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Reactivity of Platinum Iminoboryl Complexes toward Covalent Element−Hydrogen Bonds of Opposing Polarity

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Reaction of the platinum iminoboryl complex *trans*-[$(Cy_3P)_2(Br)Pt(B{\equiv}NSiMe_3)$] (Cy = cyclohexyl) toward covalent element−hydrogen bonds of inverse polarity led to regiospecific formation of the corresponding *trans* products of 1,2-dipolar addition. Hydrogen bromide reversibly adds to the B≡N triple bond, and despite the close proximity of the bromide to the trimethylsilyl substituent, the hydrobromination adduct *trans*-[$(Cy_3P)_2BrPt\{B(Br)N(H)SiMe_3\}$] did not show any signs of bromosilane elimination. Furthermore, the reaction of *trans*-[$(Cy_3P)_2(Br)Pt(B{\equiv}NSiMe_3)$] and *trans*-[$(Cy_3P)_2Pt(B{\equiv}NSiMe_3)(C{\equiv}CPh)$] with the hydroboration reagent catecholatoborane was probed, revealing in both cases clean 1:1 reaction of the reagents. Whereas the reaction product of the latter complex is inherently unstable, both the mono- and the dinuclear hydroboration products of *trans*-[$(Cy_3P)_2(Br)Pt(B{\equiv}NSiMe_3)$] could be isolated and fully characterized including X-ray diffraction analysis.

Introduction

During the past decades, transition metal complexes of boron-centered ligands have developed from intriguing laboratory curiosities to a well-established class of compounds, which continues to be extensively investigated.[1−3] The particular interest that especially boryl complexes [$L_nM{-}BR_2$] have attracted originally was rooted in their key role in catalytic functionalization of organic substrates. Thus, hydroboration,[4] diboration,[5] and C−H activation processes[6] allow for the highly selective synthesis of organoboranes, which are among the most useful reagents in synthetic chemistry.[7] Consequently, transition metal complexes of ligands with tricoordinate boron atoms are plentiful,[1,3] and the bonding situation in these compounds has been extensively investigated.[8,9] In contrast, complexes featuring dicoordinate boron centers are considerably more limited in number. Their relationship to carbyne, vinylidene, and even carbonyl

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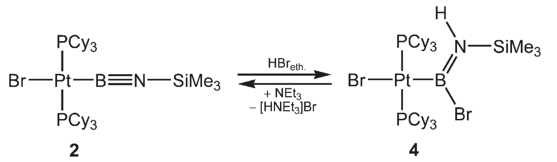
complexes stimulated great efforts in accessing and understanding the corresponding compounds. In this field, terminal borylene complexes [$L_nM{=}BR$] exhibiting a considerable metal−boron multibond character account for the largest proportion.[2,3] Preparation of the previously unprecedented oxoboryl complexes [$L_nM{-}B{\equiv}O$][10] as well as a variety of iminoboryl complexes [$L_nM{-}B{\equiv}N{-}R$][11,12] demonstrated that the electron deficiency at boron can also be compensated almost exclusively by a doubly π-donating main group substituent. The latter compounds constitute isoelectronic BN analogues of the well-established class of σ-alkynyl complexes, which have proven their relevance as rigid-rod polymers and optoelectronic materials.[13] Despite the polarity of the B≡N triple bond, the iminoboryl complexes display a remarkable stability. However, in particular the platinum derivatives undergo highly selective reactions resembling their main group-substituted analogues.[14,15] Thus, coordination of Lewis-acidic aluminum trichloride to the imino nitrogen center of *trans*-[$(Cy_3P)_2BrPt(B{\equiv}NSiMe_3)$] (**1**) yielded the first neutral borylene complex of platinum, *trans*-[$(Cy_3P)_2BrPt{=}B{=}N(SiMe_3)(AlCl_3)$],[16] whereas sodium(phenyl)acetylide leaves the iminoboryl moiety intact. Instead it reacts under substitution of the bromide, forming *trans*-[$(Cy_3P)_2Pt(B{\equiv}NSiMe_3)(C{\equiv}CPh)$] (**2**),[12] in which the two isoelectronic ligands are coordinated to the same metal center. Furthermore, different moderately Brønsted-acidic substrates react via 1,2-dipolar addition, yielding unsymmetrically substituted boryl ligands,[12,16] the generation of which otherwise would demand considerable preparative efforts. Herein, we report the extension of this chemistry to the reversible addition of hydrogen bromide to *trans*-[$(Cy_3P)_2BrPt(B{\equiv}NSiMe_3)$] (**1**) and its behavior toward hydroboration reagents.

