Syntheses and Structures of Mono- and Dinuclear Cationic Base-Stabilized Platinum Borylene Complexes

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A series of fully characterized cationic, base-stabilized borylene complexes of the type *trans*-$[(Cy_3P)_2Pt(Br)\{B(NC_5H_4\text{-}4\text{-}R)X\}][BAr^f{}_4]$ (R = Me, X = NMe_2, Pip, Br; R = *t*Bu, X = Pip) were synthesized by addition of $Na[BAr^f{}_4]$ and a pyridine Lewis base to boryl complexes *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)X\}]$, inducing a formal 1,2-bromide shift from the boron atom to the platinum center. Furthermore, the reactions of $[Pt(PCy_3)_2]$ with 1,4-$(Br_2B)_2$-C_6H_4 allowed for the isolation of the dinuclear boryl complex 1,4-*trans*-$[\{(Cy_3P)_2(Br)Pt(BBr)\}_2\text{-}C_6H_4]$ and *trans*-$[(Cy_3P)_2Pt(Br)\text{-}1\text{-}\{B(Br)\text{-}C_6H_4\text{-}4\text{-}\{BBr_2(PCy_3)\}\}]$. The former was treated with $K[B(C_6F_5)_4]$, which afforded the abstraction of both platinum-bound bromides and formation of the dicationic boryl complex 1,4-*trans*-$[\{(Cy_3P)_2Pt(BBr)\}_2\text{-}C_6H_4][B(C_6F_5)_4]_2$. This compound was converted into the base-stabilized borylene species 1,4-*trans*-$[\{(Cy_3P)_2(Br)Pt\{B(NC_5H_4\text{-}4\text{-}Me)\}\}_2\text{-}C_6H_4][B(C_6F_5)_4]_2$ by reaction with 4-methylpyridine.

Introduction

Transition metal boryl and borylene complexes have attracted considerable interest,[1] especially due to the fact that the former are important key intermediates for transition metal-catalyzed hydro-[2] and diboration,[3] as well as for the C−H functionalization[4] of organic substrates. In addition to the first bridged[5] and terminal[6] borylene complexes a wide variety of different coordination modes have been realized for B−R ligands over the past decade. These include heterodinuclear bridged,[7] semibridged,[8] metallo group,[9] and main group as well as metal base stabilized borylene species.[10]

Most commonly, salt elimination, halide abstraction, and thermally or photochemically induced borylene transfer reactions are employed for the synthesis of borylene complexes. The first method provided, for example, group 6 borylene complexes $[(OC)_5M{=}BN(SiMe_3)_2]$ (M = Cr, Mo, W),[6,11] the bridged compounds $[\{(\eta^5\text{-}C_5R_5)(OC)M\}_2\{\mu\text{-}B(NSiMe_3)_2\}(\mu\text{-}CO)]$ (M = Fe, R = H, Me; M = Ru, R = H),[12] or the metalloborylene complexes $[(\eta^5\text{-}C_5H_5)(OC)_2Fe{=}B{=}M(CO)_n]$ (M = Fe, n = 4; M = Cr, n = 5).[9] Aldridge and co-workers employed halide abstraction for the preparation of the cationic species $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe{=}BR]^+$ (R = 2,4,6-Me_3-C_6H_2, NCy_2, N*i*Pr_2) from corresponding haloboryl complexes $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\text{-}$

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Chart 1. Different Base-Stabilized Borylene Complexes

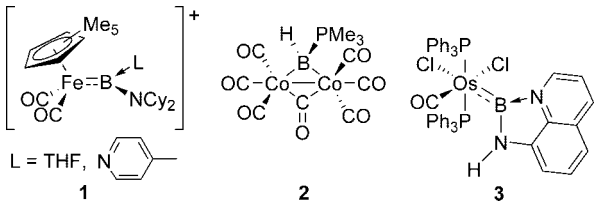
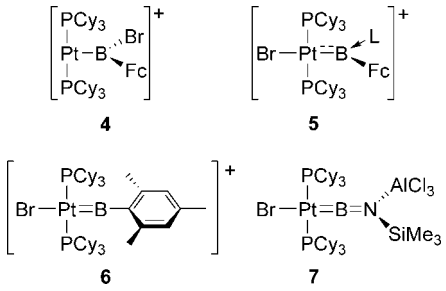


Chart 2. Diverse Platinum Boryl and Borylene Complexes



B(Hal)R] (Hal = Cl, Br),[10a,13] whereas the complexes [(η^5-C_5H_5)$(OC)_3V$=B(NSiMe$_3$)$_2$],[14] [L$(OC)_3$M{μ-BN(SiMe$_3$)$_2$}(μ-CO)M′(PCy_3)] (Cy = cyclohexyl) (L = CO, PCy_3; M = Cr, Mo, W; M′ = Pd, Pt),[8] [{(η^5-C_5H_5)(OC)Co}{μ-BN(SiMe$_3$)$_2$}{W$(CO)_5$}],[15] or [$(OC)_2$Rh(μ-Cl)$_2$Rh{μ-BN(SiMe$_3$)$_2$}$_2$(μ-CO)]$_2$[16] were prepared via partial or total borylene transfer.

However, none of these former methods are suitable for the synthesis of base-stabilized borylene complexes, which were obtained by (i) addition of a Lewis base to a borylene complex, furnishing, for example, [(η^5-C_5Me_5)$(OC)_2$Fe=B(L)NCy$_2$]$^+$ (L = THF, NC_5H_4-4-Me) (**1**),[10a] (ii) reaction of [B_2H_4(PMe_3)$_2$] with [$Co_2(CO)_8$] to give [{$(OC)_3$Co}$_2$(μ-CO)(μ-BHPMe_3)] (**2**),[10b] or (iii) addition of a Lewis base to a haloboryl complex and concomitant 1,2-halide shift, yielding osmium borylene complexes such as **3**[10c−e] (Chart 1).

Recently, we communicated preliminary results on the reactivity of the T-shaped cationic boryl complex *trans*-[$(Cy_3P)_2$Pt{B(Br)Fc}][BAr$^f_4$] (**4**; Fc = ferrocenyl) toward 4-methylpyridine.[10f] This strong Lewis base surprisingly did not coordinate to the vacant site at the platinum center in *trans*-position to the boryl ligand, but to the boron atom with formation of the cationic complex *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)Fc}][BAr$^f_4$] (**5**) and formal 1,2-shift of bromide from boron to platinum.[10f] In addition to this base-stabilized borylene complex, further platinum borylene species *trans*-[$(Cy_3P)_2$Pt-(Br){B(2,4,6-Me_3-C_6H_2)}][B(C_6F_5)$_4$] (**6**)[17] and *trans*-[$(Cy_3P)_2$-Pt(Br){BN($AlCl_3$)$SiMe_3$}] (**7**)[18] have been reported (Chart 2), which, however, display two-coordinate boron centers and, thus, are characterized by a more pronounced Pt−B multiple bond character.

Results and Discussion

Preparation of Mononuclear Base-Stabilized Borylene Complexes. To determine whether the aforementioned behavior of platinum complex **4**, which was prepared from *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)Fc}] (**8**) and Na[BAr$^f_4$], toward Lewis bases is exceptional or can be exploited as a general access to platinum borylene species, different complexes of the type *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)X}] (X = NMe_2, Pip, Br) (**9**−**11**) (Pip = piperidyl)[19a] were reacted with Na[BAr$^f_4$], yielding the corresponding cationic T-shaped boryl species, namely, *trans*-[$(Cy_3P)_2$Pt{B(Br)X}[BAr$^f_4$], as determined by multinuclear NMR spectroscopy.[19b] Subsequent addition of 4-methylpyridine induced a formal 1,2-bromide shift from the boron atom to the platinum center. $^{31}P\{^1H\}$ NMR data indicate the clean conversion of the starting materials into *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)X}][BAr$^f_4$] (X = NMe_2, Pip, Br) (**12**−**14**) by means of a resonance at around 26 ppm and a coupling constant of approximately 2500 Hz, which is significantly decreased by about 300 Hz in comparison to the neutral species **8**−**11** (Table 1). Likewise, a corresponding reaction of **10** with Na[BAr$^f_4$] and 4-*tert*-butylpyridine allowed for the isolation of *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-*t*Bu)Pip}][BAr$^f_4$] (**15**) (Scheme 1). All compounds were isolated as analytically pure, colorless, air- and moisture-sensitive solids in yields up to 84%.

