

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*-element organometallic chemistry since the remarkably early synthesis of Zeise's salt, $K[PtCl_3(C_2H_4)] \cdot H_2O$, in 1827.^[1] By contrast, boron/carbon-based π -ligand complexes have been developed only in the past 50 years. Formally monoanionic boratabenzene^[2] and dianionic borole ligands,^[2] isoelectronic with arene and cyclopentadienyl ligands (Figure 1), are now prominent 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 Piers' $[Cp_2TaL_x\{CH_2B(C_6F_5)_2\}]$ ($L = CN^iBu$ and CO ; $x = 0$ or 1) (**III** in Figure 2), and η^3 -borataallyl complexes (Figure 1)^[4] are limited to Shapiro's $[PdCl_2\{\eta^3-PhB(CHPh)_2\}]$ and $[ZrCl_4\{\eta^3-PhB(CHPh)_2\}]$ (**I-II** in Figure 2).^[5] The $PhB(CHPh)_2$ ligand may be viewed as a borane-bridged diylide or a zwitterionic 1,3-di-phosphonium-substituted 2-borataallyl ligand.

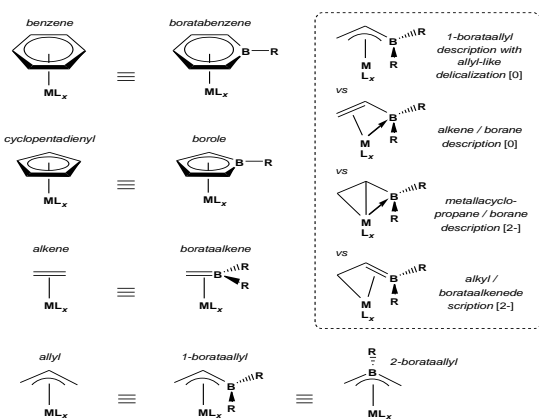


Figure 1. Structural relationships between common hydrocarbon π -ligands and their boron analogues. The inset shows 4 possible bonding descriptions for an η^3 -coordinated vinylborane, with formal charges on the ligand in square brackets.^[4]

Complexes of η^3 -coordinated R_2CCRBR_2 ligands or simple hydrocarbyl substituted R_2CBRCR_2 ligands are therefore unknown,

but are of particular interest given the generally enhanced reactivity of acyclic π -ligands relative to cyclic π -ligands (e.g. $allyl^-$ vs $C_5H_5^-$). Metal allyl complexes may be prepared by reaction of a suitable metal precursor with a source of an allyl anion or cation. Free vinylboranes are conceptually analogous to an allyl cation, and we describe herein reactions of $E-PhHC=CH-B(C_6F_5)_2$ (VB^{Ph})^[6] with low valent platinum and nickel precursors to yield η^3BCC -coordinated vinylborane complexes. Several possible bonding descriptions for an η^3 -vinylborane ligand are shown in Figure 1.

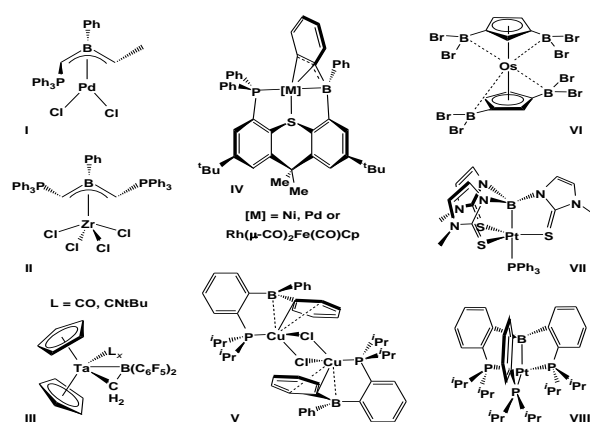


Figure 2. Selected complexes featuring $M-BR_3$ interactions. **I** and **II** are η^3 -coordinated borane-bridged diylide complexes.^[5] **III** is an η^2 -borataalkene complex. **IV** and **V** are η^3BCC -coordinated triarylborane complexes.^[7] **VI** is a metallocenylborane complex.^[8] **VII** and **VIII** are platinum η^1 -borane complexes.^[11-13]