Scheme 1. Synthesis of *trans*-[$(Cy_3P)_2BrPt\{B(Br)N(H)SiMe_3\}$] (4)



Results and Discussion

As was published previously, *trans*-[$(Cy_3P)_2BrPt(B{\equiv}NSiMe_3)$] (**1**) turned out to be surprisingly stable toward pure water. Only the presence of acidic reagents catalyzed 1,2-dipolar addition of H_2O to the B≡N triple bond. Thus, reaction with hydrobromic acid yielded exclusively the platinaborinic acid *trans*-[$(Cy_3P)_2BrPt\{B(OH)N(H)SiMe_3\}$] (**3**).[12] In the absence of protic solvents, hydrogen bromide itself undergoes instant reaction with the iminoboryl complex. Hence, addition of an ethereal hydrogen bromide solution to a toluene solution of **1** at −70 °C causes immediate formation of a colorless precipitate, which dissolves upon warming to room temperature. Analysis of the reaction mixture by means of nuclear magnetic resonance (NMR) spectroscopy reveals formation of one new compound. The boron (^{11}B) NMR resonance (38 ppm) and phosphorus (^{31}P) NMR data (20.2 ppm, $^1J_{Pt-P}$ = 2805 Hz) are indicative of a boryl complex featuring a tricoordinate boron atom.[1,9,17] However, the values markedly differ from those observed for **3** (^{11}B: 33 ppm, ^{31}P: 25.7 ppm, $^1J_{Pt-P}$ = 2894 Hz),[12] and the differences in the ^{11}B NMR chemical shifts are in the typical range observed for formal substitution of an oxygen-centered substituent by a bromide.[18] The proton (^1H) NMR spectrum of the product displays a sharp signal at 4.55 ppm with an integration of 1 with respect to the cyclohexyl (66) and trimethylsilyl (9) resonances. On the basis of $^{15}N,^1H$ NMR correlation spectroscopy this signal is assigned to a hydrogen directly bound to nitrogen. Thus, the spectroscopic data are consistent with the formation of *trans*-[$(Cy_3P)_2BrPt\{B(Br)N(H)SiMe_3\}$] (**4**) obtained by 1,2-dipolar addition of hydrogen bromide to the B≡N triple bond (Scheme 1). The product was isolated in almost quantitative yields (91%), and colorless crystals were obtained by recrystallization from a mixture of benzene and hexane.

The results of X-ray diffraction studies confirm the proposed constitution of **4** (Figure 1). The geometrical parameters around platinum are not exceptional and are in full agreement with those of other boryl complexes.[1,9,17] As was previously observed for the adducts of **1** with methanol[16] and aniline,[12] **4** exhibits a configuration at the BN moiety that corresponds to formal *trans* addition of the element

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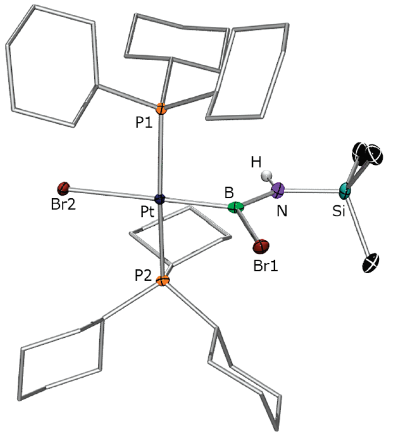


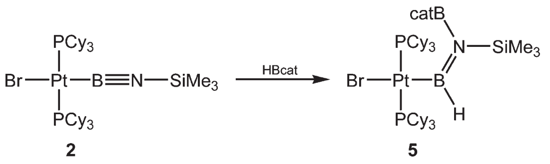
Figure 1. Molecular structure of *trans*-[$(Cy_3P)_2BrPt\{B(Br)N(H)SiMe_3\}$] (**4**). Thermal ellipsoids are represented at the 50% probability level. Ellipsoids of cyclohexyl groups were omitted for clarity. Selected bond lengths (pm) and angles (deg): Pt−B 200.1(3), Pt−Br2 259.12(2), B−N 140.9(3), B−Br1 201.9(3), N−Si 174.1(2); B−Pt−P1 89.71(7), B−Pt−P2 89.67(7), B−Pt−Br2 179.35(7), Pt−B−N 128.14(18), Pt−B−Br 120.56(13), N−B−Br 111.30(18), B−N−Si 138.01(18); P1−Pt−B−N −85.0(2), P2−Pt−B−N 86.6(2), Br−B−N−Si −1.9(3). Estimated standard deviations are given in parentheses.