The $^{13}C\{^1H\}$ NMR spectra exhibit the expected signals for the coordinated base [average values δ = 165 (s, C^{para}), 145 (s, C^{ortho}), 127 (s, C^{meta}), 22 (s, Me)/30 (s, Me, *t*Bu) ppm], and the ^1H NMR spectra two multiplets at around δ = 8.9 and 7.7 ppm for the aromatic protons. However, the bromoborylene complex **14** shows a different ^1H NMR spectrum with four broad resonances at δ = 10.66, 9.57, 7.95, and 7.83 ppm. The former signal is significantly deshielded, which most likely can be attributed to an interaction of this proton with the boron-bound bromide (Figure 1), thus accounting for the decreased symmetry observed for this species in solution.[20]

Suitable crystals for X-ray analyses were obtained for *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)X}][BAr$^f_4$] (X = NMe_2, Pip) (**12**, **13**) and *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-*t*Bu)Pip}][BAr$^f_4$] (**15**) by layering dichloromethane solutions with hexane and slow evaporation of the solvent (Figure 2).

The molecular structures of **12**, **13**, and **15** show B−N2 (Lewis base) separations [**12**, 1.585(4) Å; **13**, 1.565(5) Å; **15**, 1.581(6) Å] similar to that in *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)Fc}][BAr$^f_4$] (**5**) [B−N 1.582(6) Å].[10f] The B−N1 distances [**12**, 1.406(4) Å; **13**, 1.388(5) Å; **15**, 1.402(7) Å] are indicative of B=N double bonds and, thus, effective B−N π-donation; despite this, the boron center is still Lewis acidic and available for base coordination. The Pt−Br bond lengths [**12**, 2.5909(3) Å; **13**, 2.5986(4) Å; **15**, 2.5857(5) Å; **5**, 2.6057(5) Å] are comparable to those in neutral boryl complexes *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)X}] [X = NMe_2 (**9**), 2.6087(3) Å; X = Pip (**10**), 2.6313(5) Å; X = Fc (**8**), 2.6183(8) Å][19a,21] and demonstrate that boryl and base-stabilized borylene moieties impose a similar *trans*-influence. The pronounced steric demand of the borylene ligand =B(L)R imposes a twist of the plane containing the borylene fragment =B(L)R toward the PtP_2 plane [**12**, 79.45°; **13**, 75.56°; **15**, 73.7(4)°]; commonly an angle of approximately 90° is preferred [**9**, 88.93°; **10**, 83.83°].[19a]

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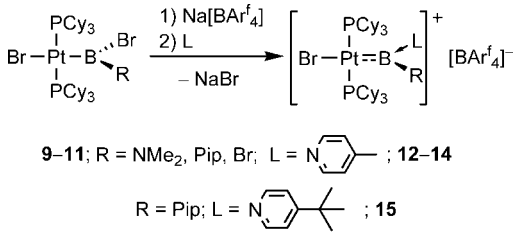
Table 1. Selected Data of the Base-Stabilized Borylene Complexes *trans*-[(Cy$_3$P)$_2$Pt(Br){B(L)X}]$^+$ (5, 12−15) Compared to the Starting Materials *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)X}] (8−11)[19a] (δ in ppm, J in Hz)

−B(L)X	compound	δ (^{31}P) ($^1J_{P-Pt}$)		starting material δ (^{31}P) ($^1J_{P-Pt}$)	yield
X = Fc, L = NC_5H_4-4-Me[10f]	**5**	25.0 (2554)	**8**	21.5 (2892)	75%
X = NMe_2, L = NC_5H_4-4-Me	**12**	26.2 (2532)	**9**	24.0 (2815)	84%
X = Pip, L = NC_5H_4-4-Me	**13**	27.0 (2548)	**10**	24.6 (2867)	65%
X = Br, L = NC_5H_4-4-Me	**14**	23.9 (2373)	**11**	19.4 (2683)	35%
X = Pip, L = NC_5H_4-4-*t*Bu	**15**	27.2 (2557)	**10**	24.6 (2867)	69%

Scheme 1. Synthesis of Different Cationic, Base-Stabilized Borylene Complexes of Platinum



The Pt−B bond distances [**12**, 2.018(4) Å; **13**, 2.046(4) Å; **15**, 2.023(5) Å] resemble those of the corresponding neutral boryl complexes *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)X}] [**9**, 2.009(3) Å; **10**, 2.021(5) Å].[19a] This phenomenon was already observed for *trans*-[(Cy$_3$P)$_2$Pt(Br){B(NC$_5$H$_4$-4-Me)Fc}][BAr$^f_4$] (**5**) [2.014(5) Å][10f] and its precursor **8** [1.9963(34) Å][21] and is in line with the coordination number of three and the steric demands of the substituents on boron. In contrast, platinum complexes with two coordinate borylene centers, *trans*-[(Cy$_3$P)$_2$Pt(Br){B(2,4,6-Me$_3$-C$_6$H$_2$)}][B(C$_6$F$_5$)$_4$] (**6**)[17] and *trans*-[(Cy$_3$P)$_2$Pt(Br){BN(AlCl$_3$)-SiMe$_3$}] (**7**),[18] are characterized by significantly decreased Pt−B separations of 1.859(3) and 1.904(3) Å, respectively. These findings emphasize the "boryl" character of the metal bound −B(L)R ligand and its decreased M−B multiple bond character. Similar observations were made for the aforementioned osmium complexes with base-stabilized borylene ligands such as **3** and for base-stabilized silylene complexes.[22]

Compounds **12**−**15** were formed by addition of pyridine bases to the boron centers with concomitant 1,2-bromide shift to the central metal, thus increasing the coordination number at platinum. Corresponding intramolecular shifts, especially of α-hydrogen atoms, were found to be kinetically favored, in case of coordinatively unsaturated metal centers.[23] This route already allowed for the first synthesis of platinum silylene complexes[24] and seems to have a similar potential for the preparation of borylene species from haloboryl complexes.

Preparation of a Dinuclear Bisboryl Complex. In order to synthesize a base-stabilized diborylene species of the type [(Cy$_3$P)$_2$Pt(Br){B(L)spacerB(L)}Pt(Br)(PCy$_3$)$_2$] in an analogous way, [Pt(PCy$_3$)$_2$] was first reacted with the bisborylated benzene derivative 1,4-(Br$_2$B)$_2$-C$_6$H$_4$ (**16**) in benzene in order to prepare the corresponding bisboryl complex. Monitoring the reaction by multinuclear NMR spectroscopy revealed the formation of different products depending on the boron−platinum ratio. In a typical experiment, 0.044 mmol of **16** was reacted with a 1.5-fold excess of [Pt(PCy$_3$)$_2$] and the ^{31}P{^{1}H} NMR spectrum revealed one dominating sharp signal at δ = 21.4 ppm flanked by platinum satellites ($^1J_{P-Pt}$ = 2829 Hz) and a broad resonance at δ = −7.9 ppm. From concentrated reaction mixtures, the air- and moisture-sensitive product precipitated and was isolated in analytically pure form. Recrystallization yielded colorless single crystals, which were analyzed by X-ray diffraction, showing that the constitution of the product was not that of the species 1,4-*trans*-[{(Cy$_3$P)$_2$(Br)Pt(BBr)}$_2$-C$_6$H$_4$] (**17**), but *trans*-[(Cy$_3$P)$_2$Pt(Br)-1-{B(Br)-C$_6$H$_4$-4-{BBr$_2$(PCy$_3$)}}] (**18**) (Figure 3).

