

B=B and B≡E (E = N and O) Multiple Bonds in the Coordination Sphere of Late Transition Metals

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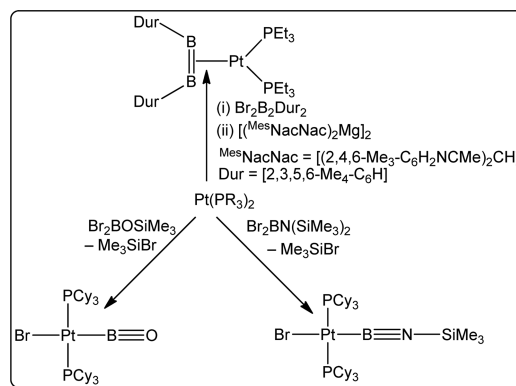
CONSPECTUS

Because of their unusual structural and bonding motifs, multiply bonded boron compounds are fundamentally important to chemists, leading to enormous research interest. To access these compounds, researchers have introduced sterically demanding ligands that provide kinetic as well as electronic stability. A conceptually different approach to the synthesis of such compounds involves the use of an electron-rich, coordinatively unsaturated transition metal fragment. To isolate the plethora of borane, boryl, and borylene complexes, chemists have also used the coordination sphere of transition metals to stabilize reactive motifs in these molecules. In this Account, we summarize our results showing that increasingly synthetically challenging targets such as iminoboryl (B=N), oxoboryl (B=O), and diborene (B=B) fragments can be stabilized in the coordination sphere of late transition metals.

This journey began with the isolation of two new iminoboryl ligands *trans*-[(Cy₃P)₂(Br)M(B=N(SiMe₃))] (M = Pd, Pt) attached to palladium and platinum fragments. The synthesis involved oxidative addition of the B–Br bond in (Me₃Si)₂N=BBr₂ to [M(PCy₃)₂] (M = Pt, Pd) and the subsequent elimination of Me₃SiBr at room temperature. Variation of the metal, the metal-bound coligands, and the substituent at the nitrogen atom afforded a series of analogous iminoboryl complexes. Following the same synthetic strategy, we also synthesized the first oxoboryl complex *trans*-[(Cy₃P)₂BrPt(BO)]. The labile bromide ligand adjacent to platinum makes the complex a viable candidate for further substitution reactions, which led to a number of new oxoboryl complexes. In addition to allowing us to isolate these fundamental compounds, the synthetic strategy is very convenient and minimizes byproducts. We also discuss the reaction chemistry of these types of compounds.

In addition to facilitating the isolation of compounds with B≡E (E = N, O) triple bonds, the platinum fragment can also stabilize a diborene (RB=BR) moiety, a bonding motif that thus far had only been accessible when stabilized by N-heterocyclic carbenes (NHCs). In the new π -diborene [(Et₃P)₂Pt(B₂Dur₂)] (Dur = 2,3,5,6-Me₄-C₆H) complex, the diborene ligand receives electron density from Pt, leading to a strong Pt–B bond and a B=B bond. We attribute this result to the very short B=B bond distance (1.51(2) Å) while coordinated to platinum.

Overall, an increasing number of chemists are examining the chemistry of multiply bound boron compounds. The isolation of an oxoboryl complex is of special interest not only from a structural standpoint but also because of its orbital similarities to the ubiquitous CO ligand. Detailed computational studies of the π -diborene complex [(Et₃P)₂Pt(B₂Dur₂)] show that the bonding properties of this molecule violate the widely accepted Dewar–Chatt–Duncanson (DCD) bonding model.

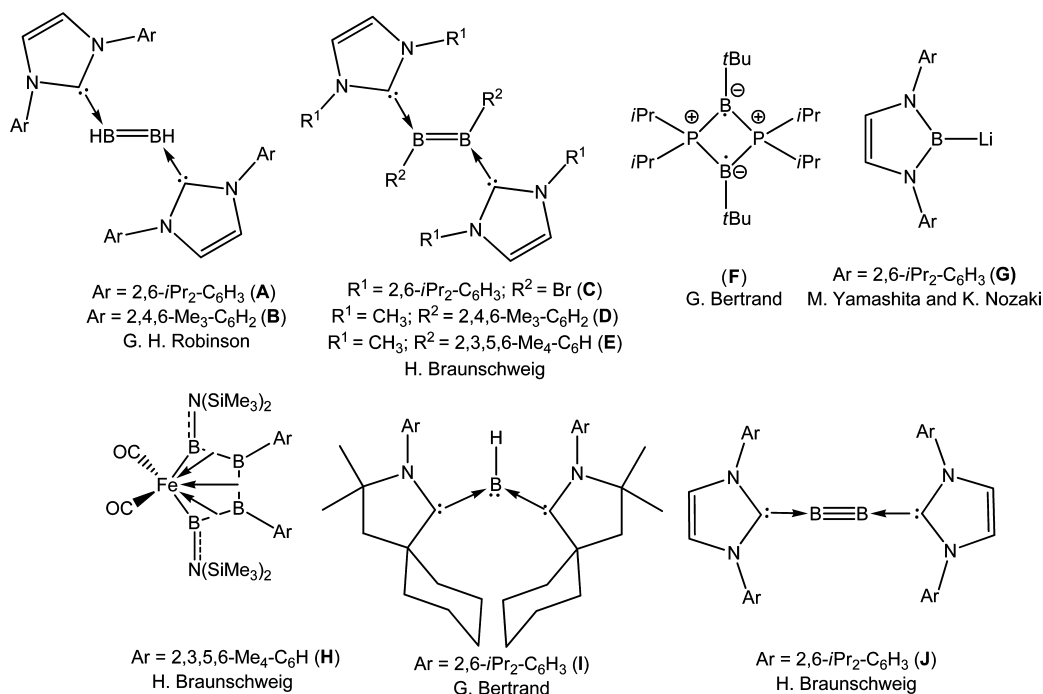


Introduction

The molecular chemistry of boron has become one of the most exciting research topics in recent years. Several unusual compounds, such as diborenes (**A–E**),^{1–4} boron diradicals (**F**),⁵ boryl anions (**G**),⁶ and complexes with homocatenated B₄ chains (**H**),⁷ have recently been experimentally realized.

Some selected examples are depicted in Chart 1. Although these fundamental compounds have already been subject of many reviews⁸ and fall outside the scope of this Account, the introduction would be lopsided without acknowledging two recent developments in low-valent boron chemistry: (i) a parent borylene stabilized by cyclic (alkyl)(amino)carbenes

CHART 1. Unique Structural Motifs Featuring Boron (A–J)



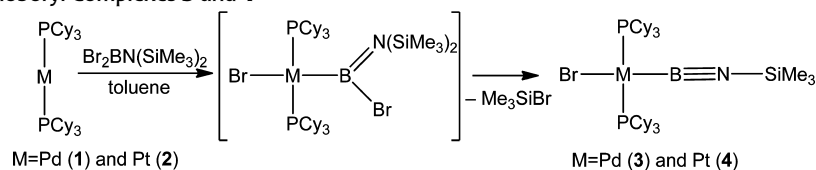
(cAACs) (I) from the group of Bertrand⁹ and (ii) a neutral diboryne supported by N-heterocyclic carbene (NHC)³ (J) from our laboratory. Such advances ensure that low valent boron chemistry will continue to thrive and that practicing boron chemistry has never been as rewarding as it is now.

