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A B–C Double Bond Unit Coordinated to Platinum: An Alkylideneboryl Ligand that Is Isoelectronic to Neutral Aminoborylene Ligands**

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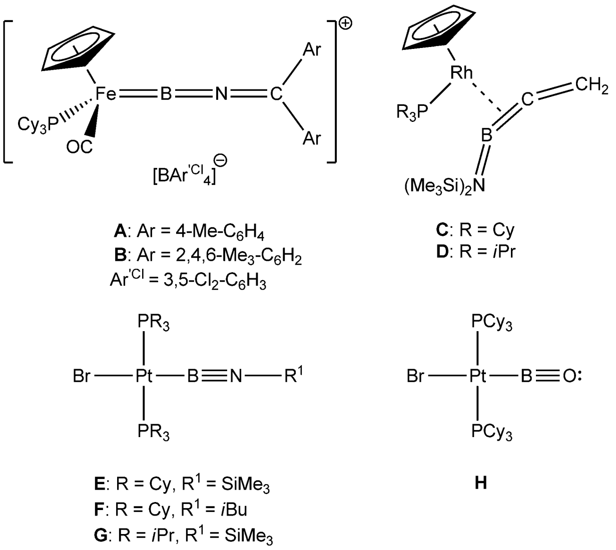
Abstract: *The reaction of [Pt(PCy$_3$)$_2$] with Br$_2$B-CH(SiMe$_3$)$_2$ resulted in generation of the first alkylideneboryl complex, trans-[Br(Cy$_3$P)$_2$Pt{B=CH(SiMe$_3$)}], with concomitant elimination of Me$_3$SiBr. The trans bromide ligand of the alkylideneboryl complex was readily substituted by a methyl group upon treatment with methyllithium, leading to another alkylideneboryl complex, trans-[Me(Cy$_3$P)$_2$Pt{B=CH(SiMe$_3$)}]. Various spectrochemical techniques, single-crystal X-ray crystallography, and quantum chemical calculations confirmed the formulation of a double bond between the boron and the carbon atom. The theoretical studies also provided evidence for the stronger trans influence of the alkylideneboryl ligand over iminoboryl and oxoboryl ligands.*



Scheme 1. Recently reported iminoborylene complexes (**A** and **B**), 1-aza-2-borabutatriene rhodium complexes (**C** and **D**), iminoboryl complexes (**E**–**G**), and an oxoboryl complex (**H**).

From merely a laboratory curiosity, multiply bound boron compounds have become key synthetic targets in recent years, a fact that can be witnessed from an exponential growth in the number of publications on the topic.[1] Among multiply bound boron systems, compounds featuring a B–C double bond are of special interest because they are electronically comparable to vinyl cations or Schrock-type alkylidene complexes.[2] The parent borene (HB=CH$_2$) has been detected only by IR spectroscopy in an argon matrix,[3] and still remains synthetically elusive. Nevertheless, a number of main-group-substituted alkylideneborane compounds have been isolated; noteworthy in this context are contributions by the groups of Berndt,[2a,4] Nöth,[5] Paetzold,[6] and others.[7] A conceptually different approach to realizing such low-coordinate main-group compounds is to stabilize them in the coordination sphere of a transition-metal fragment. Following this strategy, many recent advances have been achieved in the fields of transition-metal borylene and silylene complexes.[8] In 2011 Aldridge et al. synthesized two cationic iminoborylenes **A** and **B** (Scheme 1) in the coordination sphere of iron.[9] However, apart from our recent realization of two rhodium complexes possessing π-bound (B,C) boraallene ligands **C** and **D**, the isolation of a true B=C doubly bound compound in the coordination sphere of transition metals is still elusive.[10] Moreover, a better understanding of the electronic properties such as σ-donation, π-acceptance, *trans* influence and metal-binding abilities of alkylideneboryl systems is of significant interest, as is a quantitative comparison of them with other analogous ligands known to have strong σ-donor capabilities (for example, iminoboryl and oxoboryl ligands).[11]