hydrogen bond. The decrease in the bond order between boron and nitrogen associated with hydrobromination is reflected in the elongated B−N distance of 140.9(3) pm [cf. 126.0(4) ppm for **1**]. However, reflecting the poor π-donor abilities of the bromide substituent, this bond lengthening is less pronounced than described for *trans*-[$(Cy_3P)_2BrPt\{B(OMe)N(H)SiMe_3\}$] [143.2(3) pm][16] and *trans*-[$(Cy_3P)_2BrPt\{B(N(H)Ph)N(H)SiMe_3\}$] [144.4(5) pm].[12]

At this point we would like to emphasize that the formation of the iminoboryl complex **1** by elimination of trimethylbromosilane proceeds at ambient temperature, and the proposed intermediate *trans*-[$(Cy_3P)_2BrPt\{B(Br)N(SiMe_3)_2\}$] could not even be observed spectroscopically. In contrast, despite the close proximity of the silicon and the bromide in boryl complex **4**, benzene-D_6 solutions give no evidence for elimination of bromosilane at room temperature. Only heating the solution to 80 °C initiated a reaction. However, ^{31}P NMR spectroscopy reveals the predominant phosphorus-containing species in solution to be *trans*-[$(Cy_3P)_2Pt(H)Br$][19] and, thus, indicates cleavage of the bond between platinum and boron. To explore further the stability of **4**, its reactivity toward basic reagents was examined. Addition of triethylamine to a clear solution of **4** in benzene-D_6 is accompanied by instant formation of a colorless solid, which can be isolated by filtration and identified by ^{1}H NMR spectroscopy as [Et_3NH]Br. Multinuclear NMR spectroscopy performed on the filtrate reveals clean regeneration of *trans*-[$(Cy_3P)_2BrPt(B{\equiv}NSiMe_3)$] (**1**) (Scheme 1).

As was mentioned previously, organoboranes constitute extremely valuable intermediates in synthetic organic chemistry. Probably the most popular way to prepare those compounds is hydroboration, i.e., the addition of boron−hydrogen bonds to unsaturated substrates. In this respect, Lewis acidic boranes resemble protic acids, though often highly selectively yielding the inverse regioisomer.[7] Consequently, reactivity of main group-substituted iminoboranes has also been in the focus of research interests over many years,[15,20] and we wondered if the observed reactivity patterns would be transferable to our platinum-stabilized systems. Furthermore, the presence of two unsaturated units of different polarity as well as a different degree of sterical protection in *trans*-[$(Cy_3P)_2Pt(B{\equiv}NSiMe_3)(C{\equiv}CPh)$] (**2**) suggested to conduct competitive experiments and by chance would allow for the stepwise preparation of rigid-rod polymers by reaction of bifunctional reagents.

Scheme 2. Synthesis of *trans*-[$(Cy_3P)_2BrPt\{B(H)N(SiMe_3)Bcat\}$] (5)



Monitoring the reaction of **1** with equimolar amounts of catecholatoborane (HBcat = $HBO_2C_6H_4$) reveals subsequent consumption of the starting materials and clean formation of one new compound. ^{31}P NMR data (22.9 ppm, $^{1}J_{Pt-P}$ = 3107 Hz) once more significantly vary from those of the starting complex **1** (31.2 ppm, $^{1}J_{Pt-P}$ = 2389 Hz)[11] and clearly indicate an increase in the coordination number of the boron atom at platinum. This interpretation is also consistent with the pronounced downfield shift observed for the platinum-bound boron atom (58 ppm, cf. **1**: 26 ppm).[11] In contrast, the second signal in the ^{11}B NMR spectrum (27 ppm) appears only slightly downfield shifted with respect to the starting borane (25 ppm).[21] Besides the characteristic signals for the tricyclohexylphosphine ligands, the ^{1}H NMR spectrum of the product displays one set of signals that can be assigned to the catecholato moiety with an integration of 4 with respect to the trimethylsilyl resonance (9). Unfortunately, even ^{11}B-decoupled ^{1}H NMR experiments performed on saturated benzene solutions of **5** did not allow for the detection of a signal that can be assigned to the hydrogen at boron. This phenomenon has already been observed for a series of Lewis base (LB)-stabilized boryl complexes of the general formula [$L_nM-BH_2\cdot LB$].[22] Hence, only in very few cases could broad resonances be detected for the BH_2 moiety, and most of the signals were not observed. However, X-ray diffraction experiments performed on suitable single crystals of **5** obtained from a mixture of dichloromethane and hexane via slow diffusion left no doubt on the constitutional composition of the hydroboration product of **1** (Scheme 2).