Reaction of $E-PhHC=CH-B(C_6F_5)_2$ (VB^{Ph})^[6] with $[Pt(nb)_3]$ ($nb = \text{norbornylene}$), followed by addition of P^iBu_3 provided dark red $[(^iBu_3P)Pt(\eta^3BCC-VB^{Ph})]$ (**1**) in 68 % yield (Scheme 1). X-ray quality crystals of **1** (Figure 3) containing two independent molecules (A and B) in the unit cell were obtained from hexane at -30 °C.^[9] In both A and B, the VB^{Ph} ligand is η^3BCC -coordinated with P^iBu_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 $(Mes)_2BCH=CHPh$, $\{(F_5C_6)_2B\}_2C=CHPh$ and $B\{C(SiMe_3)=CHMe\}_3$ [1.54 - 1.57 Å], while the $C(1)-C(2)$ distances of 1.383(6) and 1.403(6) Å are slightly longer (cf. 1.33 - 1.365 Å in the vinylboranes above).^[10]

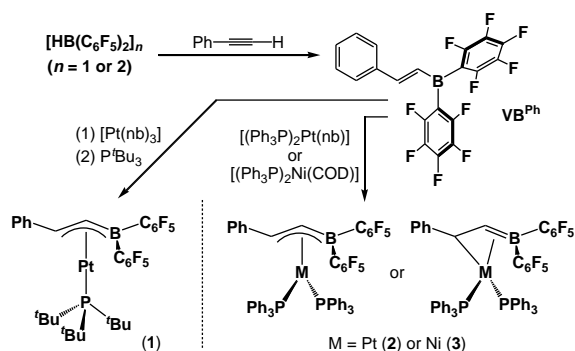
In molecule A, the $Pt-B$ distance is 2.273(5) Å, $Pt-C(1)$ is 2.130(4) Å, and $Pt-C(2)$ is 2.155(4) Å, indicative of strong η^3 -binding. In molecule B, the C_6F_5 rings lie at different angles relative to the BCC -core, leading to slightly different $Pt-B$, $Pt-C(1)$, and $Pt-C(2)$ distances [2.319(5), 2.126(4) and 2.137(4) Å, respectively]. Similar $M-B$ and $M-C$ distances were observed for **I** and **IV** ($M = Pd$ and Ni) in Figure 2, and the $M-C$ distances in **1** are comparable with those in $[Pd(\eta^3-C_3H_4Me)_2]$,^[11] $[(^iBu_3P)PtCl(\eta^3-C_3H_5)]$ ^[12] and $[(dmpe)Pt(\eta^3-C_3H_3Ph_2-1,3)][PF_6]$ ^[13] (2.13 - 2.23 Å). The $M-B$ distance in **1** is also comparable with those in η^1 -borane complexes such as **VIII** [2.296(2) Å;]^[14] in Figure 2 and is far shorter than

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[**] D.J.H.E. thanks NSERC of Canada for a Discovery Grant, the Ontario Ministry of Research and Innovation for an Early Researcher Award, and CFI and OIT for New Opportunities Grants. We are also very grateful to I. Vargas-Baca for help with DFT calculations, and J. F. Britten and H. A. Jenkins for help with X-ray crystallography.

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those in metallocenylboranes (e.g. **VI**).^[8] However, whereas boron is strongly pyramidalized in tightly bound η^1 -borane complexes, it is only modestly pyramidalized in **1** [$\Sigma(\text{C-B-C}) = 353$ and 357°].



Scheme 1. Synthesis of VB^{Ph} ,^[6] $[(^t\text{Bu}_3\text{P})\text{Pt}\{\eta^3\text{BCC-VB}^{\text{Ph}}\}]$ (**1**), $[(\text{Ph}_3\text{P})_2\text{Pt}\{\eta^3\text{BCC-VB}^{\text{Ph}}\}]$ (**2**) and $[(\text{Ph}_3\text{P})_2\text{Ni}\{\eta^3\text{BCC-VB}^{\text{Ph}}\}]$ (**3**).

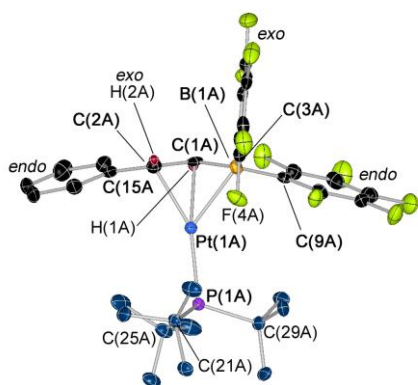


Figure 3. X-ray structure of **1** with thermal ellipsoids at 50% probability. Only molecule A (one of two independent molecules in the unit cell) is shown. Most hydrogen atoms are removed for clarity.