Very recently, our group synthesized the series of iminoboryl complexes *trans*-[(R$_3$P)$_2$BrPt(B≡NR^1)] (**E**: R = Cy, R^1 = SiMe$_3$; **F**: R = Cy, R^1 = *i*Bu; **G**: R = *i*Pr, R^1 = SiMe$_3$)[12] of platinum, which was followed by the isolation of the first oxoboryl complex *trans*-[(Cy$_3$P)$_2$BrPt(B≡O)] (**H**).[13] The preparation involved oxidative addition of a B–Br bond of (Me$_3$Si)$_2$NBBr$_2$ or Me$_3$SiOBBr$_2$ to [Pt(PCy$_3$)$_2$] (**1**) and subsequent spontaneous elimination of Me$_3$SiBr at room temperature. We anticipated that this method might be

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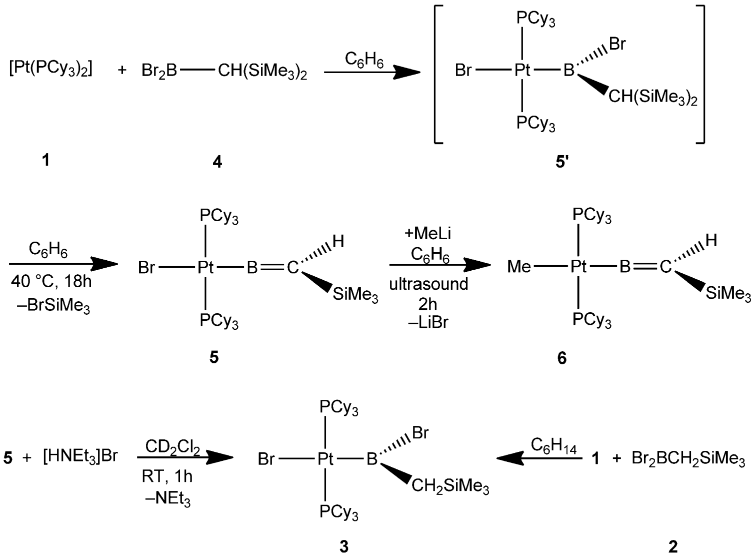
extended to isolating alkylideneboryl complexes with a platinum-bound B–C double bond unit. Herein, we describe a convenient method for the isolation of alkylideneboryl complexes.

At the outset of our investigation, we reasoned that any precursor borane suitable for alkylideneborane synthesis should contain a trimethylsilyl group to induce halosilane elimination. Accordingly, the known dibromoborane, $Br_2BCH_2SiMe_3$ (**2**)[14] was treated with **1**, resulting in isolation of the platinum(II) boryl complex *trans*-[Br($Cy_3P)_2Pt\{B(Br)CH_2SiMe_3\}$] (**3**) in 88% yield (Scheme 2). In the $^{31}P\{^1H\}$ NMR spectrum, **3** shows an upfield shift (δ = 21.0 ppm $^1J_{PPt}$ = 2933 Hz) with respect to **1** (δ = 62.3 ppm, $^1J_{PPt}$ = 4160 Hz), indicating the formation of a square-planar Pt^{II} complex.[15] However, despite the proximity of the bromide and the trimethylsilyl substituent, **3** did not eliminate bromosilane even at 150 °C in various solvents or under irradiation. The molecular structure of **3** (see Figure S1 in the Supporting Information)[26] reveals that the Pt–B and Pt–Br distances are 1.995(5) and 2.628(3) Å, respectively, which are similar to those reported for *trans*-[Br($Cy_3P)_2Pt\{B(Fc)Br\}$] (Fc = ferrocenyl)[16] and other related boryl complexes.[15,17]



Scheme 2. Syntheses of the platinum(II) alkylboryl complex **3**, the platinum(II) alkylideneboryl complexes **5** and **6**, and a 1,2-dipolar addition to **5**.

As the synthesis of a platinum alkylideneboryl complex was not successful with borane **2**, we then sought to increase the steric demand of the dibromoborane. Stoichiometric reaction of $LiCH(SiMe_3)_2$ with BBr_3 in hexane at −78 °C resulted in the formation of a bulkier borane, $Br_2BCH(SiMe_3)_2$ (**4**), which was characterized by means of multinuclear NMR spectroscopy (see the Supporting Information).