The molecular structure (Figure 2) unequivocally reveals addition of the catecholatoboryl moiety to the former imino

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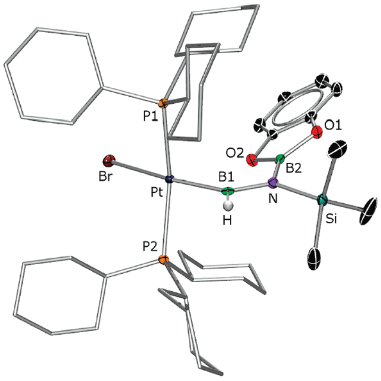
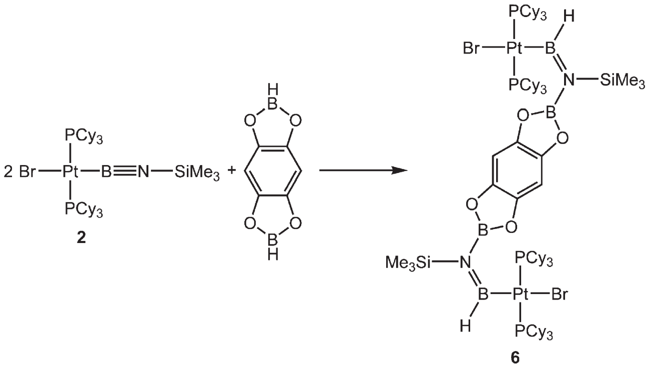


Figure 2. Molecular structure of *trans*-[$(Cy_3P)_2BrPt\{B(H)N(SiMe_3)Bcat\}$] (**5**). Thermal ellipsoids are represented at the 50% probability level. Ellipsoids of cyclohexyl groups were omitted for clarity. Selected bond lengths (pm) and angles (deg): Pt−B1 202.0(3), Pt−Br 263.19(3), B1−H 121(3), B1−N 145.2(3), N−B2 142.6(3), B2−O1 140.0(3), B2−O2 140.0(3), N−Si 178.1(2); B1−Pt−P1 90.17(7), B1−Pt−P2 89.81(7), B−Pt−Br2 167.32(8), Pt−B1−N 125.74(17), Pt−B1−H 121.5(14), N−B1−H 112.7(14), B1−N−B2 123.2(2), B1−N−Si 119.15(16), B2−N−Si 117.41(17), P1−Pt−B1−N −95.92(19), Pt−B1−N−Si −175.68(12), Pt−B1−N−B2 9.8(3), B1−N−B2−O1 147.7(2), B1−N−B2−O2 −33.0(4); ∠(B1B2NSi,B1B2O1O2) 30.19(7). Estimated standard deviations are given in parentheses.

nitrogen atom. Furthermore, an electron residual peak (0.74 e^-) at the vacant site of the triangle around the boron at platinum was obtained from Fourier analysis, indicating the presence of a hydrogen atom. Thus, the structural data clearly let us conclude the formation of a hydrogen-substituted boryl complex, which to the best of our knowledge represents the first example of its kind. Even though the examples of compounds with multicenter transition metal−boron interactions (e.g., σ-hydroborane,[23] σ-hydroborate,[24] σ-hydroborinium,[25] polyborane, and carborane complexes[26]) are plentiful, complexes of boron-centered ligands in electron-precise coordination modes with B−H bonds are limited to one bridging borylene complex[27] and the boryl complexes mentioned above.[22] However, in all of these compounds the boron center was stabilized by coordination of a Lewis base.

The enlarged Pt−B [202.0(3) pm] and Pt−Br [263.19(3) pm] separations in **5** with respect to the hydrobromination adduct **4** are in full agreement with the previously described dependence of the *trans* influence from the electronegativity of the substituents at boron.[9,28] The boryl ligand exhibits a nearly planar geometry [$\angle_{Pt-B1-N-B2} = 9.8(3)°$, $\angle_{Pt-B1-N-Si} = -175.68(12)°$] and is oriented almost perpendicular to the platinum bisphosphine axis [$\angle_{B1-Pt-P1} = 90.17(7)°$]. The catecholatoboryl moiety is twisted out of this plane by 30.19(7)°, which should antagonize a multiple-bond character to the nitrogen atom. Nevertheless, probably due to hybridization effects, this B−N bond [142.6(3) pm] is considerably shorter than the bond between nitrogen and the boron atom at platinum [145.2(3) pm].