The η^3 -coordination mode in **1** contrasts the η^2 -alkene coordination mode in previously reported $[(\text{CO})_4\text{Fe}\{\text{H}_2\text{C}=\text{CH}-\text{BR}(\text{NMe}_2)\}]$ ($\text{R} = \text{Br}$ and Me)^[15] and $[\text{Cp}_2\text{Ti}(\text{ArH}=\text{CH}-\text{BCat})]$ ($\text{Ar} = \text{Ph}$ and $\text{C}_6\text{H}_4\text{OMe-}p$; $\text{Cat} = \text{O}_2\text{C}_6\text{H}_4$ or $\text{O}_2\text{C}_6\text{H}_3^t\text{Bu-4}$),^[16] likely due to much greater borane Lewis acidity in **1**. Related $[(\text{CO})_3\text{Fe}(\text{H}_2\text{C}=\text{CH}-\text{BR}-\text{NMe}_2)]$ ($\text{R} = \text{Br}$, Me and ^tBu)^[15] and $[(\text{CO})_4\text{Cr}\{\text{BuHC}=\text{CH}-\text{BH}-\text{N}(\text{SiMe}_3)_2\}]$ ^[17] complexes are also known, but in both cases the vinylborane is η^4 -coordinated and acts as a 4-electron donor; the former is a boron-nitrogen analogue of butadiene, while the latter binds via 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, while the *endo* [C(9) and C(15)] and central [H(1)] substituents bend towards the metal.^[22] Similar distortions were observed in $[\text{PdCl}_2\{\eta^3\text{-PhB}(\text{CHPPH}_3)_2\}]$,^[5] and are typical of late transition metal allyl complexes.^[18] 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 peak at 15.6 ppm; far upfield of free VB^{Ph} (58.3 ppm),^[6] and significantly upfield of **I**, **IV** (Pd and Ni) and **VIII** in Table 1 (35–18 ppm). In addition, ^{195}Pt satellites are observed for the *BCHCHPh* atoms ($^1J_{^{13}\text{C},^{195}\text{Pt}} = 196$ Hz; $^2J_{^1\text{H},^{195}\text{Pt}} = 47$ and 80 Hz) in the ^1H and ^{13}C NMR spectra of **1**. These data are consistent with tight $\eta^3\text{BCC}$ -coordination of VB^{Ph} .

To examine the generality of the $\eta^3\text{BCC}$ -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 phosphine co-ligands, $[(\text{Ph}_3\text{P})_2\text{Pt}\{\eta^3\text{BCC-VB}^{\text{Ph}}\}]$ (**2**) and $[(\text{Ph}_3\text{P})_2\text{Ni}\{\eta^3\text{BCC-VB}^{\text{Ph}}\}]$ (**3**), were prepared as shown in Scheme 1.^[24] Significant $^1J_{^{13}\text{C},^{195}\text{Pt}}$ (171 Hz), $^2J_{^1\text{H},^{195}\text{Pt}}$ (40 and 49 Hz) and $^2J_{^{13}\text{C},^{31}\text{P}}$ (30 and 16 Hz) couplings for the *BCHCHPh* atoms are indicative of strong metal–carbon interactions in **2** and **3**. However, the ^{11}B NMR signals for **2** and **3** (25 and 34 ppm, respectively) are shifted to higher frequency of complex **1**. By ^{31}P NMR, complexes **2** and **3** exhibit hindered rotation of VB^{Ph} around the metal–ligand axis. Substantial barriers to acyclic π -ligand rotation are also encountered in 16-electron allyl complexes such as $[(\text{Ph}_3\text{P})\text{ClPt}(\eta^3\text{-C}_3\text{H}_5)]$,^[19] and in a broad range of late transition metal alkene complexes.^[20]

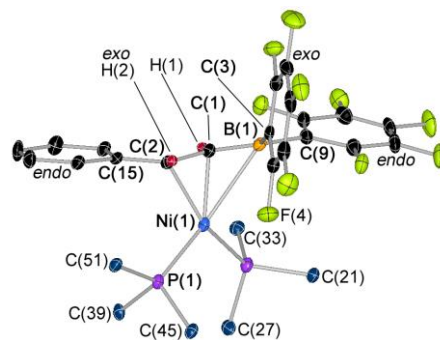


Figure 4. X-ray structure of **3** with thermal ellipsoids at 50% probability. Most hydrogen atoms are removed for clarity.