Monitoring the reaction of the newly prepared borane **4** with **1** by $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of a colorless complex assumed to be *trans*-[Br($Cy_3P)_2Pt\{B(Br)CH(SiMe_3)_2\}$] (**5′**) initially, which eventually led to the yellow platinum alkylideneboryl complex *trans*-[Br($Cy_3P)_2Pt\{B{=}CH(SiMe_3)\}$] (**5**; Scheme 2). Although platinum boryl complex **5′** could not be isolated owing to spontaneous liberation of Me_3SiBr at room temperature, the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures initially showed a resonance at δ = 17.1 ppm ($^1J_{PPt}$ = 3066 Hz), which matches well with those of **3** (Scheme 2). The intensity of the resonances for **5′** started to decrease rapidly and a new peak appeared at δ = 30.4 ppm ($^1J_{PPt}$ = 2482 Hz). It was also observed from ^1H NMR spectroscopy that the conversion rate from **5′** to **5** can be increased by heating the reaction mixture to 40 °C. The new signal corresponds to the alkylideneboryl complex **5** and the coupling constant was in the range of those found for reported platinum(II) iminoboryl complexes (**E**: 2389 Hz, **F**: 2427 Hz, **G**: 2412 Hz; Scheme 1), indicating that the boron atom in **5** is two-coordinate.[12] The ^{11}B NMR signal of **5** appeared at δ = 41 ppm as a broad singlet, at a lower frequency than that of **4** (δ = 56 ppm). The IR spectrum of **5** shows an absorption band at 1442 cm^{-1}. Complex **5** did not show any propensity towards oligomerization or decomposition even after heating to 60 °C for 48 h. At 80 °C, it started to decompose slowly and as a result, the commonly observed byproducts *trans*-[Br($Cy_3P)_2PtH$] and *trans*-[($Cy_3P)_2PtBr_2$], along with **1**, could be detected in the $^{31}P\{^1H\}$ NMR spectrum. Recrystallization from various solvents (toluene, hexane, benzene, fluorobenzene, and binary solutions thereof) afforded yellow single crystals of **5**, from which we were able to confirm its constitution by single-crystal X-ray crystallography. However, from all of these crystalline samples, the obtained structural parameters were unreliable owing to massive disorder in the single crystals resulting from the superposition of the bromide atom and the alkylideneboryl ligand. It should be noted that we encountered a similar crystallographic problem while determining the molecular structure of the oxoboryl complex, *trans*-[Br($Cy_3P)_2PtB{\equiv}O$] (**H**).[13]

Although alkylideneboryl complex **5** is thermally less-stable than the iminoboryl (**E**) and oxoboryl (**H**) complexes, it reacts with an excess of methyllithium in [D_6]benzene. After 2 h in an ultrasound bath, the yellow color of the solution was retained; however, a colorless precipitate formed. The signals for complex **5** disappeared and new signals at δ = 27.0 ppm ($^1J_{PPt}$ = 2606 Hz) were detected in the $^{31}P\{^1H\}$ NMR spectrum. The ^{11}B NMR spectrum exhibits a very broad singlet at δ = 52 ppm. On account of these NMR data, we proposed the formulation of *trans*-[Me($Cy_3P)_2Pt\{B{=}CH(SiMe_3)\}$] (**6**; Scheme 2). Replacement of the *trans* bromide ligand by a methyl group led to a marginally upfield chemical shift for **6** (δ = 27.0 ppm) in the $^{31}P\{^1H\}$ NMR spectrum with respect to those of **5** (δ = 30.4 ppm).[13] In contrast, the ^{11}B NMR signal (δ = 52 ppm) was found at much higher frequency than that observed for **5** (δ = 41 ppm), which is presumably due to a lesser degree of shielding of the boron atom in complex **6**. Complex **6** also shows an absorption band at 1442 cm^{-1}, which can be assigned to the B=C stretching vibration. This result corresponds very well with the B=C stretching mode of $HB{=}CH_2$ in the gas phase at 1470 cm^{-1}.[3]

The platinum(II) complexes **5** and **6**, together with the amino(neopentylidene)borane (*t*Bu)HC=B=N(SiMe$_3$)(*t*Bu) (**I**)[18] reported by Paetzold et al., are the only neutral alkylideneboranes with a hydrogen atom bound to the carbon atom of the B–C double bond. However, reliable X-ray data for compound **I** were not obtained.