Due to their isoelectronic relationships with alkynes and nitriles, respectively, iminoboranes (L–B≡N–R) and oxoboranes (L–B≡O) have garnered intense research interest. However, the situation regarding their synthesis remains very delicate. The typical reduction of haloboranes, by far the best method for constructing B–B multiple bonds, is not very useful for synthesizing compounds with B≡E (E = N and O) triple bonds. Decades ago, the groups of Paetzold, Klingebiel, and Elter independently reported the elimination of halosilanes from sterically encumbered aminoboranes leading to main-group-substituted iminoboranes.¹⁰ However, the elimination of halosilanes generally requires forcing conditions (~400–500 °C), and in some cases, there are issues with side products and poor yields. Before this work, the formation of oxoboranes had only been detected in gas phase or matrix isolation studies,¹¹ and a structurally characterized oxoborane remained elusive.

Until now, the majority of the synthetic approaches to the isolation of stable compounds with multiply bound boron atoms involved the use of sterically demanding neutral (NHCs or cAACs)¹² or monoanionic (β -diketiminato) ligands

as stabilizing groups. The exploitation of such sterically demanding ligands circumvents the kinetic instability as well as populates the vacant orbitals on the boron atoms. In addition to these classical approaches, a promising alternative route is to stabilize such transient species in the coordination sphere of an electron-rich, coordinatively unsaturated transition metal fragment. Such a synthetic strategy can be evidenced in the fields of transition metal borylene and silylene complexes, where the borylene and silylenes moieties are directly bound to the transition metals.¹³ A further impetus comes from the contributions of Hartwig, Marder, Yamashita, Nozaki, Aldridge, and others on the stabilization of borane and boryl complexes in the coordination sphere of early and late transition metals.¹⁴ The stability of these complexes stems from the strong σ -donation ability of boryls or borylenes to the transition metals. Theoretical studies indicated that like borylenes, iminoboryl (B≡N⁻) and oxoboryl (B≡O⁻) moieties are also strong σ -donors.¹⁵ Therefore, it seemed valid to envisage the isolation of transition metal complexes with iminoboryl and oxoboryl ligands.

While investigating the chemistry of transition metal boryl and borylene complexes, we observed that the reaction of Na[(η^5 -C₅H₅)Ru(CO)₂] with [(Me₃Si)₂N=BCl₂] led to a boryl complex [(η^5 -C₅H₅)Ru(CO)₂–B(Cl)=N(SiMe₃)–B(Cl)=N(SiMe₃)₂] with subsequent elimination of Me₃SiCl at ambient temperature.¹⁶ An iminoboryl complex [(η^5 -C₅H₅)Ru(CO)₂–B≡N(SiMe₃)]

SCHEME 1. Synthesis of Iminoboryl Complexes **3** and **4**TABLE 1. Essential Spectroscopic and Structural Features of Iminoboryl Complexes **3**, **4**, **6**, **7**, and **9** and Complexes **10**–**18** Derived Therefrom

compound	¹¹ B (ppm)	³¹ P, ppm (¹ J _{P,Pt} , Hz)	B–N (Å)	M–B (Å)	M–Br (Å)
<i>trans</i> -[(Cy ₃ P) ₂ BrPd(B≡N(SiMe ₃))] (3)	22.0	34.3	1.255 ^a	1.963 ^a	2.538 ^a
<i>trans</i> -[(Cy ₃ P) ₂ BrPt(B≡N(SiMe ₃))] (4)	25.9	31.2 (2389)	1.260(4)	1.960(3)	2.552(1)
<i>trans</i> -[(iPr ₃ P) ₂ BrPt(B≡N(SiMe ₃))] (6)	16.9	42.7 (2412)	1.265(7)	1.959(3)	2.544(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt(B≡N <i>i</i> Bu)] (7)	33.6	31.5 (2427)			
<i>cis,mer</i> -[(Me ₃ P) ₃ Br ₂ Rh(B≡NSiMe ₃)] (9)	27.0	1.6 (126), –13.9 (89)	1.255(7)	1.956(6)	2.623(1), 2.586(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{BN(SiMe ₃)(AlCl ₃)}] (10)	45.6	31.2 (2135)	1.330(3)	1.904(3)	2.528(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{BH(N(Bcat)(SiMe ₃))}] (11)	58.0 (Pt–B), 27.0 (Bcat)	22.9 (3107)	1.452(3)	2.020(3)	2.632(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{BHN(SiMe ₃)BO ₂ }] ₂ C ₆ H ₂] (12)	^b	22.8 (3087)	1.456(6)	2.010(5)	2.631(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{B(OH)(NH(SiMe ₃))}] (13)	32.5	25.7 (2894)			
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{B(Br)(NH(SiMe ₃))}] (14)	38.0	20.2 (2805)	1.409(3)	2.001(3)	2.591(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{B(OMe)(NH(SiMe ₃))}] (15)	30.3	25.4 (2923)	1.432(3)	2.053(2)	2.635(1)
<i>trans</i> -[(Cy ₃ P) ₂ BrPt{B(NHPh)(NH(SiMe ₃))}] (16)	31.7	21.3 (2907)	1.444(5)	2.048(4)	2.658(1)
1,4- <i>trans</i> -[(Cy ₃ P) ₂ BrPt{B(NH <i>i</i> Bu)(NH)}] ₂ C ₆ H ₄] (17)	^b	21.5 (2957)	1.429(7)	2.048(4)	2.631(1)
<i>trans</i> -[(Cy ₃ P) ₂ Pt(B≡NSiMe ₃)(C≡CPh)] (18)	^b	30.3 (2397)			

^aMean. ^bNot found.

was assumed as an intermediate, which presumably underwent a 1,2-dipolar addition reaction with one equivalent of [(Me₃Si)₂N=BCl₂] to yield the final product. We reasoned that the key step for the formation of iminoborane would be the elimination of halosilane and contemplated that the reactions of boranes comprising trimethylsilyl substituents with electron-rich unsaturated transition metal fragments may lead to imino- and oxoboranes. However, the key question arises regarding how to deal with the polarization of the B≡N and B≡O triple bond, assumed to be responsible for their susceptibility toward dipolar reactions or oligomerization. DFT calculations suggested that the introduction of π -donor ligands in the transition metal scaffold would enhance the backbonding from metal to boron and provide electronic stability. Thus, Na[(η^5 -C₅H₅)Ru(CO)₂] was replaced with [M(PCy₃)₂] (M = Pd (**1**) and Pt (**2**)). The reaction of **1** and **2** with [(Me₃Si)₂N=BBr₂] led to complexes with a B≡N triple bond. The reactions proceed via oxidative addition of the B–Br bond of the aminoborane to the metal fragments, followed by subsequent elimination of bromosilane. The synthetic protocol was further extended to the preparation of a complex with a B≡O triple bond. In this Account, we will present our findings on the synthetic, spectroscopic, and structural features of late-transition-metal-supported multiply bound boron compounds. We will also discuss our findings regarding the subsequent reactivity of the iminoboryl and oxoboryl complexes.