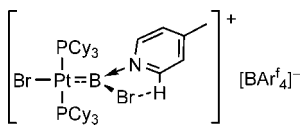


Figure 1. Schematic picture of a possible bromine hydrogen interaction in **14**.

Obviously, only one B−Br bond was oxidatively added to platinum and a PCy$_3$ molecule coordinated to the second boron center. The abstraction of PCy$_3$ from platinum with Lewis acidic boranes with formation of corresponding phosphine boranes was reported before[25] and accounts for the formation of **18**. The gradual darkening of the reaction mixture observed here is attributed to the deposition of Pt(0). The ^{11}B{^{1}H} NMR spectrum of **18** features two broad signals for both distinct boron centers [δ = 73 (Pt−B), −5 ppm (P−B)]. The former one shows a value typical for arylboryl complexes,[19a] and the high-field shifted signal is characteristic for a four-coordinated boron atom.

However, treatment of 1,4-(Br$_2$B)$_2$-C$_6$H$_4$ (**16**) with a larger excess of [Pt(PCy$_3$)$_2$] led to the buildup of another resonance in the ^{31}P{^{1}H} NMR spectrum at δ = 23.5 ppm ($^1J_{P-Pt}$ = 2845 Hz), which indicated the formation of the target product 1,4-*trans*-[{(Cy$_3$P)$_2$(Br)Pt(BBr)}$_2$-C$_6$H$_4$] (**17**). Precipitated material (predominantly **18**) was removed from the mixture, and the remaining solvent was allowed to evaporate slowly in order to isolate pure, air- and moisture-sensitive **17**, which resembles a rare example of a dinuclear, boryl-bridged complex (Scheme 2). The only other fully characterized examples are [(η^5-C$_5$R$_5$)(OC)$_2$FeB-spacer-BFe(CO)$_2$(η^5-C$_5$R$_5$)] (R$_5$ = H$_5$, H$_4$Me, Me$_5$, B-spacer-B = BO$_2$C$_6$H$_2$O$_2$B; R$_5$ = H$_5$, B-spacer-B = *spiro*-B(OCH$_2$)$_2$C(CH$_2$O)$_2$B), which were reported by Aldridge[26] and 1,4-*trans*-[{(Cy$_3$P)$_2$(Br)Pt(B{NH*i*Bu}NH)}$_2$-C$_6$H$_4$], which was synthesized by a 1,2 dipolar addition of 1,4-(H$_2$N)$_2$-C$_6$H$_4$ to the B≡N triple bond of 2 equiv of the iminoboryl complex *trans*-[(Cy$_3$P)$_2$Pt(Br)(BN*i*Bu)] (Chart 3).[27]

The ^{11}B{^{1}H} NMR spectrum of **17** shows one broad resonance at δ = 75 ppm for both boron centers, and thus a similar chemical shift to the platinum-bound boron in **18**. Likewise, in the ^{1}H NMR spectrum only one signal [δ = 8.46 ppm] was detected for the aromatic protons, indicating an increased symmetry in comparison to **18**. Pale yellow, single

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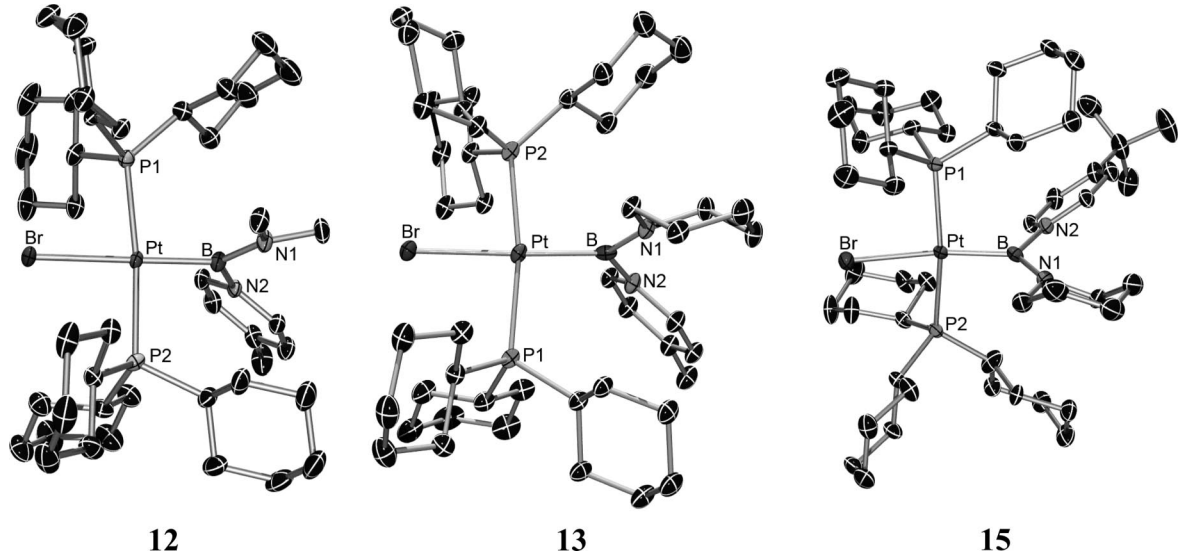


Figure 2. Molecular structures of the cationic, base-stabilized borylene complexes **12**, **13**, and **15**. Counterions, hydrogen atoms, and cocrystallized solvent molecules (**12**, 2 CH_2Cl_2; **13**, 2 C_6H_{14}) are omitted for clarity. In **15** two cyclohexyl groups bound to P2 are disordered. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å] and angles [deg]: **12**, Pt−B 2.018(4), Pt−Br 2.5909(3), B−N1 1.406(4), B−N2 1.585(4), P1−Pt−P2 173.30(3), B−Pt−Br 179.29(11), P2−Pt−B−N1 79.3(3); **13**, Pt−Br 2.5986(4), Pt−B 2.046(4), B−N1 1.388(5), B−N2 1.565(5), P1−Pt−P2 170.13(3), B−Pt−Br 178.17(11), P1−Pt−B−N1 76.6(4); **15**, Pt−Br 2.5857(5), Pt−B 2.023(5), B−N1 1.402(7), B−N2 1.581(6), P1−Pt−P2 165.63(4), B−Pt−Br 164.92(16), P1−Pt−B−N1 106.3(4).