Crystallization of **6** from a hexane solution by diffusion with benzene/toluene resulted in yellow crystals suitable for X-ray diffraction analysis (Figure 1).[26] Complex **6** crystallizes in the monoclinic space group $P2_1/c$ and shows a square planar geometry around the platinum center. The methyl group, the platinum atom, the boron atom, and the alkylidene carbon atom (C2) are roughly linear. Carbon atom C2 is sp^2-hybridized, although the B-C2-Si angle (134.5(3)°) is slightly larger than 120°, which is presumably due to the low steric demand of the hydrogen atom at C2. The boron atom is sp-hybridized, exhibits a linear geometry, and the [B=CR$_2$]$^-$ ligand is isoelectronic to the [B=NR$_2$] unit in *trans*-[(Cy$_3$P)$_2$BrPt{=B=N(AlCl$_3$)(SiMe$_3$)}] or [(OC)$_2$CpFe={B=N(Cy)$_2$}][BAr^F] (Cp = η^5-cyclopentadienyl, Ar^F = 3,5-bis(trifluoromethyl)phenyl).[19] The B=C bond length (1.373(5) Å) is similar to those reported for main-group-substituted alkylideneboranes (that is, *t*BuB=C(SiMe$_3$)$_2$ (**J**) 1.361(5) Å; {Me$_2$(MeDurB)C}B=C(SiMe$_3$)(SiMe$_2$Dur) (Dur = 2,3,5,6-Me$_4$C$_6$H) (**K**) 1.363(9) Å), thus unequivocally confirming the formation of a B–C double bond.[4c,20]

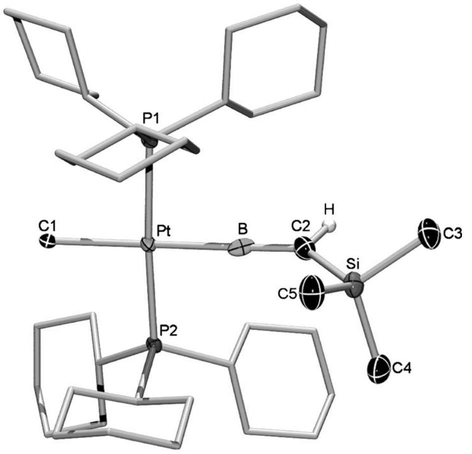


Figure 1. Molecular structure of *trans*-[Me(Cy$_3$P)$_2$Pt{B=CH(SiMe$_3$)}] (**6**). Ellipsoids are set at 50% probability. Hydrogen atoms (except for the proton at the alkylideneboryl moiety), solvent molecules, and ellipsoids of cyclohexyl groups have been omitted for clarity. Relevant bond lengths [Å] and angles [°]: Pt–B 2.033(4), Pt–C1 2.195(3), B–C2 1.373(5); C1-Pt-B 174.8(13), Pt-B-C2 177.5(3), P1-Pt-P2 176.2(1), B-C2-Si 134.5(3).[26]

Comparison of the B=C bond length of compound **6** with the aforementioned rhodium π-alkylideneborane complex **C** (1.489(12) Å) shows that the σ-coordinated B=C unit in platinum complex **6** is almost 12 pm shorter than in **C**. This finding is attributed to the presence of back-bonding from the rhodium to an antibonding π* orbital of the double-bond-containing ligand, which also results in a bent coordination of the 1-aza-2-bora-butatriene in **C**.[10]

Very recently, Zhu, Lin, and Marder presented an in-depth computational evaluation of the *trans* influence of boryl, aminoboryl, and related ligands,[21] while our group has covered the same topic experimentally.[15a] To better understand the electronic structure of **6** as well as to comprehend the *trans*-influence of the alkylideneboryl ligand, we carried out density functional theory calculations at the B3LYP level (see the Supporting Information for more details).[22] The calculated structure of **6** is in excellent agreement with the observed structure (Figure 2; Supporting Information, Figure S3). The Pt–B bond is single in nature with a Wiberg Bond Index (WBI) of 0.812. The HOMO corresponds to the B–C π bond with some amount of Pt–B antibonding contribution stemming from the Pt d orbital. We also observed a MO (HOMO−6) that corresponds to the interaction of the Pt (d$_{xy}$) orbital with the B in-plane (p$_x$) orbital. However, this interaction is not strong enough to form a Pt–B π bond. The inability of the strong σ-donating alkylideneboryl ligand to form a π bond with the Pt atom is traced to the high energies of its π acceptor orbitals (ca. 3.70 eV and 4.13 eV respectively; Supporting Information, Figure S2). Also, the calculated bond length and order of the B–C double bond of **6** (bond length = 1.416 Å; WBI = 1.415) is similar to that of the free ligand (bond length = 1.443 Å; WBI = 1.416), further highlighting the lack of back-bonding interactions between Pt and the alkylideneboryl ligand. Such a bonding model incorporating little or no Pt–B back-bonding is consistent with the previous theoretical studies carried out on **H**.[23]