Synthesis, Spectroscopic, and Structural Elucidation of Iminoboryl Complexes

Electron-rich complexes **1** and **2** were chosen as transition metal fragments to initiate the study for the following reasons: (i) they were easy to synthesize,¹⁷ (ii) they bind strongly to boron and provide adequate steric bulk, as observed in our contemporaneous isolation of a boryl cation *trans*-[(Cy₃P)₂Pt{B(Fc)Br}][BAR^F₄] and a base-stabilized borylene complex *trans*-[(Cy₃P)₂PtBr{B(Fc)(NC₅H₄-4-Me)}][BAR^F₄] (Ar^F = 3,5-(CF₃)₂C₆H₃),¹⁸ (iii) they provide the opportunity to fine-tune the transition metal fragments by alteration of the phosphine alkyl substituents, and (iv) they are easy to monitor by NMR spectroscopy due to ³¹P NMR resonances associated with ¹⁹⁵Pt satellites. The reactions of **1** and **2** with [(Me₃Si)₂N=BBr₂] smoothly resulted in *trans*-[(Cy₃P)₂BrM(B≡N(SiMe₃))] (M = Pd (**3**) and Pt (**4**)) with concomitant liberation of Me₃SiBr [Scheme 1].¹⁹ It can be assumed that the reactions proceed through the formation of intermediate boryl complexes *trans*-[(Cy₃P)₂BrM{B(Br)(N(SiMe₃)₂)}], although these were not spectroscopically detected. Essential spectroscopic and structural features of iminoboryl and related complexes are summarized in Table 1. The presence of B≡N triple bonds was authenticated by X-ray crystallographic studies, which revealed that the B≡N bond lengths in **3** and **4** are 1.255 (mean) and 1.260(4) Å [Figure 1]. The relatively short M–B bonds [**3**, 1.963 (mean) and **4**, 1.960(3) Å] compared with boryl complexes¹⁴ can be rationalized in

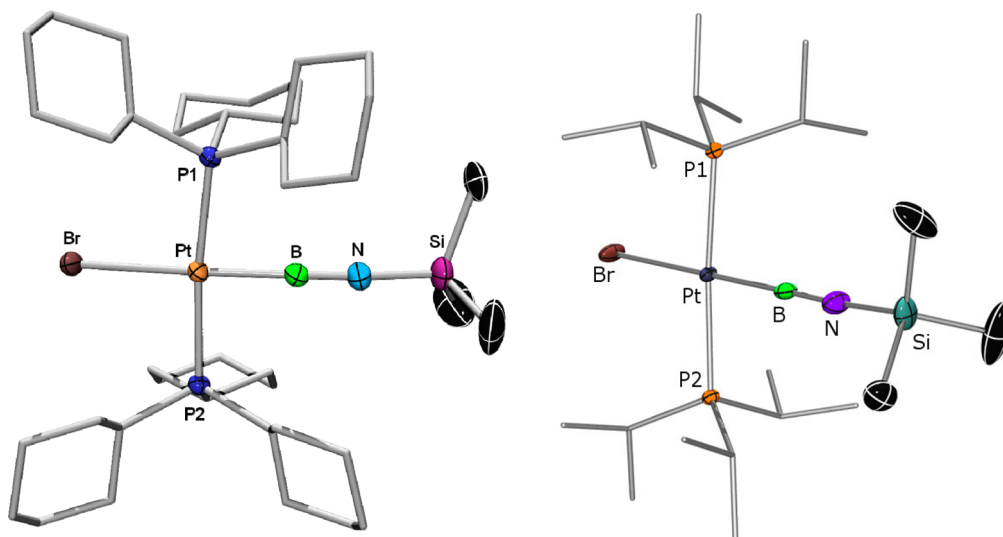
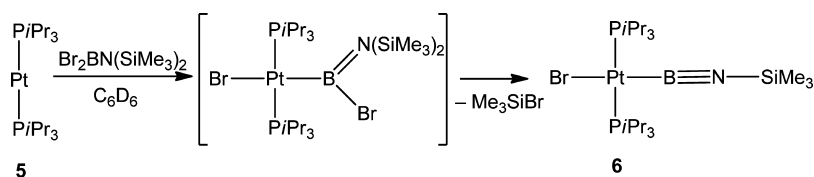
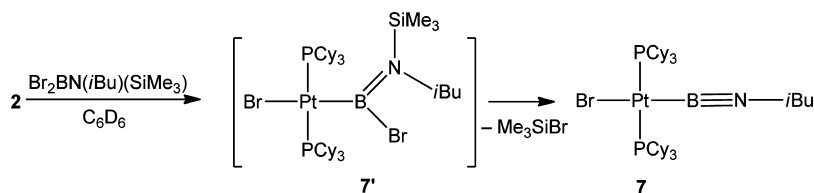


FIGURE 1. Molecular structures of **4** and **6**.

SCHEME 2. Synthesis of Iminoboryl Complex **6**



SCHEME 3. Synthesis of Iminoboryl Complex **7**



terms of hybridization of the boron atoms. Unlike boryl complexes where the boron atoms are three-coordinate and assume sp^2 hybridization, the boron atoms in **3** and **4** are sp hybridized, leading to contraction of not only the M–B bonds but also the M–Br bonds [**3** (2.538 (mean)) and **4** (2.552(1)) Å]. The astounding thermal stability of these iminoboryl complexes was verified by irradiating C_6D_6 solutions of **3** and **4** at room temperature for 12 h, which did not induce any change in their respective NMR spectra. This implies significant electronic and kinetic stabilization of the iminoboryl moieties upon coordination to the transition metals.

In order to understand the role of the metal-bound coligands, we replaced the PCy_3 ligands with the less bulky $PiPr_3$, and observed that the reaction of $[Pt(PiPr_3)_2]$ (**5**)

with the same aminoborane $[(Me_3Si)_2N=BBR_2]$ resulted in the analogous iminoboryl complex $trans\text{-}[(iPr_3P)_2BrPt(B≡NSiMe_3)]$ (**6**) [Scheme 2], with a B=N bond distance of 1.265(7) Å [Figure 1].²⁰ Next, we carried out the reaction of **2** with a slightly modified aminoborane $[(Me_3Si)(iBu)N=BBR_2]$ [Scheme 3]. The reaction led to the formation of a boryl complex $trans\text{-}[(Cy_3P)_2BrPt\{B(SiMe_3)(iBu)Br\}]$ (**7'**) initially, which in due course resulted in the expected iminoboryl complex $trans\text{-}[(Cy_3P)_2BrPt(B≡NiBu)]$ (**7**) with the liberation of Me_3SiBr . The hypothesis of boryl intermediates during the formation of iminoboryl complexes was hereby confirmed on the basis of the ^{31}P and ^{11}B NMR evidences.

To this end, it seemed reasonable to probe the formation of iminoboryl complexes with a late transition metal other than Pd and Pt. Treatment of $[(Me_3Si)_2N=BBR_2]$ with

$[(\text{Me}_3\text{P})_3\text{RhCl}]$ resulted in the first group 9 iminoboryl complex *cis,mer*- $[(\text{Me}_3\text{P})_3\text{Br}_2\text{Rh}(\text{B}=\text{NSiMe}_3)]$ (**9**) [Scheme 4].²⁰ The boron–nitrogen bond distance of 1.255(7) Å in **9** justifies the formulation of a B≡N triple bond.

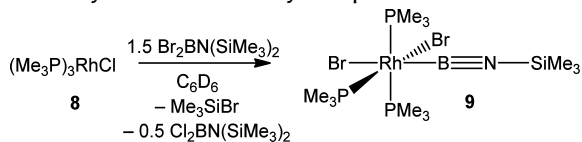
Reactivities of Iminoboryl Complexes

Investigating the chemistry of stable iminoboryl complexes promises to be a rewarding exercise. Organic iminoboranes ($\text{RB}=\text{NR}'$) have been reported to form coordination complexes and undergo hydroboration, hydrozirconation, and metal-mediated cyclization and cycloaddition reactions.²¹ The iminoboryl complexes are also expected to show enhanced reactivity due to an electron-rich B≡N triple bond and modest steric shielding surrounding the B≡N moiety, which allows the reagents to react. Three modes of reactivity can be anticipated: (i) reactivity through the lone pair of electrons on nitrogen, (ii) reactivity involving the B≡N unit, and (iii) substitution reactions through the bromide atom adjacent to the platinum center. The reactivity of **4** toward various substrates is outlined in Schemes 5 and 6. The first mode of reactivity was observed with AlCl_3 , which afforded a Lewis acid–base adduct **10** [Scheme 5].²² A single-crystal