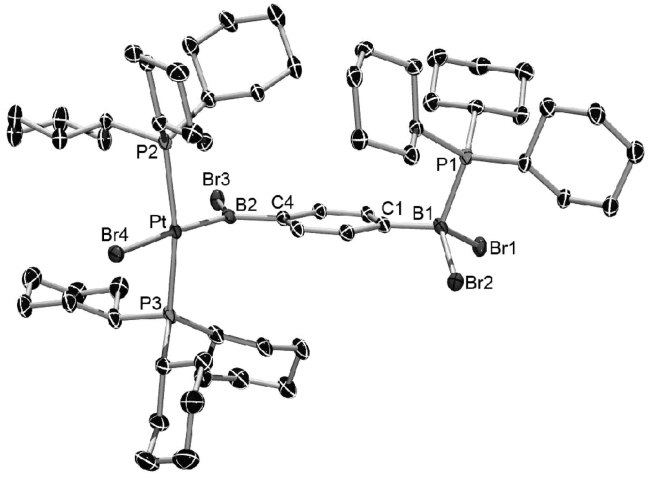
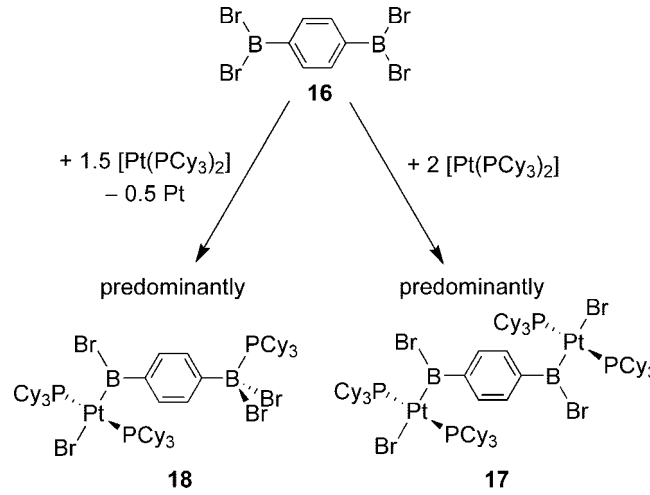


Figure 3. Molecular structure of *trans*-[$(Cy_3P)_2$Pt(Br)-1-{B(Br)-C_6H_4-4-{$BBr_2(PCy_3)$}}] (**18**). Solvent molecules (2.5 C_6H_6 and 0.5 C_6H_{14}) and hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å] and angles [deg]: B1−P1 2.036(5), B1−Br1 2.047(5), B1−Br2 2.055(6), B1−C1 1.608(7), B2−Br3 1.994(5), B2−C4 1.567(7), Pt−B2 1.986(5), Pt−Br4 2.6287(5), C1−B1−P1 112.3(3), C1−B1−Br1 111.1(3), C1−B1−Br2 111.2(3), P3−Pt−P2 165.82(4), Br4−Pt−B2 167.55(15), P2−Pt−B2−C4 96.5(4), Pt−B2−C4−C5 176.6(3).

crystals of **17** were obtained by recrystallization and analyzed by X-ray diffraction, identifying the expected product (Figure 4).

In the solid state the platinum centers of **17** and **18** exhibit slightly distorted square-planar geometries [**17**, P1−Pt−P2 165.61(3)°, B−Pt−Br2 162.51(9)°; **18**, P3−Pt−P2 165.82(4)°, Br4−Pt−B2 167.55(15)°] and are bound to three-coordinate boron atoms. The boryl ligands are oriented almost perpendicular to the PtP_2 plane [**17**, P1−Pt−B−C1 98.8(2)°; **18**, P2−Pt−B2−C4 96.5(4)°]. Relatively long Pt−Br bonds indicate [**17**, 2.6153(3) Å; **18**, 2.6287(5) Å] the expected degree of *trans*-influence for boryl groups with this particular substitution pattern.[19a] The significantly decreased Pt−B distances in **17** [1.965(3) Å] and **18** [1.986(5) Å]

Scheme 2. Synthesis of the Boryl Complexes 17 and 18

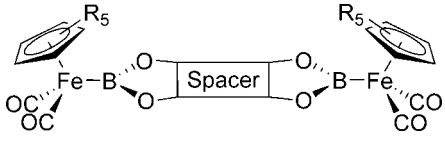


are comparable to the ones in *trans*-[$(Cy_3P)_2$Pt(Br)(BBr_2)] [1.963(6) Å][19a] or *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)*t*Bu}] [1.983(5) Å][19a] and provide evidence for an effective Pt−B π-back-donation due to less effective π-stablization of the boron by its substituents. The B−Br and B−C bond lengths [**17**, 1.994(5) and 1.567(7) Å; **18**, B2−Br3 2.006(3) and B2−C4 1.567(7) Å] are comparable to those in related boryl complexes.[19a]

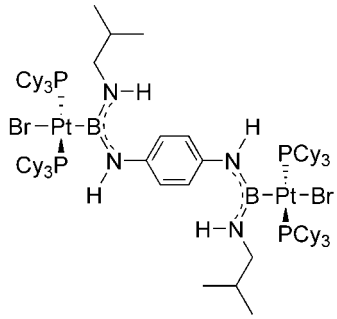
Boron atom B1 in **18** is tetrahedrally coordinated [C1−B1−P1 112.3(3)°, C1−B1−Br1 111.1(3)°, C1−B1−Br2 111.2(3)°] and displays B−P [2.036(5) Å] and B−Br distances [B1−Br1 2.047(5), B1−Br2 2.055(6) Å] that are slightly longer than in known phosphine borane adducts [Me_3P−BBr_3: B−P 1.924(12) Å, B−Br 2.021(10) Å;[28] Pr_3P−BBr_3: B−P 1.95(1) Å, B−Br 2.009(3) Å][29] most likely due to the increased steric demands of the phosphine and the aryl substituent. The B−C distance [B1−C1 1.608(7) Å] is in line with a typical carbon−boron single bond.[30]

Stepwise Preparation of a Bridged Base-Stabilized Diborylene Complex. Reaction of the dinuclear complex **17** with 2 equiv of $K[B(C_6F_5)_4]$ yielded 1,4-*trans*-[{$(Cy_3P)_2$Pt(BBr)}$_2$-

Chart 3. Bridged Iron (top) and Platinum (bottom) Diboryl Complexes



Spacer = C_6H_2, $R_5 = H_5$, H_4Me, Me_5
Spacer = C_5H_8, $R_5 = H_5$



$C_6H_4][B(C_6F_5)_4]_2$ (**19**) (Scheme 3) with abstraction of both platinum-bound bromide ligands, as indicated by a typical downfield shift of about 20 ppm[10f,31] in the $^{31}P\{^1H\}$ NMR spectrum [$\delta = 43.0$ ppm ($^1J_{P-Pt} = 2776$ Hz)] compared to the starting material.

The ^1H NMR spectrum shows only one resonance for the aromatic protons at $\delta = 8.29$ ppm, and the $^{11}B\{^1H\}$ NMR spectrum exhibits a sharp signal for the anion at $\delta = -17.6$ ppm. A signal for the platinum-bound boron atoms was not detected, most likely due to high dilution and unresolved coupling to platinum and posphorus nuclei, as observed before in many cases.[10f,32] Suitable crystals for X-ray analysis were obtained by layering hexane on concentrated reaction mixtures and storage at −35 °C (Figure 5).