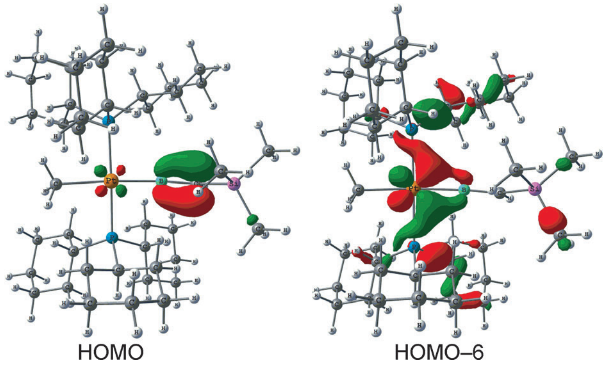


Figure 2. Important molecular orbitals contributing to the electronic structure of *trans*-[Me(Cy$_3$P)$_2$Pt{B=CH(SiMe$_3$)}] (**6**).

To compare the relative *trans* influences of imino-, oxo-, and alkylideneboryl ligands, we have optimized the geometries of the bare ligands and that of **E**, **H**, and the platinum alkylideneboryl complex *trans*-[Br(Cy$_3$P)$_2$Pt{B=CH(SiMe$_3$)}] (**5**) at the same level of theory (Supporting Information, Figures S2, S3). The calculated energies of the σ-symmetric HOMO, which is mainly concentrated at the B atom of these ligands, are −0.34, −0.23, and −0.20 eV for imino-, oxo-, and alkylideneboryl ligands, respectively. Thus, of these ligands, the alkylideneboryl ligand exhibits the strongest *trans* influence, in accordance with the calculated Pt–Br distances of **E** (2.633 Å), **H** (2.613 Å), and **5** (2.650 Å).

With an interest in investigating the reactivity of the title compound further, we reacted **5** with various unsaturated organic substrates, such as diphenylacetylene, adamantylphosphaalkyne, trimethylsilylazide, and *N*,α-diphenylnitrone. However, unlike main-group-substituted alkylideneboranes, **5** did not show any propensity towards cycloaddition reactions.[5a,6a,24] Instead, resembling the reactivity pattern of iminoboryl complex **E**, **5** underwent a 1,2-dipolar addition reaction with anhydrous ethereal HCl, leading to *trans*-$[Br(Cy_3P)_2Pt\{B(Cl)CH_2SiMe_3\}]$.[25] Multinuclear NMR spectroscopy verified the formation of the latter but also indicated the formation of several side-products, such as *trans*-$[Cl(Cy_3P)_2PtH]$ and *trans*-$[Br(Cy_3P)_2PtH]$. Despite using a variety of reaction conditions, the aforementioned boryl complex could not be obtained on a preparative scale, and as a result a full characterization of the latter was not possible. Therefore, we treated **5** with $[HNEt_3]Br$, resulting in isolation of the boryl complex **3**, along with the release of triethylamine (Scheme 2). The formation of **3** by this method was indicated by NMR spectroscopy and was verified by comparison with a pure sample of **3** prepared according to Scheme 2. Note that, unlike **E**, the addition of hydrogen bromide to the B–C double bond of **5** in this manner was found to be irreversible.[25]

In summary, we have demonstrated the systematic reaction of an electron-rich, coordinatively unsaturated transition metal complex with custom-designed haloboranes, leading to the first transition-metal complex with a terminally bound $B{=}CR_2$ ligand that is isoelectronic to aminoborylene ligands. Additionally, we have described the reactivity of an alkylideneboryl complex (**5**), which undergoes facile σ-bond metathesis to afford another alkylideneboryl complex (**6**), and a 1,2-dipolar addition reaction to give rise to a boryl complex (**3**). Quantum-chemical calculations on complexes **5** and **6** showed that the alkylideneboryl ligand is a strong σ-donor and thus exhibits a very strong *trans* influence. These findings invite the construction of many more multiply bound boron complexes and provide a snapshot of their manifold reactivity.

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[26] CCDC 966870 (**3**) and CCDC 966871 (**6**) 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.