Scheme 3. Synthesis of [{*trans*-$(Cy_3P)_2BrPt(B(H)N(SiMe_3)BO_2)\}_2C_6H_2$] (6)



As was determined by NMR spectroscopy, *trans*-[$(Cy_3P)_2Pt(B{\equiv}NSiMe_3)(C{\equiv}CPh)$] (**2**), too, initially cleanly reacts with equimolar amounts of HBcat. Thus, after 30 min ^{31}P NMR data indicate formation of one new compound (23.4 ppm, $^1J_{Pt-P}$ = 2896 Hz). Although we cannot completely rule out hydroboration at the acetylide ligand, the observed ^{11}B NMR resonance at 28 ppm rather implies reaction at the more polar iminoboryl moiety, as we would expect a carbon-substituted catecholatoborane to exhibit a slightly higher chemical shift.[18] Moreover, the $SiMe_3$ resonance (0.61 ppm) appears considerably shifted to low field in comparison to **2** (0.42 ppm) and therefore supports the conclusion of severe changes in its immediate chemical environment. Addition of another equivalent of HBcat does not cause any further changes that would indicate a second hydroboration of **2**. Instead, a set of signals for unreacted HBcat can be observed.

In contrast to *trans*-[$(Cy_3P)_2BrPt\{B(H)N(SiMe_3)Bcat\}$] (**5**) the reaction product of HBcat and **2** turned out to be inherently unstable. Thus, even handled exclusively under glovebox conditions and in J-Young NMR tubes to ensure absolute exclusion of air, a slow decrease of the signal at 23.4 ppm could be observed in the ^{31}P NMR spectrum. Hence, after 60 h at room temperature, multinuclear NMR spectroscopy performed on a benzene-D_6 solution indicated complete decomposition, and several signals could be observed in the ^{31}P NMR spectrum. One of the three most prominent singlets was assigned to *trans*-[$(Cy_3P)_2Pt(H)_2$] (52.9 ppm, $^1J_{Pt-P}$ = 2873 Hz) by comparison with literature values.[29] The other two signals (46.3 ppm, $^1J_{Pt-P}$ = 2695 Hz and 38.3 ppm, $^1J_{Pt-P}$ = 2721 Hz, respectively) eventually can be assigned to the products of Pt−B and Pt−C bond cleavage. Especially the latter signal strongly resembles that of the hydrogen bromide adduct *trans*-[$(Cy_3P)_2Pt(H)Br$] (38.3 ppm, $^1J_{Pt-P}$ = 2721 Hz),[30] which we often identified as a decomposition product of bromide-substituted boryl complexes. Thus, obviously the increased σ-donor properties that come along with hydroboration destabilize the whole system, where the two strong *trans* influence ligands are forced in a *trans* position because of sterically extremely demanding co-ligands.

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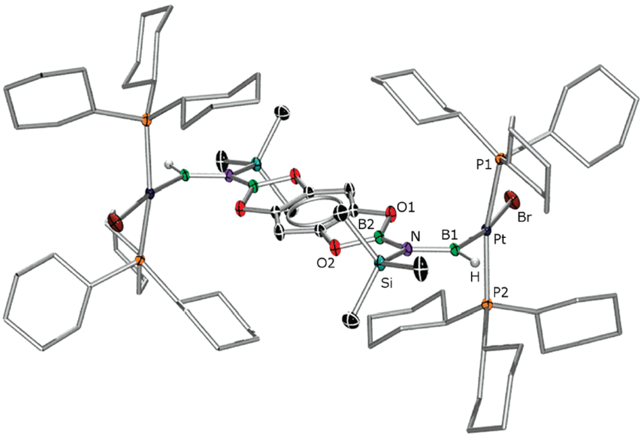

Figure 3. Centrosymmetrical molecular structure of [{*trans*-(Cy$_3$P)$_2$BrPt(B(H)N(SiMe$_3$)BO$_2$)}$_2$C$_6$H$_2$] (**6**)·3C$_6$H$_6$. Thermal ellipsoids are represented at the 50% probability level. Solvent molecules, ellipsoids, and disorder of cyclohexyl groups were omitted for clarity. Selected bond lengths (pm) and angles (deg): Pt−B1 201.0(5), Pt−Br 263.10(4), B1−N 145.6(6), N−B2 142.3(6), B2−O1 140.2(5), B2−O2 139.3(6), N−Si 178.7(4); B1−Pt−P1 88.97(14), B1−Pt−P2 89.65(14), B−Pt−Br2 169.40(14), Pt−B1−N 125.1(3), B1−N−B2 122.1(4), B1−N−Si 119.15(16), B2−N−Si 115.5(3), P1−Pt−B1−N −94.4(4), Pt−B1−N−Si −174.4(2), Pt−B1−N−B2 4.8(6), B1−N−B2−O1 −18.5(7), B1−N−B2−O2 163.5(4); ∠(B1B2NSi,B1B2O1O2) 18.81(8). Estimated standard deviations are given in parentheses.