In **19** both platinum fragments adopt a slightly distorted T-shaped geometry [P1−Pt−P2 166.717(17)°], and the platinum(II) atoms are only three-coordinate. The plane containing the boryl ligand is twisted by 108° toward the PtP_2 plane [P2−Pt−B1−C1 107.87(16)°]. Compared to the starting material **17** the Pt−B bond length is slightly shorter [**19**, 1.938(2) Å; **17**, 1.965(3) Å], which is in line with observations made for other cationic boryl complexes.[10f,31] The B−Br and B−C1 bonds [1.939(2) and 1.563(3) Å] lie in the range of similar boryl complexes.[19a] The shortest Pt···H(C) and Pt···C distances amount to Pt···H(C9) 2.572 Å and Pt···C9 3.232 Å and, thus, prove the absence of notable agostic interactions.[10f,33]

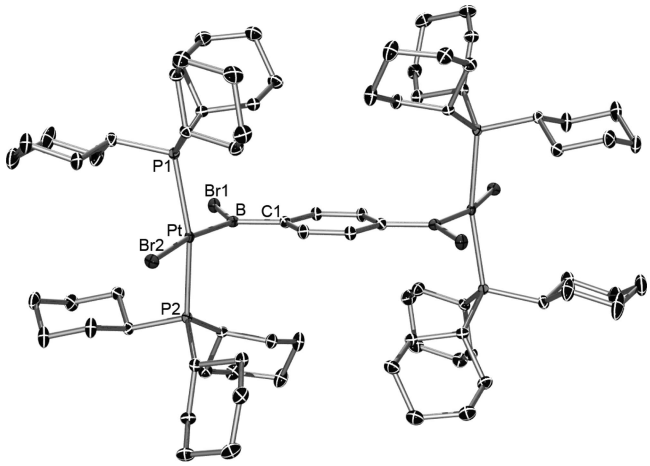


Figure 4. Molecular structure of 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt(BBr)}$_2$-C_6H_4] (**17**). Solvent molecules (3 CH_2Cl_2) and hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å] and angles [deg]: Pt−Br2 2.6153(3), Pt−B 1.965(3), B−Br1 2.006(3), B−C1 1.570(4), P1−Pt−P2 165.61(3), B−Pt−Br2 162.51(9), C1−B−Br1 114.9(2), C1−B−Pt 121.5(2), Pt−B−Br1 123.6(2), P1−Pt−B−C1 98.8(2), Pt−B−C1−C3 177.6(2).

Treatment of **19** with 2 equiv of 4-methylpyridine afforded the expected 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt{B(NC_5H_4-4-Me)}}$_2$-C_6H_4][$B(C_6F_5)_4]_2$ (**20**) (Scheme 4), which was identified by NMR spectroscopy and elemental analysis.

The ^1H NMR spectrum exhibits three signals in the aromatic region [$\delta = 9.4$ (4H, 2 NC_5H_4-4-Me), 8.08 (4H, C_6H_4), 7.91 (4H, 2 NC_5H_4-4-Me)]. The corresponding resonances for the pyridine ligand in the $^{13}C\{^1H\}$ NMR spectrum were detected at $\delta = 165.5$ (s, C^{para}), 144.1 (s, C^{ortho}), 128.2 (s, C^{meta}), and 23.1 (s, Me) ppm and lie in the range of the signals observed for **5** and **12**−**14**, verifying the coordination of the base at the boron center.

Conclusions

In conclusion we have described a series of fully characterized cationic, base-stabilized borylene complexes of the type *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-R)X}][BAr^f_4] (R = Me, X = NMe_2, Pip, Br; R = *t*Bu, X = Pip). These compounds were obtained from bromo boryl comlexes of the general formula *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)X}] upon removal of the bromide with Na[BAr^f_4] and coordination of the Lewis base to the boron center, thus indicating a general applicability of this method. Furthermore, the dinuclear boryl complexes 1,4-*trans*-[{$(Cy_3P)_2$-(Br)Pt(BBr)}$_2$-C_6H_4] and *trans*-[$(Cy_3P)_2$Pt(Br)-1-{B(Br)-C_6H_4-4-{$BBr_2(PCy_3)$}}] were isolated. The former was reacted with K[$B(C_6F_5)_4$] with formation of the dicationic boryl complex 1,4-*trans*-[{$(Cy_3P)_2$Pt(BBr)}$_2$-C_6H_4][$B(C_6F_5)_4]_2$, which was converted into the diborylene base-stabilized species 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt{B(NC_5H_4-4-Me)}}$_2$-C_6H_4][$B(C_6F_5)_4]_2$ by addition of 4-methylpyridine. In agreement with previous results, the structural data of the cationic species **12**, **13**, and **15** indicate that ligands of the type =B(R)L, while formally representing base-stabilized borylenes, are characterized by a metal−boron linkage of little multiple bond character and, thus, resemble boryl ligands $-BR_2$.

Experimental Section

Synthesis of *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)NMe_2}][BAr^f_4] (12). *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)NMe_2}] (**9**) (0.020 g, 0.021 mmol) and [$NaBAr^f_4$] (0.018 g, 0.021 mmol) were loaded in a J. Young NMR tube and dissolved in CD_2Cl_2 (0.6 mL). The reaction mixture immediately turned yellow, and some fine powder (NaBr) precipi-

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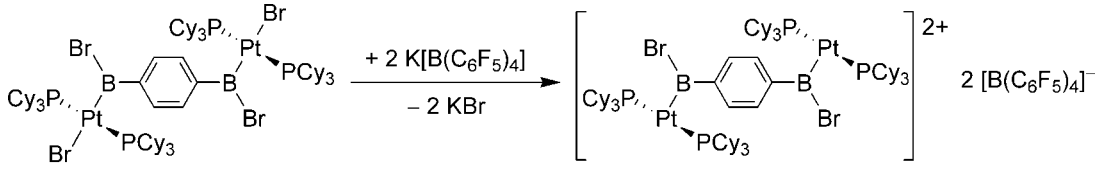
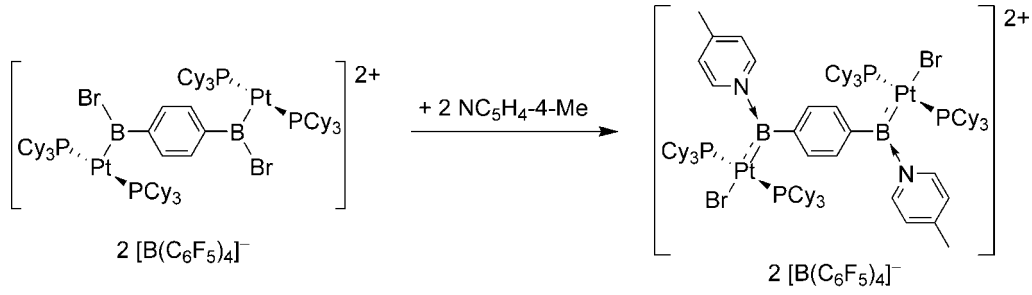
Scheme 3. Synthesis of the Spacer-Bridged Dicationic Diboryl Complex 19



17 **19**

Scheme 4. Synthesis of the Spacer-Bridged Dicationic Base-Stabilized Diborylene Complex 20



19 **20**

tated. After filtering over glass fiber filter paper 4-methylpyridine (0.002 g, 0.021 mmol) was added. After 8 h the solution was layered with hexane (2 mL) and allowed to evaporate slowly. After 3 weeks and several recrystallization cycles pure *trans*-[$(Cy_3P)_2Pt(Br)\{B(NC_5H_4$-4-Me$)NMe_2\}][BAr^f_4]$ (**12**) precipitated (0.031 g, 84%).