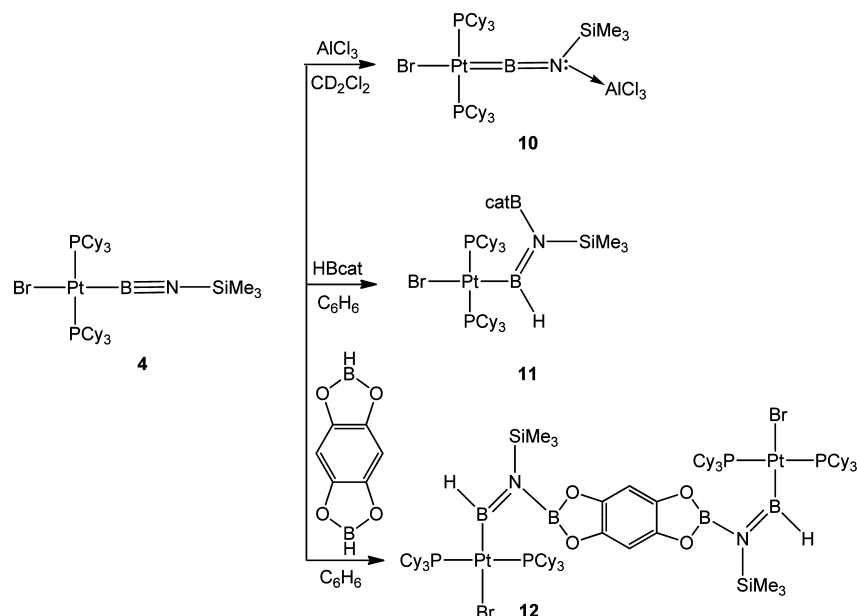
X-ray study on **10** revealed that the coordination of **4** to AlCl_3 resulted in a decrease of electron density from the boron atom leading to a slight elongation of the B–N bond [1.330(3) (**10**) vs 1.260(4) Å (**4**)] but considerable shortening of the Pt–B bond [1.904(3) (**10**) vs 1.960(3) Å (**4**)] [Figure 2]. The reactions of **4** with catecholatorborane (HBcat) and 1,2,4,5-benzenetetrolatobis(borane) led to regioselective addition of the B–H bonds to the B≡N bond and afforded the corresponding 1,2-dipolar addition products **11** and **12** [Scheme 5].²³ As expected, the 1,2-addition led to significant elongation of the B–N [1.452(3) Å (**11**), 1.456(6) Å (**12**)] and Pt–B [2.020(3) (**11**), 2.010(5) Å (**12**)] bonds with respect to those of **4** and **10**. A comparison of the Pt–Br distances in **11** [2.632(1) Å] and **12** [2.631(1) Å] with the corresponding distances in **4** [2.552(1) Å] and **10** [2.528(1) Å] provides evidence for a stronger *trans* influence of boryl ligands over iminoboryl or borylene ligands, which is in accordance with the computationally evaluated *trans* influence of various ligands by Zhu, Lin, and Marder.²⁴

Iminoboryl complex **4** was also seen to undergo 1,2-dipolar addition reactions with protic reagents such as H_2O , HBr, MeOH, and PhNH_2 leading to *trans*- $[(\text{Cy}_3\text{P})_2\text{BrPt}\{\text{B}(\text{X})\text{-(NH}(\text{SiMe}_3))\}]$ (X = OH (**13**), Br (**14**), OMe (**15**), and NHPH (**16**)) [Scheme 6] with the retention of the Pt–B bond under protic conditions.²⁰ The cleavage of H_2O into H^+ and OH^- took place only when a catalytic amount of HBr was added into the reaction mixture. However, in the absence of H_2O , HBr underwent 1,2-dipolar addition with **4** and yielded

SCHEME 4. Synthesis of Iminoboryl Complex **9**



SCHEME 5. Reactions of Iminoboryl Complex **4**



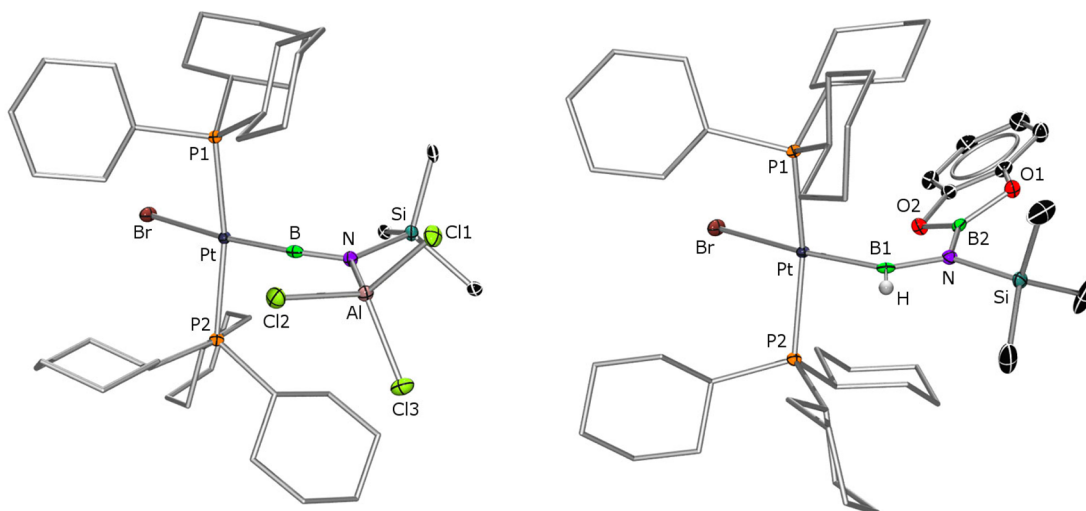
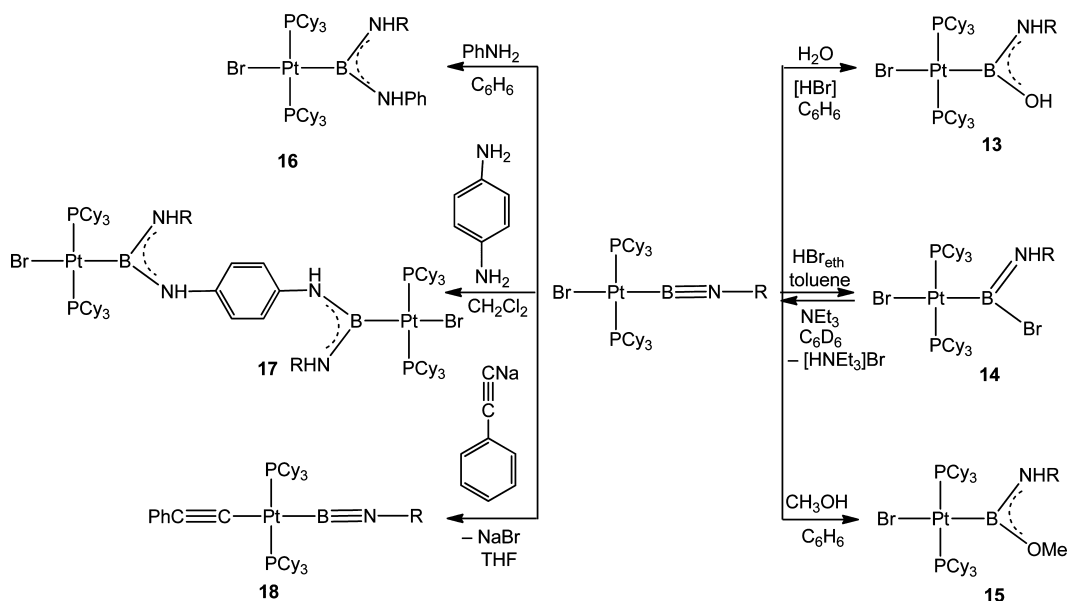


FIGURE 2. Molecular structures of **10** and **11**.