Linking two iminoboryl moieties by reaction with bifunctional reagents provides facile access to dinuclear complexes connected by bridging boryl ligands.[12] Compounds of this type still are very limited in number, although they have been proposed to serve as model substances for transition metal containing π-conjugated polymers.[31] Reaction of HBO$_2$C$_6$H$_2$O$_2$BH and two equivalents of **1** in benzene solution (Scheme 3) affords a colorless crystalline solid, which was identified as [{*trans*-(Cy$_3$P)$_2$BrPt(B(H)N(SiMe$_3$)BO$_2$)}$_2$C$_6$H$_2$] (**6**)·2C$_6$H$_6$ by means of X-ray diffraction studies (Figure 3). The relevant structural parameters are in very good agreement with those observed for the mononuclear hydroboration product **5**. Only the bridging bis(boryl) unit is twisted to a lesser extent with respect to the (silylamino)boryl moiety [18.81(8)°]. However, the separations between nitrogen and the boron atoms are identical within the 3σ-criterion to those of **5**, as are all other important bond lengths. Due to the poor solubility of **6**, no signals could be observed in the ^{11}B NMR spectrum. Nevertheless, the spectral data clearly indicate clean formation of the dinuclear complex **6**.

Conclusions

In this work we described an experimental study on the reactivity of platinum iminoboryl complexes toward covalent element−hydrogen bonds of opposing polarity regiospecifically yielding the *trans* products of 1,2-dipolar addition. Hence, hydrogen bromide reversibly adds to the B≡N triple bond of *trans*-[(Cy$_3$P)$_2$(Br)Pt(B≡NSiMe$_3$)] (**1**). Despite the close proximity of the bromide to the trimethylsilyl substituent, the reaction product *trans*-[(Cy$_3$P)$_2$BrPt{B(Br)N(H)SiMe$_3$}] (**4**) did not show any signs of elimination of bromosilane. Furthermore, the reaction of **1** and the bifunctional complex *trans*-[(Cy$_3$P)$_2$Pt(B≡NSiMe$_3$)(C≡CPh)] (**2**) with hydroboration reagents was probed, revealing in both cases clean 1:1 reaction of the reagents. Whereas the reaction product of **2** and catecholatoborane is inherently unstable, both the mono- and the dinuclear hydroboration products of **1** could be isolated and fully characterized.

Experimental Details

General Considerations. All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk-line or glovebox techniques. Dichloromethane, hexane, and toluene were purified and dried using an M. Braun solvent purification system. Deuterated solvents were dried over molecular sieves and degassed by three freeze−pump−thaw cycles before use. Other solvent were distilled from appropriate drying agents.[32] All solvents were stored over activated molecular sieves. NMR spectra of isolated compounds were acquired on a Bruker Avance 500 NMR spectrometer. ^{15}N,^{1}H COSY spectra were recorded on a DRX 300 spectrometer, and routine NMR measurements were performed on a Bruker Avance 200 spectrometer. Chemical shifts (δ) are given in ppm. NMR spectra were referenced to external SiMe$_4$ via the residual protio solvent (^{1}H) or the solvent itself (^{13}C), BF$_3$·OEt$_2$ (^{11}B), MeNO$_2$ (^{15}N), and 85% H$_3$PO$_4$ (^{31}P), respectively. Microanalyses were performed on either a Leco CHNS-932 or an Elementar Vario Micro cube elemental analyzer. *trans*-[(Cy$_3$P)$_2$(Br)Pt(B≡NSiMe$_3$)] (**1**)[11] and HBO$_2$C$_6$H$_2$O$_2$BH[33] were prepared according to published literature procedures. All other compounds were purchased from commercial sources and degassed in vacuo.

Preparation of *trans*-[(Cy$_3$P)$_2$(Br)Pt{B(Br)N(H)SiMe$_3$}] (4). A solution of *trans*-[(Cy$_3$P)$_2$(Br)Pt(B≡NSiMe$_3$)] (**1**) (303.2 mg, 325 μmol) in toluene (5 mL) was cooled to −70 °C, and a solution of hydrogen bromide in diethyl ether (1.2 mL, 0.31 M, 372 μmol) was added, causing the formation of a colorless solid. The stirred reaction mixture was allowed to warm to room temperature and the precipitate dissolved. All volatile components were removed in vacuo, yielding a pale yellow powder (299.4 mg, 91%). Recrystallization from a mixture of benzene and hexane gave colorless crystals suitable for X-ray diffraction studies.