Crystals of **3** were obtained from a benzene/hexane mixture at -30 °C (Figure 4).^[9] 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, [3] a shorter B(1)–C(1) bond of 1.483(4) Å (*vide infra*), [4] a somewhat longer C(1)–C(2) distance of 1.431(3) Å, [5] less pronounced distortions of the *exo*-H, *exo*-C₆F₅, *endo*-C₆F₅ and 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**.^[21]

Returning to point 3 above, the B–C distance in **3** is in fact more similar to that found in free $\text{R}_2\text{B}=\text{CR}_2^-$ or $\text{R}_2\text{B}=\text{C}=\text{BR}_2^{2-}$ anions (1.39–1.51 Å)^[22] than in vinylboranes (*vide infra*), and is also shorter than those in Piers' tantalum borataalkene complexes (1.51–1.53 Å).^[23] These data, and distortion of both substituents on C(2) away from the metal, are indicative of more alkyl/borataalkene-like coordination (see inset in 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 metal–ligand bonding in $\text{H}_2\text{C}=\text{CH}-\text{BH}_2$, VB^{Ph} , **1**, and **3**. All geometries were fully optimized, and those of **1** and **3** match the solid state structures, including shortening of the B–C(1) bond in **3** by 0.035 Å relative to that in **1**. Metal–boron distances were however over-estimated by 3% in **1** and 9% in **3**, although this is not expected to alter significantly the overall analysis. Bonding in **1** and **3** was then investigated using a fragment approach that considered the interaction of an uncharged ($^t\text{Bu}_3\text{P}$)Pt or $(\text{Ph}_3\text{P})_2\text{Ni}$ fragment with the neutral VB^{Ph} ligand (all fragments were generated from the geometry optimized structures of **1** and **3**).

In free $\text{H}_2\text{C}=\text{CH}-\text{BH}_2$, 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, due to the lower electronegativity of boron relative to carbon, the vinylborane LUMO

is bonding in character between B and C(1), and antibonding in character between C(1) and C(2). 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.

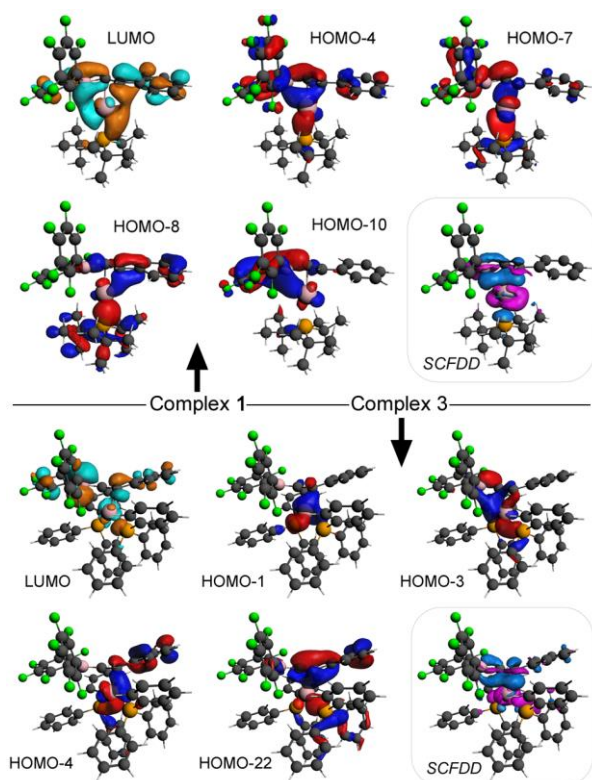


Figure 5. Key MOs involved in metal–VB^{Ph} bonding in **1** and **3**. Insets show SCF deformation density isosurfaces (SCF electron density for the molecule minus the sum of the SCF electron density for the two fragments; blue is increased and pink is depleted electron density).