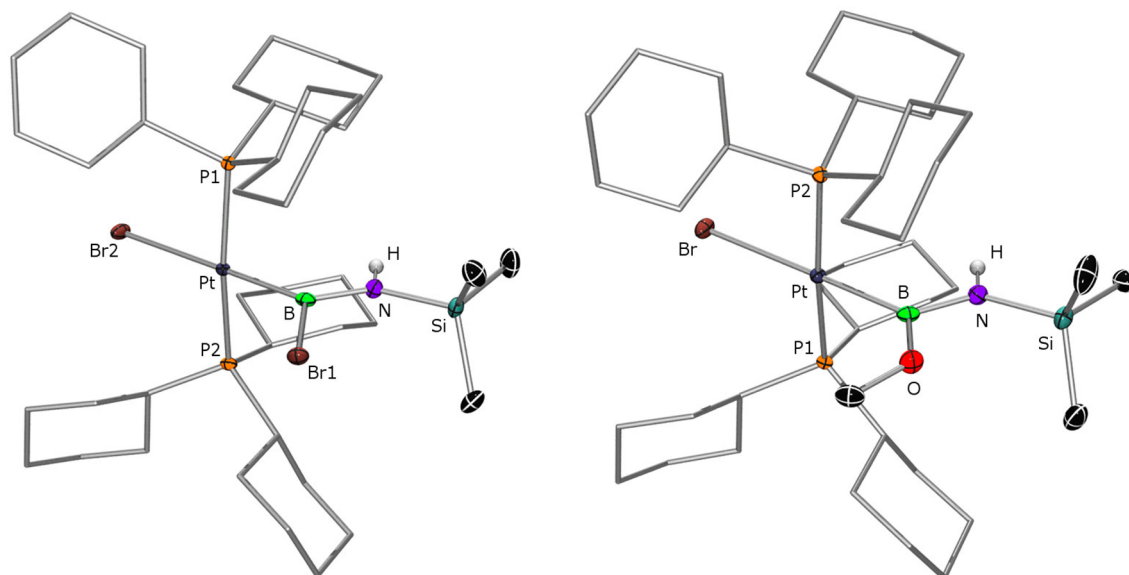
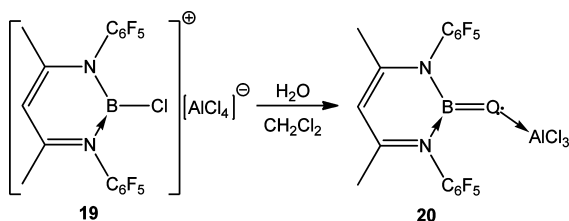
SCHEME 6. Reactions of Iminoboryl Complexes **4** and **9** with Various Substrates (R = SiMe₃ for **13–16, 18**, and R = *i*Bu for **17**)



trans-[(Cy₃P)₂BrPt{B(Br)(NH(SiMe₃))}] (**14**). Even though the bromide atom and trimethylsilyl substituent reside in close proximity in **14**, the complex did not show any tendency toward bromosilane elimination even at elevated temperatures. Addition of triethylamine to **14** instantly afforded the precursor **4** along with the formation of [Et₃NH]Br. The reaction of **4** with *p*-phenylenediamine was not only slow but yielded a mixture of products that could not be identified. However, using a less bulky iminoboryl complex **7**, we cleanly isolated 1,4-*trans*-[[(Cy₃P)₂BrPt{B{NH*i*Bu}NH}]₂C₆H₄] (**17**) stemming from 1,2-dipolar addition of *p*-phenylenediamine to the B≡N bond of **7**.²⁰ The addition of sodium(phenylacetylide) to **4** provided straightforward salt elimination

instead of putative [2 + 2] cycloaddition leading to *trans*-[(Cy₃P)₂(PhC≡C)Pt(B≡NSiMe₃)] (**18**), a complex where iso-electronic σ -alkynyl and iminoboryl ligands [C≡C and B≡N] are bound to platinum.

Inspection of the B–N bond lengths in **14–17** [(1.409(3) (**14**), 1.432(3) (**15**), 1.444(5) (**16**), and 1.429(7) (**17**) Å] [Figure 3] revealed that these addition reactions resulted in the decrease of the B–N bond order and subsequent elongation of the B–N bond as observed in the cases of **11** and **12**. Similar elongation was also observed for the adjacent Pt–B and Pt–Br bonds [2.001(3) and 2.591(2) (**14**), 2.053(2) and 2.635(1) (**15**), 2.048(4) and 2.658(1) (**16**), 2.048(6) and 2.631(1) (**17**) Å] with respect to their precursors. In fact, the Pt–Br bond

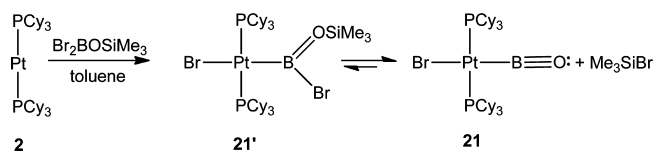
FIGURE 3. Molecular structures of **14** and **15**.SCHEME 7. Synthesis of a Complex with a B=O Double Bond (**20**)

length in **16** is the longest Pt–Br bond reported so far for a boryl complex [2.562(2)–2.645(1) Å].²⁵

Synthesis, Structural Elucidation, and Reactivities of Oxoboryl Complexes

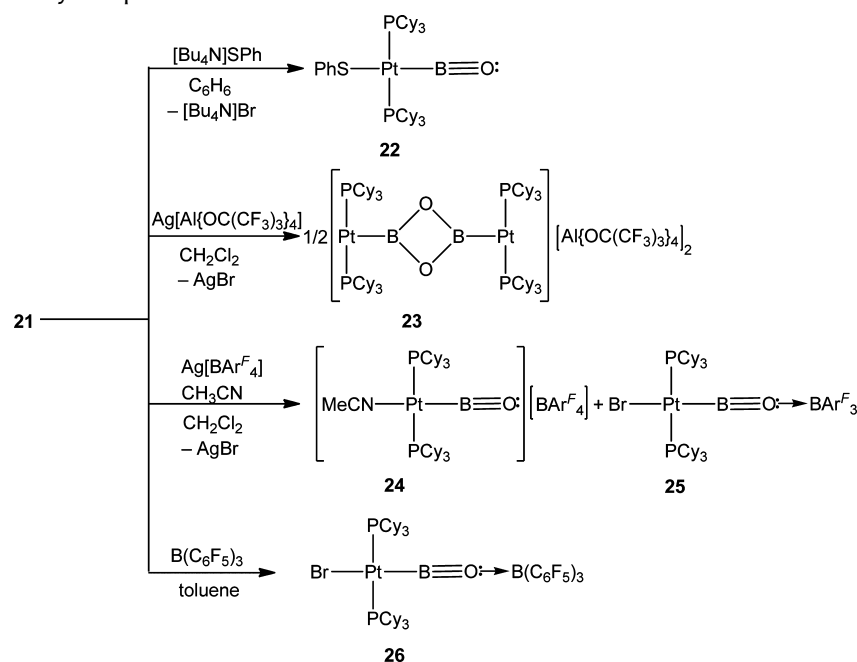
With the isolation of B≡N triple bonds in the coordination sphere of Pt, Pd, and Rh, our research was extended to analogous complexes with B–O multiple bonds. The propensity of the extremely polar B–O bond toward oligomerization even under ambient conditions is attributed to the scarcity of complexes featuring B–O multiple bonds. In 2005, Cowley et al. prepared the first well-defined boranone [$\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{BO}\text{---}\text{AlCl}_3$] (**20**) featuring a B=O double bond from the reaction of [$\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{BCl}\}\text{[AlCl}_4\text{]}^-$] (**19**) with one equivalent of H₂O [Scheme 7].²⁶ A combination of XRD and computational studies revealed that the B=O bond in **20** is 1.304(2) Å in length and possesses considerable double bond character.