^{1}H NMR (500 MHz, CD_2Cl_2, 24 °C): δ 8.83 (d, $^3J_{H-H} = 7$ Hz, 2H, NC_5H_4-4-Me), 7.64 (m, 8H, BAr^f_4), 7.62 (d, $^3J_{H-H} = 7$ Hz, 2H, NC_5H_4-4-Me), 7.48 (br s, 4H, BAr^f_4), 3.16 (s, 3H, NMe_2), 2.68 (s, 3H, NMe_2), 2.51 (s, 3H, Me, NC_5H_4-4-Me), 2.05−1.05 (m, 66H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): δ 162.0 (q, $^1J_{C-B} = 50$ Hz, C^{ipso}, BAr^f_4), 161.0 (s, C^{para}, NC_5H_4-4-Me), 146.6 (s, C^{ortho}, NC_5H_4-4-Me), 135.1 (br s, C^{ortho}, BAr^f_4), 129.1 (qq, $^2J_{C-F} = 32$ Hz, $^3J_{C-B} = 3$ Hz, C^{meta}, BAr^f_4), 127.1 (s, C^{meta}, NC_5H_4-4-Me), 124.9 (q, $^1J_{C-F} = 272$ Hz, CF_3, BAr^f_4), 117.7 (sep, $^3J_{C-F} = 4$ Hz, C^{para}, BAr^f_4), 47.0 (s, NMe_2), 40.6 (s, NMe_2), 37.0 (vt, $N = |^1J_{C-P} + {}^3J_{C-P}| = 28$ Hz, C^1, Cy), 31.1 (br s, $C^{3,5}$, Cy), 30.4 (br s, $C^{3,5}$, Cy), 28.0 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 27.7 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 10$ Hz, $C^{2,6}$, Cy), 26.5 (s, C^4, Cy), 22.3 (s, Me, NC_5H_4-4-Me). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): δ −7.6 (s, BAr^f_4). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): δ 26.2 (s, $^1J_{P-Pt} = 2532$ Hz). Anal. Calcd for $C_{76}H_{91}N_2B_2BrF_{24}P_2Pt$: C, 49.42; H, 4.97; N, 1.52. Found: C, 49.09; H, 5.08; N, 1.48.

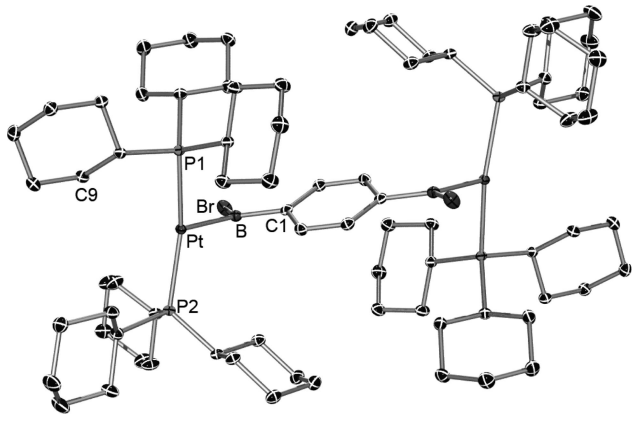


Figure 5. Molecular structure of 1,4-*trans*-[$\{(Cy_3P)_2Pt(BBr)\}_2$-C_6H_4][$B(C_6F_5)_4]_2$ (**19**). Couterions, solvent molecules (2 CH_2Cl_2), and hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å] and angles [deg]: Pt−B 1.938(2), B−C1 1.563(3), B−Br 1.939(2), P1−Pt−P2 166.717(17), P2−Pt−B-C1 107.87(16), Pt−B−C1−C2 158.18(15).

Synthesis of *trans*-[$(Cy_3P)_2Pt(Br)\{B(NC_5H_4$-4-Me$)Pip\}][BAr^f_4]$ (13). *trans*-[$(Cy_3P)_2Pt(Br)\{B(Br)Pip\}$] (**10**) (0.025 g, 0.025 mmol) and [$NaBAr^f_4$] (0.022 g, 0.025 mmol) were put in a vial in the glovebox and dissolved in CD_2Cl_2 (0.6 mL). The reaction mixture immediately turned yellow, and some fine powder (NaBr) precipitated. After 2 h the suspension was filtered over glass fiber filter paper, and 4-methylpyridine (0.002 g, 0.025 mmol) was added to the solution. Over 1−2 h the mixture turned colorless. Crystals of *trans*-[$(Cy_3P)_2Pt(Br)\{B(NC_5H_4$-4-Me$)Pip\}][BAr^f_4]$ (**13**) were obtained by layering the solution with hexane (2 mL) and slow evaporation of the solvent, yielding 0.026 g (65%).

^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): δ 8.99 (br d, $^3J_{H-H} = 6$ Hz, 2H, NC_5H_4-4-Me), 7.72 (m, 8H, BAr^f_4), 7.69 (d, $^3J_{H-H} = 6$ Hz, 2H, NC_5H_4-4-Me), 7.56 (br s, 4H, BAr^f_4), 3.71 (m, 2H, NCH_2, Pip), 3.02 (m, 2H, NCH_2, Pip), 2.61 (s, 3H, Me, NC_5H_4-4-Me), 2.05 (m, 6H, Cy), 1.85−1.16 (m, 60H+6H, Cy and Pip). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): δ 162.1 (q, $^1J_{C-B} = 50$ Hz, C^{ipso}, BAr^f_4), 161.3 (s, C^{para}, NC_5H_4-4-Me), 146.7 (br s, C^{ortho}, NC_5H_4-4-Me), 135.2 (s, C^{ortho}, BAr^f_4), 129.2 (qq, $^2J_{C-F} = 31$ Hz, $^3J_{C-B} = 3$ Hz, C^{meta}, BAr^f_4), 127.1 (s, C^{meta}, NC_5H_4-4-Me), 125.0 (q, $^1J_{C-F} = 272$ Hz, CF_3, BAr^f_4), 117.8 (sep, $^3J_{C-F} = 4$ Hz, C^{para}, BAr^f_4), 55.0 (s, NCH_2, Pip), 50.7 (s, NCH_2, Pip), 36.9 ($N = |^1J_{C-P} + {}^3J_{C-P}| = 26$ Hz, C^1, Cy), 31.1 (br s, $C^{3,5}$, Cy), 30.6 (br s, $C^{3,5}$, Cy), 28.1 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 27.9 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 10$ Hz, $C^{2,6}$, Cy), 27.7 (s, Pip), 26.6 (s, C^4, Cy), 26.1 (s, Pip), 24.9 (s, Pip), 22.6 (s, Me, NC_5H_4-4-Me). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 23 °C): δ −7.6 (s, BAr^f_4). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 23 °C): δ 27.0 (s, $^1J_{P-Pt} = 2548$ Hz). Anal. Calcd for $C_{79}H_{95}N_2B_2BrF_{24}P_2Pt$: C, 50.28; H, 5.07; N, 1.48. Found: C, 50.18; H, 4.76; N, 1.44.

Synthesis of *trans*-[$(Cy_3P)_2Pt(Br)\{B(NC_5H_4$-4-Me$)Br\}][BAr^f_4]$ (14). *trans*-[$(Cy_3P)_2Pt(Br)(BBr_2)$] (**11**) (0.015 g, 0.015 mmol) and Na-[BAr^f_4] (0.013 g, 0.015 mmol) were loaded in a J. Young NMR tube and dissolved in CD_2Cl_2 (0.6 mL). The reaction mixture immediately turned orange, and some fine powder (NaBr) precipitated. After filtering over glass fiber filter paper 4-methylpyridine (0.001 g, 0.015 mmol) was added. After 3 h the yellow solution was layered with hexane (1 mL) and stored at −35 °C, and after 2 weeks yellow crystals of *trans*-[$(Cy_3P)_2Pt(Br)\{B(NC_5H_4$-4-Me$)Br\}$]-[$BAr^f_4$] (**14**) were isolated (0.010 g, 35%).