In complex **1** (Figure 5), the LUMO receives major contributions from the VB^{Ph} LUMO and both filled and empty (Bu₃P)Pt orbitals of Pt 5*d*- or 6*p*-character. Similarly, the HOMO-4 in **1** involves the VB^{Ph} HOMO and both filled and empty (Bu₃P)Pt orbitals of Pt 5*d*- or 6*s*/6*p*-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 acceptor interactions dominating as evidenced by a value of –0.255 for the VB^{Ph} fragment by Hirshfeld charge analysis. Regions of depleted or increased electron density arising from combination of the (Bu₃P)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 donor and acceptor (Figure 5). However, the frontier metal orbitals of (Ph₃P)₂Ni are higher in energy than those of (Bu₃P)Pt,^[25] leading to a value of –0.404 for the VB^{Ph} fragment in 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 backdonation 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.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: Boranes · Isoelectronic analogues · Lewis acids · Pi ligands · Transition metals

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- [9] **Crystal data for 1:** C₃₂H₃₄BF₁₀Pt, *M_r* = 845.47, 0.43 x 0.22 x 0.15 mm, triclinic, space group *P*-1, *a* = 10.4467(7), *b* = 16.4391(11), *c* = 19.1813(14) Å, α = 99.1070(10), β = 97.1550(10), γ = 101.7510(10), *V* = 3142.2(4) Å³, *Z* = 4, ρ_{calc} = 1.787 Mg m⁻³, $\mu(\text{MoK}\alpha)$ = 0.71073 mm⁻¹, *T* = 100(2) K, 2 θ_{max} = 57°, 42232 reflections, 15473 indep. (*R*_{int} = 0.0530), *R*₁ = 0.0350 & *wR*₂ = 0.0641 [*I* > 2 σ (*I*)], max. res. density peaks: 1.13 to –1.28 eÅ⁻³. **Crystal data for 3:** C₅₆H₃₇BF₁₀P₂Ni, *M_r* = 1031.34, 0.58 x 0.32 x 0.30 mm, triclinic, space group *P*-1, *a* = 10.1954(9), *b* = 13.3921(11), *c* = 17.7377(15) Å, α = 96.319(2), β = 103.476(2), γ = 98.237(2), *V* = 2304.9(3) Å³, *Z* = 2, ρ_{calc} = 1.486 Mg m⁻³, $\mu(\text{MoK}\alpha)$ = 0.71073 mm⁻¹, *T* = 100(2) K, 2 θ_{max} = 53°, 22713 reflections, 9340 indep. (*R*_{int} = 0.0301), *R*₁ = 0.0351 & *wR*₂ = 0.0786 [*I* > 2 σ (*I*)], max. res. density peaks: 0.560 to –0.356 eÅ⁻³. Structures refined with Patterson methods. VB^{Ph} and PPh₃ H atoms located and refined isotropically with thermal parameters set to 1.2 x *C*_{attached}. H atoms in P'Bu₃ placed at calculated positions on C_{attached} but with methyl group rotation refined to match highest points of electron density. CCDC 757289 (**1**) and 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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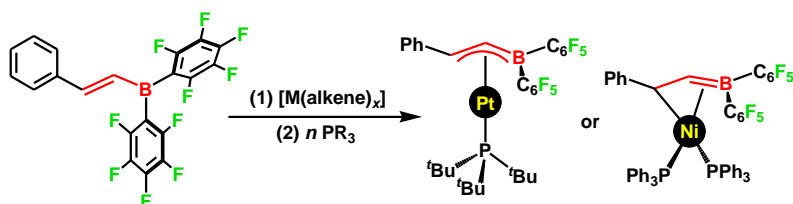
Entry for the Table of Contents (Please choose one layout)

Layout 2:

Anyone for Pie? It's Acyclic Borocarbon.

Kristopher B. Kolpin and David J. H. Emslie* _____ Page – Page

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



The vinylborane $\text{PhHC}=\text{CH}-\text{B}(\text{C}_6\text{F}_5)_2$ reacts with zero-valent Group 10 transition metal precursors to form η^3 -vinylborane complexes. The platinum tri-*tert*-butylphosphine complex exhibits an η^3 -borataallyl-like coordination mode whereas the nickel bis-triphenylphosphine complex tends towards alkyl/borataalkene coordination.