With the quest for B=O doubly bound compounds partially fulfilled, attention turned toward a B≡O triple bond. Such species had only been detected in the gas phase or by

SCHEME 8. Synthesis of a Complex with a B≡O Triple Bond (**21**)

low-temperature matrix isolation studies and posed a formidable synthetic challenge. The intermediacy of oxoboranes RBO [R = 2,4,6-*t*Bu₃-C₆H₂, 2,4,6- $\{\text{CH}(\text{SiMe}_3)_2\}_3\text{-C}_6\text{H}_2$, or C(SiMe₃)₃] during the combustion of a number of boron compounds had been ascertained by trapping experiments.²⁷ This quest came to an end in 2010 with the isolation of the first oxoboryl complex *trans*-[(Cy₃P)₂BrPt(BO)] (**21**) from the reaction between [Br₂BOSiMe₃] and [Pt(PCy₃)₂] (**2**) [Scheme 8].²⁸ As in the case of **7**, a platinum(II) boryl complex *trans*-[(Cy₃P)₂BrPt{B(Br)OSiMe₃}] (**21'**) is initially formed, which in due course resulted in **21** with concomitant liberation of Me₃SiBr. A reversibility was observed when **21** was treated with an excess of Me₃SiBr.

Unfortunately, due to massive disorder as a result of superposition of the Br and BO ligands, the crystallographic data of **21** were not completely reliable. Therefore, the only way to authenticate the B≡O triple bond crystallographically was to synthesize new oxoboryl derivatives. Due to the presence of a labile bromide ligand at the platinum center, **21** was expected to be a versatile precursor for further substitution chemistry, which was potentially an easy way to prepare new oxoboryl complexes. The reaction of **21** with [Bu₄N]SPh led to *trans*-[(Cy₃P)₂(PhS)Pt(BO)] (**22**),²⁸ whereas

SCHEME 9. Reactions of Oxoboryl Complex **21**TABLE 2. Important Spectroscopic and Structural Details of Complexes **21–26**

compound	^{11}B (ppm)	^{31}P ppm ($^1J_{\text{P,Pt}}$, Hz)	IR (cm^{-1})	B–O (Å)	Pt–B (Å)
<i>trans</i> -[(C_3P) $_2$ BrPt(BO)] (21)	17.0	32.5 (2294)	1853, 1797		
<i>trans</i> -[(C_3P) $_2$ (PhS)Pt(BO)] (22)	24.0	28.9 (2309)	1849, 1793	1.210(3)	1.983(3)
[(C_3P) $_2$ Pt(B_2O_2)Pt(PCy_3) $_2$] $^{2+}$ [Al{OC(CF $_3$) $_3$ } $_4$] $^{2-}$ (23)	15.0	50.1 (2512)		1.413 ^a	1.950 ^a
<i>trans</i> -[(C_3P) $_2$ (MeCN)Pt(BO)][BAR F_4] (24)	12.0	35.9 (2294)	1885, 1828	1.197(6)	1.971(5)
<i>trans</i> -[(C_3P) $_2$ BrPt(B=O→BAR F_3)] (25)		33.4 (2048)	1784, 1732	1.234(2)	1.928(3)
<i>trans</i> -[(C_3P) $_2$ BrPt(B=O→B(C $_6$ F $_5$) $_3$)] (26)	22.0, –2.0	33.7 (2065)	1773, 1721		

^aMean.

the analogous reaction with $\text{Ag}^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ afforded the ionic complex $[(\text{C}_3\text{P})_2\text{Pt}(\text{B}_2\text{O}_2)\text{Pt}(\text{PCy}_3)_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]_2$ (**23**)²⁹ stemming from cyclodimerization of two B=O ligands [Scheme 9]. Formation of an analogous cationic dioxodiborethane-diy-bridged dimeric complex was also assumed from the reaction between **21** and $\text{Ag}[\text{BAR}^F_4]$, [$\text{Ar}^F = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$], but the product was not fully characterized because of its oily nature. Surprisingly, when the latter reaction was carried out in the presence of four equivalents of acetonitrile, it resulted in *trans*-[(C_3P) $_2$ (MeCN)Pt(BO)][BAR F_4] (**24**) as a main product along with the formation of *trans*-[(C_3P) $_2$ BrPt(B=O→BAR F_3)] (**25**) as a minor product.³⁰ Adduct **25** was unable to be satisfactorily characterized by spectroscopy, but fortuitously single-crystal X-ray study authenticated its constitution. The isolation of **25** prompted the reaction of **21** with the well-known Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$, which afforded the expected Lewis adduct *trans*-[(C_3P) $_2$ BrPt(B=O→B(C $_6$ F $_5$) $_3$)] (**26**).³⁰ It is apparent from these reactions that the bromide substitution of **21** ultimately results in a

range of products, depending mainly on the halide abstracting reagent.

In their ^{31}P NMR spectra, **22–26** display resonances at $\delta = 28.9$ ($^1J_{\text{P,Pt}} = 2309$ Hz), 50.1 ($^1J_{\text{P,Pt}} = 2512$ Hz), 33.4 ($^1J_{\text{P,Pt}} = 2048$ Hz), 35.9 ($^1J_{\text{P,Pt}} = 2294$ Hz), and 33.7 ($^1J_{\text{P,Pt}} = 2065$ Hz) ppm, respectively [Table 2]. The substantial downfield chemical shift of **23** is indicative of a T-shaped cationic complex with tricoordinate Pt atoms. The differing ^{11}B NMR chemical shifts reflect the π -donor ability of the substituents attached to Pt: a low-field shift was reported for thiolate-substituted oxoboryl complex **22** ($\delta = 24$ ppm), with successively higher-field resonances being observed for bromide- **26** ($\delta = 22$ ppm) and **21** ($\delta = 17$ ppm)] and acetonitrile-substituted [**24** ($\delta = 12$ ppm)] oxoboryl complexes. This is further mirrored in the lowest B=O stretching frequencies being measured for **22** [1849 and 1793 cm^{-1}] with gradually higher B=O stretching frequencies for **21** [1853 and 1797 cm^{-1}] and **24** [1885 and 1828 cm^{-1}]. The molecular structures of **22** and **24** show an almost square-planar geometry