^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): δ 10.66 (br s, 1H, NC_5H_4-4-Me, H···Br), 9.57 (br s, 1H, NC_5H_4-4-Me), 7.95 (br s, 1H, NC_5H_4-4-Me), 7.83 (br s, 1H, NC_5H_4-4-Me), 7.71 (m, 8H, BAr^f_4), 7.55 (br s, 4H, BAr^f_4), 2.70 (s, 3H, Me, NC_5H_4-4-Me), 2.61 (br s, 6H, Cy), 2.13−2.02 (m, 6H, Cy), 1.85−1.78 (m, 6H, Cy),

1.70−1.48 (m, 30H, Cy), 1.30−1.15 (m, 12H, Cy), 1.00−0.90 (br s, 6H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ 166.7 (s, C^{para}, NC_5H_4-4-Me), 162.0 (q, $^1J_{C-B} = 49$ Hz, C^{ipso}, BAr^f_4), 144.2 (br s, C^{ortho}, NC_5H_4-4-Me, HMQC), 135.1 (s, C^{ortho}, BAr^f_4), 129.1 (qq, $^2J_{C-F} = 32$ Hz, $^3J_{C-B} = 3$ Hz, C^{meta}, BAr^f_4,), 128.4 (br s, C^{meta}, NC_5H_4-4-Me), 124.9 (q, $^1J_{C-F} = 272$ Hz, CF_3, BAr^f_4), 117.7 (sep, $^3J_{C-F} = 4$ Hz, C^{para}, BAr^f_4), 36.3 (br s, C^1, Cy), 30.9 (s, $C^{3,5}$, Cy), 30.8 (s, $C^{3,5}$, Cy), 27.8 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 27.7 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 26.5 (s, C^4, Cy), 23.3 (s, Me, NC_5H_4-4-Me). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): δ −7.6 (s, BAr^f_4). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): δ 23.9 (s, $^1J_{P-Pt} = 2373$ Hz). Anal. Calcd for $C_{74}H_{85}B_2Br_2F_{24}NP_2Pt$: C, 47.20; H, 4.55; N, 0.74. Found: C, 47.09; H, 4.56; N, 0.67.

Synthesis of *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-*t*Bu)Pip}][BAr^f_4] (15). Similarly to the synthesis of *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)Pip}][BAr^f_4] (**12**) *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-*t*Bu)Pip}]-[BAr^f_4] (**15**) (0.033 g, 69%) was isolated starting from *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)(Pip)}] (**10**) (0.025 g, 0.025 mmol), Na[BAr^f_4] (0.022 g, 0.025 mmol), and NC_5H_4-4-*t*Bu (0.003 g, 0.025 mmol).

^1H NMR (500 MHz, CD_2Cl_2, 23 °C): δ 8.99 (m, 2H, NC_5H_4-4-*t*Bu), 7.86 (m, 2H, NC_5H_4-4-*t*Bu), 7.72 (m, 8H, BAr^f_4), 7.56 (br s, 4H, BAr^f_4), 3.71 (br s, 2H, NCH_2, Pip), 3.04 (br s, 2H, NCH_2, Pip), 2.05 (m, 6H, Cy), 1.85−1.16 (m, 60H+6H, Cy and Pip) 1.41 (s, 9H, *t*Bu, NC_5H_4-4-*t*Bu). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): δ 173.45 (s, C^{para}, NC_5H_4-4-*t*Bu), 162.1 (q, $^1J_{C-B} = 50$ Hz, C^{ipso}, BAr^f_4,), 147.0 (br s, C^{ortho}, NC_5H_4-4-*t*Bu), 135.2 (s, C^{ortho}, BAr^f_4), 129.2 (qq, $^2J_{C-F} = 31$ Hz, $^3J_{C-B} = 3$ Hz, C^{meta}, BAr^f_4), 125.0 (q, $^1J_{C-F} = 273$ Hz, CF_3, BAr^f_4), 123.7 (s, C^{meta}, NC_5H_4-4-*t*Bu), 117.8 (sep, $^3J_{C-F} = 4$ Hz, C^{para}, BAr^f_4), 54.9 (s, NCH_2, Pip), 50.5 (s, NCH_2, Pip), 37.2 (s, C, *t*Bu), 36.9 (vt, $N = |^1J_{C-P} + {}^3J_{C-P}| = 27$ Hz, C^1, Cy), 31.1 (br s, $C^{3,5}$, Cy), 30.6 (br s, $C^{3,5}$, Cy), 30.0 (s, Me, *t*Bu), 28.1 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 27.8 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 27.6 (s, Pip), 26.6 (s, C^4, Cy), 26.0 (s, Pip), 24.9 (s, Pip). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 23 °C): δ −7.6 (s, BAr^f_4). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 23 °C): δ 27.2 (s, $^1J_{P-Pt} = 2557$ Hz). Anal. Calcd for $C_{82}H_{101}N_2B_2BrF_{24}P_2Pt$: C, 51.05; H, 5.28; N, 1.45. Found: C, 51.38; H, 5.73; N, 1.42.

Synthesis of 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt(BBr)}$_2$-C_6H_4] (17). 1,4-$(BBr_2)_2$-C_6H_4 (**16**) (0.014 g, 0.033 mmol) and [$Pt(PCy_3)_2$] (0.050 g, 0.066 mmol) were added to a J. Young NMR tube and dissolved in C_6D_6 (0.6 mL). A white solid of *trans*-[$(Cy_3P)_2$Pt(Br)-1-{B(Br)-C_6H_4-4-{$BBr_2(PCy_3)$}}] (**18**) precipitated, and the solution turned brown-yellow. After 2 days the solid was separated (0.014 g) and discarded. The remaining solution was allowed to evaporate slowly in the glovebox. The first crystallized fraction (0.007 g) still contained side products and was therefore discarded, whereas the second fraction was pure 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt(BBr)}$_2$-C_6H_4] (**17**) (0.015 g, 24%).

^1H NMR (500 MHz, CD_2Cl_2, 24 °C): δ 8.46 (br s, 4H, CH, C_6H_4), 2.65 (br s, 12H, Cy), 2.16 (br s, 12H, Cy), 1.90−1.50 (m, 72H, Cy), 1.40−1.00 (m, 36H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): δ 35.9 (br s, C^1, Cy), 30.8 (s, $C^{3,5}$, Cy), 30.2 (s, $C^{3,5}$, Cy), 28.0 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 27.8 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 26.8 (s, C^4, Cy) (due to high dilution and unresolved coupling to the boron atoms, no signals were deteted for the C_6H_4 group). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): δ 75 (br s). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): δ 23.2 (s, $^1J_{P-Pt} = 2833$ Hz). Anal. Calcd for $C_{78}H_{136}B_2Br_4P_4Pt_2$: C, 48.56; H, 7.11. Found: C, 49.10; H, 7.24.

Synthesis of *trans*-[$(Cy_3P)_2$Pt(Br)-1-{B(Br)-C_6H_4-4-{$BBr_2(PCy_3)$}}] (18). 1,4-$(BBr_2)_2$-C_6H_4 (**16**) (0.018 g, 0.044 mmol) was added to a solution of [$Pt(PCy_3)_2$] (0.050 g, 0.066 mmol) in C_6D_6 (0.6 mL). The resulting precipitate was separated from the yellow solution and extracted twice with toluene (2 × 0.5 mL). The solvent was allowed to evaporate slowly in the glovebox, and the precipitated solid was washed with hexane (2 × 0.5 mL) and dried (19 mg, 30%). Single crystals of **18** suitable for X-ray analysis were obtained by recrystallization from a C_6H_6/hexane mixture and slow evaporation.