^{1}H NMR (500 MHz, C$_6$D$_6$, 295.0 K): δ 4.55 (s, 1H, N*H*), 2.87 (br m, 6H, *Cy*), 2.26−1.21 (m, 60H, *Cy*), 0.38 (s, 9H, Si*Me*$_3$). ^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$, 295.7 K): δ 38 (br s). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 295.0 K): δ 35.6 (vt, $N = |^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P-C}}| = 28$ Hz, C$_1$ *Cy*), 31.3 (s, C$_{3,5}$ *Cy*), 30.7 (s, C$_{3,5}$ *Cy*), 27.9 and 27.8 (two overlapping vt, $N = |^2J_{\mathrm{P-C}} + {}^4J_{\mathrm{P-C}}| = 11$ Hz, C$_{2,6}$ *Cy*), 27.1 (s, C$_4$ *Cy*), 2.3 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$, 295.9 K): δ 20.2 (s, $^1J_{\mathrm{Pt-P}} = 2805$ Hz). ^{15}N,^{1}H COSY (^{15}N: 30 MHz, ^{1}H: 300 MHz, C$_6$D$_6$, 296.2 K): cross-peak between −260.5 (^{15}N) and 4.55 (^{1}H). Anal. Calcd for C$_{39}$H$_{76}$BBr$_2$NP$_2$PtSi: C 46.16, H 7.55, N 1.38. Found: C 46.10, H 7.63, N 1.39.

Reaction of *trans*-[(Cy$_3$P)$_2$(Br)Pt{B(Br)N(H)SiMe$_3$}] (4) with Triethylamine. A solution of triethylamine (1.0 mg, 10 μmol) in benzene-D$_6$ (0.1 mL) was added to a solution of *trans*-[(Cy$_3$P)$_2$(Br)Pt{B(Br)N(H)SiMe$_3$}] (**4**) (10.1 mg, 10 μmol) in benzene-D$_6$ (0.3 mL), affording the precipitation of a colorless solid. After 40 min the precipitate was removed via filtration and by ^{1}H

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NMR spectroscopy identified as $[Et_3NH]Br$. Multinuclear NMR experiments of the filtrate revealed almost quantitative formation of *trans*-$[(Cy_3P)_2(Br)Pt(B{\equiv}NSiMe_3)]$ (**1**).

Preparation of *trans*-$[(Cy_3P)_2BrPt\{B(H)N(SiMe_3)(Bcat)\}]$ (5). A solution of HBcat (4.3 mg, 35.9 μmol) in benzene (0.4 mL) was added to *trans*-$[(Cy_3P)_2(Br)Pt(B{\equiv}NSiMe_3)]$ (**1**) (30.3 mg, 32.4 μmol). After 3 h the reaction mixture was layered with hexane (0.8 mL) and the solvent mixture was allowed to evaporate slowly. Within two days a colorless solid had precipitated (32.4 mg, 95%). Recrystallization from dichloromethane/hexane via diffusion yielded colorless crystals.

^{1}H NMR (500 MHz, C_6D_6, 296.2 K): δ 7.21 (m, 2H, *cat*), 6.84 (m, 2H, *cat*), 2.60 (br m, 6H, *Cy*), 2.35−1.06 (m, 60H, *Cy*), 0.55 (s, 9H, Si*Me*$_3$), *H*B could not be observed. ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 296.9 K): δ 58 (br s, Pt*B*), 27 (br s, *B*cat). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 296.0 K): δ 149.1 (s, $C_{1,2}$ *cat*), 123.2 (s, $C_{4,5}$ *cat*), 112.9 (s, $C_{3,6}$ *cat*), 36.2 (vt, $N = |^1J_{P-C} + {}^3J_{P-C}| = 27$ Hz, C_1 *Cy*), 30.8 (s, $C_{3,5}$ *Cy*), 30.5 (s, $C_{3,5}$ *Cy*), 28.5 (vt, $N = |^2J_{P-C} + {}^4J_{P-C}| = 11$ Hz, $C_{2,6}$ *Cy*), 28.3 (vt, $N = |^2J_{P-C} + {}^4J_{P-C}| = 10$ Hz, $C_{2,6}$ *Cy*), 27.4 (s, C_4 *Cy*), 3.2 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 296.1 K): δ 22.9 (s, $^1J_{Pt-P} = 3107$ Hz). Anal. Calcd for $C_{45}H_{80}B_2BrNO_2P_2PtSi$: C 51.29, H 7.65, N 1.33. Found: C 51.22, H 7.56, N 1.16.

Preparation of $[\{$*trans*-$(Cy_3P)_2BrPt(B(H)N(SiMe_3)BO_2)\}_2C_6H_2]$ (6). A solution of $HBO_2C_6H_2O_2BH$ (8.7 mg, 53.7 μmol) in benzene (0.2 mL) was added to a solution of *trans*-$[(Cy_3P)_2(Br)Pt(B{\equiv}NSiMe_3)]$ (**1**) (100.0 mg, 107.2 μmol) in benzene (0.4 mL). During 16 h a crystalline solid precipitated. The mixture was layered with hexane (1 mL), and after 24 h the supernatant solution was decanted off. The colorless solid was washed with hexane to yield spectroscopically pure *trans*-$[\{(Cy_3P)_2(Br)Pt(B(H)N(SiMe_3)BO_2)\}_2C_6H_2]$ (**6**) (92.4 mg, 85%).