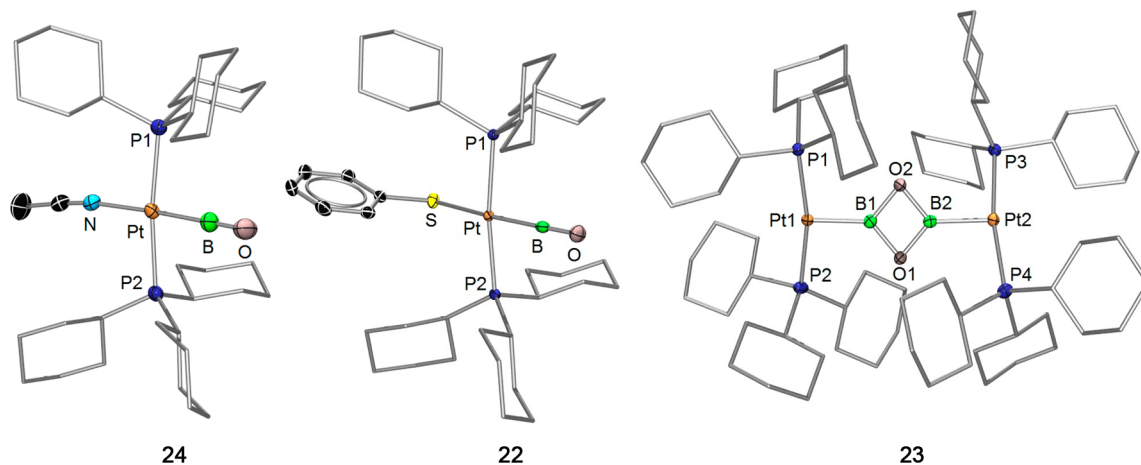


FIGURE 4. Molecular structures of **22**–**24**.

at the platinum center with Pt–B bond lengths of 1.983(3) and 1.971(5) Å, respectively [Figure 4]. The B≡O bond lengths in **22** [1.210(3) Å] and **24** [1.197(6) Å] are similar, consistent with the distance calculated from microwave data of gaseous HBO [1.200(3) Å],³¹ but substantially shorter than that of **20** [1.304(2) Å]. The lengthening of the B≡O [1.234(2) Å] and shortening of the Pt–B [1.928(3) Å] bonds in **25** suggest that it exists as a resonance hybrid of (a) Pt–B≡O→BAR^F₃ and (b) Pt=B=O→BAR^F₃, with the higher contribution coming from the second canonical form. Such variations in the bond distances are in line with those found for **10**.

The molecular structure of **23** displays a B₂O₂ quadrangle with B–O bonds of 1.404(9)–1.424(9) Å resembling the previously reported 2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-dioxodiboretane.³² The four-membered B₂O₂ ring can be termed a rhombus within the 3 σ -criterion. The relatively long B–O single bonds suggest the strong antibonding cross-ring interactions between two oxygen atoms, while the quite short B···B separation [1.846(10) Å] indicates an electronic interaction. Another striking feature of **23** is its unique helical structure resulting from twisting of the B₂O₂ plane with respect to two platinum bis(tricyclohexylphosphine) moieties by 20.84(37)° and 36.82(25)°.

The isolation of **21** raised fascinating questions regarding its bonding situation. It was previously known that the B≡O group is kinetically labile due to its high polarity and small HOMO–LUMO separation; however, complexation to a [PtX(PCy₃)₂] fragment increases the HOMO–LUMO gap and thereby increases the kinetic stability of the moiety. Steric hindrance from the six cyclohexyl substituents also plays a part in the stabilization, but is unlikely to be a major factor. Preliminary theoretical calculation by Zeng and Sakaki³³ on model compound *trans*-[(Me₃P)₂BrPt(BO)]

revealed that the formation of the oxoboryl complex is endothermic [$\Delta H^\circ = 20.48$ kJ/mol]. In line with the earlier computational studies by Baerends and co-workers,¹⁵ they reported that the major interaction is the σ -donation from the formally anionic BO[−] to Pt, with weak π -backdonation from the HOMO of the metal to the p-orbital of boron. This supports the convention of assigning the Pt–B bond in **21** as a single bond. The molecular orbitals are localized slightly more on the oxygen atom than the boron atom, manifesting the polar nature of the B=O bond [Figure 5]. Quantum chemical calculations also revealed two π -type interactions between the boron and oxygen atom, which is in line with the calculated B–O bond order of 2.83.²⁸

The formation of **21** involves a four-atom metallacyclic transition state where B ^{δ +}–Br ^{δ −} bond polarization and Br→Si and O(P _{π})→B(P _{π}) charge transfer takes place, leading to the cleavage of the B–Br and Si–O bonds and elimination of Me₃SiBr. The phosphine ligands are assumed to facilitate the B–Br bond polarization. In an effort to assess the role of the phosphines, Zeng and Sakaki mentioned that the phosphine ligands destabilize the boryl intermediate more than the oxoboryl product because (i) the intermediate boryl ligand [B(Br)(OSiMe₃)][−] is a better σ -donor than the oxoboryl ligand BO[−] and (ii) the boryl ligand is sterically more hindered than the oxoboryl ligand. The phosphines also provide electron density to platinum, which in turn augments the d _{π} → p _{π} backdonation, leading to a strong Pt–B bond. This is evident in the differences in the theoretically calculated Pt–B bond lengths in *trans*-[(R₃P)₂BrPt(BO)] [R = CF₃ (2.001 Å), CH₃ (1.970 Å), and CH(CH₃)₂ (1.958 Å)]. A comparison of σ -donor and π -acceptor properties of BO[−] with isoelectronic CN[−], CO, and NO⁺ ligands resulted in gradual decline of σ -donation in the order: BO[−] > CN[−] > CO > NO⁺, which is also indicative of strong *trans*-influence of the B≡O moiety.

A π -Diborene Complex

Over the past few years, computational chemistry has proven itself an indispensable predictive tool in synthetic chemistry.

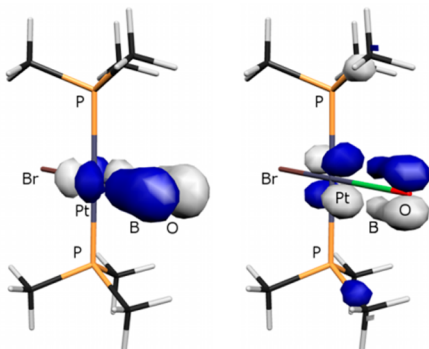


FIGURE 5. π -MOs of the model complex $trans\text{-}[(\text{Me}_3\text{P})_2\text{BrPt}(\text{BO})]$.

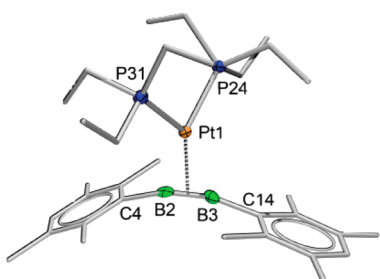
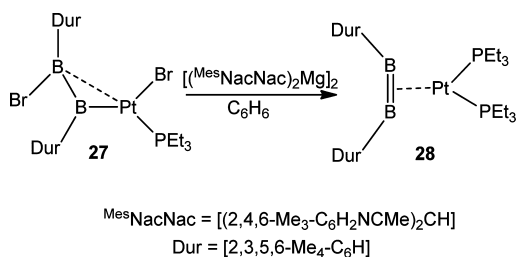


FIGURE 6. Molecular structure of **28**.

SCHEME 10. Synthesis of π -Diborene **28**



This was further manifested in our recent isolation and publication of a π -diborene ligand (**28**) in the coordination sphere of platinum.³⁴ It is noteworthy that **28** was initially theoretically devised and only later experimentally realized.

