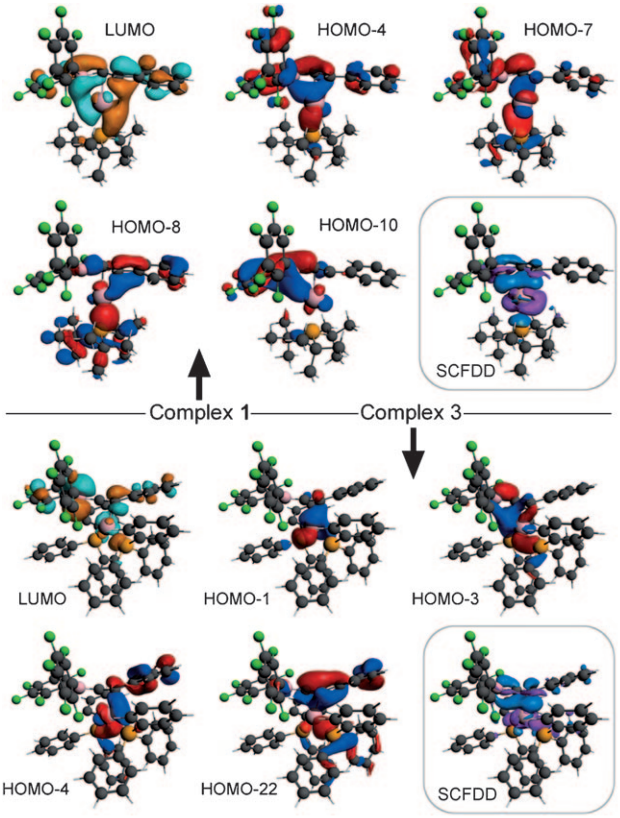

Figure 5. Key MOs involved in metal–VB^{Ph} bonding in **1** and **3**. Insets show SCF deformation density (SCFDD) isosurfaces (SCF electron density for the molecule minus the sum of the SCF electron density for the two fragments; blue is increased and pink is depleted electron density).

In complex **1** (Figure 5), the LUMO receives major contributions from the VB^{Ph} LUMO and both filled and empty $(tBu_3P)Pt$ orbitals that have Pt 5d or 6p character. Similarly, the HOMO-4 in **1** involves the VB^{Ph} HOMO and both filled and empty $(tBu_3P)Pt$ orbitals that have Pt 5d or 6s/6p character. The HOMO-7, HOMO-8, and HOMO-10 also play an important role in Pt–VB^{Ph} bonding and are shown in Figure 5. Overall, the VB^{Ph} ligand in **1** functions as both a donor and an acceptor, with dominating acceptor interactions, as shown by a value of −0.255 for the VB^{Ph} fragment obtained from Hirshfeld charge analysis. Regions of depleted or increased electron density, which arise from a combination of the $(tBu_3P)Pt$ and VB^{Ph} fragments, are also illustrated in the SCF deformation density isosurface in Figure 5.

The VB^{Ph} ligand in **3** also functions as both a donor and acceptor (Figure 5). However, the frontier metal orbitals of $(Ph_3P)_2Ni$ are higher in energy than those of $(tBu_3P)Pt$,[25] leading to a value of −0.404 for the VB^{Ph} fragment from the Hirshfeld charge analysis. Large contributions from the LUMO of the VB^{Ph} ligand to both the HOMO-3 and HOMO-4 of **3** are also observed, and more effective back-donation into the VB^{Ph} LUMO is consistent with the shorter B–C(1) distance observed experimentally and by DFT for **3**.

In summary, the first η^3-coordinated vinylborane complexes have been prepared, and adopt unique 1-borataallyl- or alkyl/borataalkene-like coordination modes. Future studies will explore the reactivity of these complexes with a focus on the availability of boron to interact with external substrates.

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[10] Crystal data for **1**: $C_{32}H_{34}BF_{10}PPt$, $M_r = 845.47$, $0.43 \times 0.22 \times 0.15\ mm^3$, triclinic, space group $P\bar{1}$; $a = 10.4467(7)$, $b = 16.4391(11)$, $c = 19.1813(14)$ Å, $\alpha = 99.1070(10)$, $\beta = 97.1550(10)$, $\gamma = 101.7510(10)$, $V = 3142.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.787\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 0.71073\ mm^{-1}$, $T = 100(2)$ K, $2\theta_{max} = 57°$, 42232 reflections, 15473 indep. ($R_{int} = 0.0530$), $R_1 = 0.0350$ and $wR_2 = 0.0641$ $[I > 2\sigma(I)]$, max. res. density peaks: 1.13 to −1.28 e Å^{-3}. Crystal data for **3**: $C_{56}H_{37}BF_{10}P_2Ni$, $M_r = 1031.34$, $0.58 \times 0.32 \times 0.30\ mm^3$, triclinic, space group $P\bar{1}$; $a = 10.1954(9)$, $b = 13.3921(11)$, $c = 17.7377(15)$ Å, $\alpha = 96.319(2)$, $\beta = 103.476(2)$, $\gamma = 98.237(2)$, $V = 2304.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.486\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 0.71073\ mm^{-1}$, $T = 100(2)$ K, $2\theta_{max} = 53°$, 22713 reflections, 9340 indep. ($R_{int} = 0.0301$), $R_1 = 0.0351$ and $wR_2 = 0.0786$ $[I > 2\sigma(I)]$, max. res. density peaks: 0.560 to −0.356 e Å^{-3}. Structures refined with Patterson methods. Hydrogen atoms in VB^{Ph} and PPh_3 were located and refined isotropically with thermal parameters set to $1.2 \times C_{attached}$. Hydrogen atoms in $PtBu_3$ were placed at calculated positions on $C_{attached}$ but with methyl group rotation refined to match highest points of electron density. CCDC 757289 (**1**) and CCDC 757290 (**3**) 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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[22] For molecule A in the unit cell of **1**, the *exo* H, *exo* C_6F_5, *endo* Ph, *endo* C_6F_5 and central H substituents are distorted from the BCC plane by 24.1°, 43.7°, −11.6°, −16.1° and −20.8°, respectively. For molecule B, these same distortions are 25.6°, 31.9°, −10.5°, −15.0° and −13.4°, and for **3** they are 9.0°, 17.2°, 11.2°, −5.2° and −1.0°.

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