^{1}H NMR (500 MHz, C_6D_6, 296.1 K): δ 7.48 (s, 2H, O_4C_4(CH)$_2$), 2.63 (br s, 12H, Cy), 2.34−1.13 (m, 120H, Cy), 0.57 (s, 18H, Si*Me*$_3$), *H*B could not be observed. ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 296.2 K): no signals observed. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 295.9 K): δ 143.5 (s, $O_4C_4(CH)_2$), 98.1 ($O_4C_4(CH)_2$, from HMBC), 35.6 (br s, C_1 *Cy*), 30.5 (s, $C_{3,5}$ *Cy*), 30.1 (s, $C_{3,5}$ *Cy*), 28.0 (br s, $C_{2,6}$ *Cy*), 27.1 (s, C_4 *Cy*), 3.0 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 296.1 K): δ 22.8 (s, $^1J_{Pt-P} = 3087$ Hz). Anal. Calcd for $C_{84}H_{154}B_4Br_2N_2O_4P_4Pt_2Si_2$: C 49.71, H 7.65, N 1.38. Found: C 50.21, H 7.66, N 1.43.

Crystal Structure Determinations. The crystal data were collected on a Bruker X8 Apex II diffractometer with a CCD area detector and multilayer mirror monochromated Mo Kα radiation. The structures were solved using direct methods, refined with the Shelx software package,[34] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except that bound to the boron atom in **5** were assigned to idealized positions and were included in structure factor calculations. Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, under reference nos. CCDC 777340 (**4**), 777341 (**5**), and 777342 (**6**), respectively.

Crystal data for *trans*-$[(Cy_3P)_2BrPt\{B(Br)N(H)SiMe_3\}]$ (4): $C_{39}H_{76}BBr_2NP_2PtSi$, $M_r = 1014.76$, colorless block, $0.31 \times 0.28 \times 0.22$ mm^3, monoclinic space group *Pc*, $a = 10.0348(3)$ Å, $b = 14.1218(3)$ Å, $c = 18.4385(4)$ Å, $\beta = 121.0080(10)°$, $V = 2239.51(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.505$ g cm^{-3}, $\mu = 5.041$ mm^{-1}, $F(000) = 1028$, $T = 100(2)$ K, $R_1 = 0.0168$, $wR_2 = 0.0411$, 13 220 independent reflections [$2\theta \le 65.72°$] and 427 parameters.

Crystal data for *trans*-$[(Cy_3P)_2BrPt\{B(H)N(SiMe_3)Bcat\}]$ (5): $C_{45}H_{80}B_2BrNO_2P_2PtSi$, $M_r = 1053.75$, colorless block, $0.31 \times 0.29 \times 0.275$ mm^3, triclinic space group $P\bar{1}$, $a = 10.7535(9)$ Å, $b = 12.1267(10)$ Å, $c = 20.7160(15)$ Å, $\alpha = 101.182(3)°$, $\beta = 96.291(3)°$, $\gamma = 113.253(3)°$, $V = 2382.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.469$ g cm^{-3}, $\mu = 3.912$ mm^{-1}, $F(000) = 1080$, $T = 100(2)$ K, $R_1 = 0.0206$, $wR_2 = 0.0501$, 9217 independent reflections [$2\theta \le 52.12°$] and 499 parameters.

Crystal data for $[\{$*trans*-$(Cy_3P)_2BrPt(B(H)N(SiMe_3)BO_2)\}_2C_6H_2]$ (6)$\cdot 3C_6H_6$: $C_{102}H_{172}B_4Br_2N_2O_4P_4Pt_2Si_2$, $M_r = 2263.72$, colorless plate, $0.115 \times 0.10 \times 0.045$ mm^3, triclinic space group $P\bar{1}$, $a = 11.4059(4)$ Å, $b = 12.1420(4)$ Å, $c = 20.5196(7)$ Å, $\alpha = 82.860(2)°$, $\beta = 76.086(2)°$, $\gamma = 78.028(2)°$, $V = 2690.09(16)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.397$ g cm^{-3}, $\mu = 3.470$ mm^{-1}, $F(000) = 1164$, $T = 100(2)$ K, $R_1 = 0.0423$, $wR_2 = 0.1069$, 12 728 independent reflections [$2\theta \le 62.14°$] and 646 parameters.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. A.S. thanks the Fonds der Chemischen Industrie for a doctoral fellowship.

Supporting Information Available: Crystallographic data of compounds **4**−**6** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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