In order to synthesize a π -diborene complex, we presumed that dihalodiboran(4)yl complexes³⁵ of platinum might serve as better precursors than $trans\text{-}[(\text{Cy}_3\text{P})_2\text{XPt}(\text{BX}_2)]$ (X = Cl and Br) due to the presence of a preformed B–B bond in the former. Precedence for this approach comes from the aforementioned preparation of a B≡B triply bonded compound (**1**, Chart 1), in which reduction of a B–B-bound precursor led to a triply bound product, in contrast to a failed earlier method that lacked B–B bond preformation.³ The reduction of a distorted σ -diboran(4)yl complex (**27**) with [LMg^I–Mg^IL] (L = (2,4,6-Me₃-C₆H₂NCMe)₂CH)³⁶ produced the first π -diborene (**28**) stabilized by a [Pt(PiPr₃)₂] fragment [Scheme 10]. The key structural feature of **28** is its B=B bond distance [1.510(14) Å] [Figure 6]. Note that the B=B bond length in **28** is shorter than that of all diborenes (**A–E**) shown in Chart 1 but longer than in diboryne **1**. This finding is unprecedented because M → L π -backdonation often results in elongation of E–E bonds as seen in the cases of alkenes and alkynes. Moreover, the B–B bond axis is situated perpendicular to the P–Pt–P plane in **28**, whereas the C–C axis lies almost coplanar with the P–Pt–P framework in π -alkyne complexes of zerovalent platinum.³⁷ A comparative DFT study of π -alkyne and π -diborene complexes revealed their dichotomy in π -backdonation [Figure 7]. Diborenes [R–B=B–R] feature two π -bonding SOMOs that are lower in energy than their π^* orbitals, and hence these SOMOs could accept the π -backdonation from platinum, whereas alkynes can receive electron density from the metal only into their antibonding π^* orbital. In order to maximize the overlap with the d-orbital of platinum, the π -SOMOs are oriented orthogonally to the P–Pt–P plane leading to an

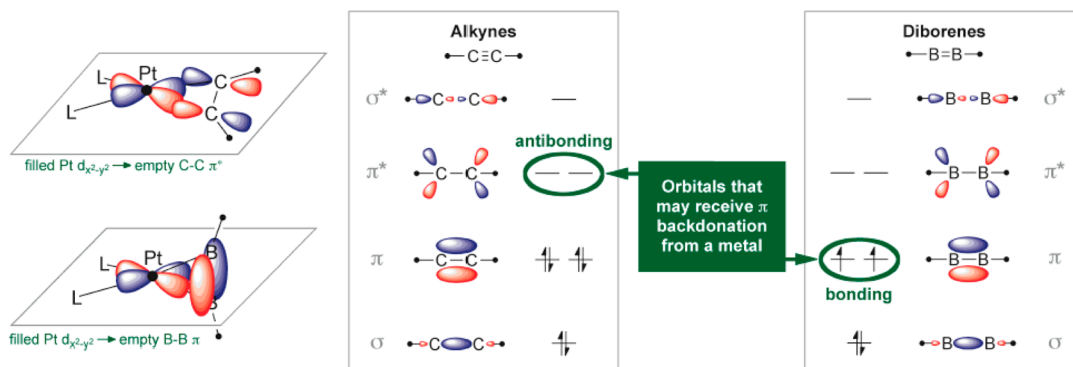


FIGURE 7. (left) Orientations of π -alkyne and π -diborene ligands. (right) Simplified diagram of the frontier orbitals of generic alkynes and diborenes in π -alkyne and π -diborene complexes.

out-of-plane backdonation into a bonding π orbital, which is presumably responsible for the shortening of the B=B double bond in **28**. The high degree of π -backdonation was further apparent in the nearly linear C–B–B bond angles [166.0(8)° and 164.2(8)°] in **28** implying that the degree of σ -donation from diborene to platinum was almost counterbalanced by π -backbonding.

Conclusion and Future Scope

The isolation of complexes featuring B=B double and B≡E (E = N and O) triple bonds in the coordination sphere of transition metal fragments (mainly platinum) launched the credentials of [Pt(PR₃)₂] as an avant-garde scaffold for the generation of B=E multiple bonds. The protocol that led to the isolation of B≡E bonds involves the oxidative addition of amino- or oxoboranes to the zerovalent platinum fragment, accompanied by elimination of bromosilane. Oxoboryl complex **21** bears the first ever well-defined B=O triple bond, and the complex surprisingly shows no tendency toward oligomerization or decomposition even at 100 °C or upon irradiation. In addition to its synthesis, the reactivities of *trans*-[(Cy₃P)₂BrPt(B≡N(SiMe₃))] (**4**) and *trans*-[(Cy₃P)₂BrPt(B=O)] (**21**) are quite remarkable and will spur more interest among researchers in the field.

From a synthetic perspective, many exciting challenges lie ahead in this area. Currently, the most common coligands used with this platinum scaffold are electron-rich trialkylphosphines. The use of N-heterocyclic carbenes as an alternative to phosphines is emerging.³⁸ It would be a rewarding exercise to study whether [Pt(NHC)(PR₃)] or [Pt(NHC)₂] can stabilize iminoboryl or oxoboryl complexes. Although platinum is currently in the spotlight, examination of other transition metals will also be important. For example, Zeng and Sakaki theoretically examined the formation reactions of oxoboryl complexes with a variety of transition metals and predicted [(R₃P)₂ClBrM(B=O)(CO)] (M = Rh, Ir) to be viable candidates. Note that unlike for **21**, the calculated enthalpy change for the formation of [(iPr₃P)₂ClBrM(B=O)(CO)] is exothermic [–5.99 (M = Rh) and –7.56 (M = Ir) kJ/mol], presenting them as potential synthetic targets.³³ Simultaneously, Li and King pointed out that in all aforementioned examples the BO ligand is monoanionic and no neutral BO derivative has either been experimentally or theoretically considered. For this reason, they published an extensive theoretical study on neutral transition metal boronyl derivatives; however, experimental realization of such compounds still remains elusive.³⁹ It would also be of significant interest to determine whether the synthetic methodology

that has been used for iminoboryl and oxoboryl complexes can be extended to third or higher row elements with the aim of isolating complexes with B–X [X = Si, Ge, P, and S] multiple bonds. The construction of a π -diborene complex (**28**) is an important development in the area of main group analogues of alkenes and alkynes, and the isolation of many other such molecules is also expected. Additionally, the reactivity studies of iminoboryl, oxoboryl, and π -diborene complexes need further input.

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BIOGRAPHICAL INFORMATION

Johannes Brand was born in Würzburg, Germany, in 1985. He graduated with a diploma degree in chemistry from the Julius-Maximilians-University of Würzburg in 2010. Supported by the Fonds der Chemischen Industrie with a fellowship, he is currently working on his doctoral degree with Professor Holger Braunschweig in the field of stabilizing low-coordinate boron-centered ligands in the coordination sphere of late transition metal complexes.

Holger Braunschweig (born 1961 in Aachen) obtained his Ph. D. (1991) and Habilitation (1998) from the RWTH Aachen with Prof. P. Paetzold and stayed for a Postdoctoral fellowship with Prof. M. F. Lappert, FRS, at the University of Sussex, Brighton. After 2 years at Imperial College as Senior Lecturer and Reader, he moved to a chair in inorganic chemistry at Julius-Maximilians-University, Würzburg, in 2002. In 2009, he was awarded the Gottfried Wilhelm Leibniz prize of the DFG, was elected as a member to the Bavarian Academy of Sciences and became member of the National Academy of Sciences (Leopoldina) in 2011. His research interests lie in the area of boron chemistry, organometallic synthesis, and catalysis and are currently focused on borametallophenanes, boron heterocycles, boron–boron multiple bonds, and transition metal complexes of boron.

Sakya S. Sen was born in Kolkata, India, in 1983. After finishing his M.Sc. from IIT Kharagpur in 2006, he joined the research group of Prof. Herbert W. Roesky at the University of Göttingen and received the title “Dr. rer. nat.” in 2010. He is currently a postdoctoral researcher supported by the Alexander von Humboldt Foundation in the laboratory of Prof. Holger Braunschweig at the University of Würzburg. His research interests lie in main group chemistry with low-valent elements and bio-organometallic chemistry.

FOOTNOTES

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