^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 8.88 (br s, 1H, CH, C_6H_4), 8.13 (br s, 1H, CH, C_6H_4), 7.84 (2 overlapping s, 2H, CH, C_6H_4), 2.60 (m, 6H, Cy), 2.37 (m, 3H, Cy), 2.24−2.11 (m, 12H, Cy), 1.87−1.50 (m, 51H, Cy), 1.30−0.94 (m, 27H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ 134.8 (br s, CH, C_6H_4), 35.6 (br s, C^1, Cy^{Pt}), 32.8 (d, $^1J_{C-P} = 29$ Hz, C^1, Cy^B), 30.9 (s, $C^{3,5}$, Cy^{Pt}), 30.1 (s, $C^{3,5}$, Cy^{Pt}), 28.7 (d, $^3J_{C-P} = 4$ Hz, $C^{3,5}$, Cy^B), 28.0 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy^{Pt}), 27.8 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 10$ Hz, $C^{2,6}$, Cy^{Pt}), 27.6 (d, $^2J_{C-P} = 10$ Hz, $C^{2,6}$, Cy^B), 26.9 (s, C^4, Cy^{Pt}), 26.3 (s, C^4, Cy^B) (due to the poor solubility, the dilution of the sample, and unresolved coupling to boron atoms, not all signals of the C_6H_4 group were detected). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 73 (br s, B-Pt), −5 (br s, B-P). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 25 °C): δ 21.4 (s, $^1J_{P-Pt} = 2829$ Hz), −7.9 (br s, P-B). Anal. Calcd for $C_{60}H_{103}B_2Br_4P_3Pt$: C, 49.57; H, 7.14. Found: C, 50.05; H, 6.94.

Synthesis of 1,4-*trans*-[{$(Cy_3P)_2$Pt(BBr)}$_2$-C_6H_4][$B(C_6F_5)_4$]$_2$ (19). 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt(BBr)}$_2$-C_6H_4] (**17**) (0.015 g, 0.008 mmol) and K[$B(C_6F_5)_4$] (0.012 g, 0.016 mmol) in CD_2Cl_2 (0.6 mL) were reacted in a J. Young NMR tube and dissolved in CD_2Cl_2 (0.6 mL). The reaction mixture immediately turned yellow, and some fine solid (KBr) precipitated. After filtering over glass fiber filter paper the yellow solution was layered with hexane (1 mL) and stored at −35 °C. After 1 week crystals of 1,4-*trans*-[{$(Cy_3P)_2$Pt(BBr)}$_2$-C_6H_4][$B(C_6F_5)_4$]$_2$ (**19**) (0.016 g, 62%) were isolated.

^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 8.29 (s, 4H, CH, C_6H_4), 2.25 (m, 12H, Cy), 2.00−1.70 (m, 60H, Cy), 1.60−1.48 (m, 24H, Cy), 1.27−1.16 (m, 36H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ 148.5 (br d, $^1J_{C-F} = 244$ Hz, C^{para}, $B(C_6F_5)_4$), 143.2 (s, C^{ipso}, C_6H_4, HMBC), 138.6 and 136.7 (2 overlapping br d, $^1J_{C-F} = 243$ Hz, $C^{ortho,meta}$, $B(C_6F_5)_4$), 138.1 (s, CH, C_6H_4, HMQC), 124.2 (br s, C^{ipso}, $B(C_6F_5)_4$), 34.9 (vt, $N = |^1J_{C-P} + {}^3J_{C-P}| = 27$ Hz, C^1, Cy), 30.6 (s, $C^{3,5}$, Cy), 30.4 (s, $C^{3,5}$, Cy), 27.4 (2 overlapping vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 11$ Hz, $C^{2,6}$, Cy), 26.0 (s, C^4, Cy). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ −17.6 (s, $B(C_6F_5)_4$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 25 °C): δ 43.0 (s, $^1J_{P-Pt} = 2776$ Hz). Anal. Calcd for $C_{126}H_{136}B_4Br_2F_{40}P_4Pt_2 \cdot 2(CH_2Cl_2)$: C, 46.62; H, 4.28. Found: C, 45.91; H, 3.66.

Synthesis of 1,4-*trans*-[{$(Cy_3P)_2$Pt(B(NC_5H_4-4-Me)Br)}$_2$-C_6H_4]-[$B(C_6F_5)_4$]$_2$ (20). Similarly to the above-described procedures the reaction of 1,4-*trans*-[{$(Cy_3P)_2$(Br)Pt(BBr)}$_2$-C_6H_4] (**17**) (0.015 g, 0.008 mmol) and K[$B(C_6F_5)_4$] (0.012 g, 0.016 mmol) afforded 1,4-*trans*-[{$(Cy_3P)_2$Pt(BBr)}$_2$-C_6H_4][$B(C_6F_5)_4$]$_2$ (**19**), which was treated with NC_5H_4-4-CH_3 (0.002 g, 0.016 mmol). The mixture was layered with hexane (1 mL) and stored at −35 °C, yielding yellow crystals of 1,4-*trans*-[{$(Cy_3P)_2$Pt(B(NC_5H_4-4-Me)Br)}$_2$-C_6H_4][$B(C_6F_5)_4$]$_2$ (**20**) (0.010 g, 39%).

^1H NMR (500 MHz, CD_2Cl_2, 23 °C): δ 9.45 (br s, 4H, 2 NC_5H_4-4-Me), 8.08 (s, 4H, CH, C_6H_4), 7.91 (br s, 4H, 2 NC_5H_4-4-Me), 2.71 (s, 6H, 2 NC_5H_4-4-Me), 2.10−1.10 (m, 132H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): δ 165.5 (s, C^{para}, NC_5H_4-4-Me), 148.5 (br d, $^1J_{C-F} = 244$ Hz, C^{para}, $B(C_6F_5)_4$), 144.1 (s, C^{ortho}, NC_5H_4-4-Me), 138.6 and 136.6 (2 overlapping br d, $^1J_{C-F} = 243$ Hz, $C^{ortho,meta}$, $B(C_6F_5)_4$), 137.0 (s, CH, C_6H_4, HMQC), 128.2 (br s, C^{meta}, NC_5H_4-4-Me), 37.4 (br s, C^1, Cy), 30.8 (br s, $C^{3,5}$, Cy), 27.7 (br s, $C^{2,6}$, Cy), 26.2 (br s, C^4, Cy), 23.1 (s, Me, NC_5H_4-4-Me). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 23 °C): δ −17.6 (s, $B(C_6F_5)_4$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 23 °C): δ 43.0 (s, $^1J_{P-Pt} = 2776$ Hz); due to the high dilution of the sample and unresolved couplings, not all signals were detected in the $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra. Anal. Calcd for $C_{138}H_{150}B_4Br_2F_{40}N_2P_4Pt_2$: C, 50.02; H, 4.56; N, 0.85. Found: C, 49.42; H, 4.52; N, 1.06.

Crystal Structure Determination. The crystal data of **12**, **13**, **15**, and **17**−**19** were collected on a Bruker X8APEX diffractometer with 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. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystal data for **12**: $C_{78}H_{95}B_2BrCl_4F_{24}N_2P_2Pt$, M_r = 2016.92, colorless bar, 0.19 × 0.18 × 0.09 mm^3, triclinic space group $P\bar{1}$, a = 13.0986(7) Å, b = 17.2349(7) Å, c = 20.2400(10) Å, α = 101.036(2)°, β = 102.763(2)°, γ = 94.732(2)°, V = 4336.6(4) Å^3, Z = 2, ρ_{calcd} = 1.545 g·cm^{-3}, μ = 2.333 mm^{-1}, $F(000)$ = 2028, T = 100(2) K, R_1 = 0.0444, wR_2 = 0.1079, 24 755 independent reflections [$2\theta \leq 61.12°$] and 1085 parameters.

Crystal data for **13**: $C_{91}H_{123}B_2BrF_{24}N_2P_2Pt$, M_r = 2059.47, colorless plate, 0.20 × 0.11 × 0.03 mm^3, triclinic space group $P\bar{1}$, a = 13.4787(10) Å, b = 19.3931(14) Å, c = 19.6039(14) Å, α = 102.695(4)°, β = 104.641(4)°, γ = 97.209(4)°, V = 4746.9(6) Å^3, Z = 2, ρ_{calcd} = 1.441 g·cm^{-3}, μ = 2.024 mm^{-1}, $F(000)$ = 2104, T = 100(2) K, R_1 = 0.0744, wR_2 = 0.1187, 27 746 independent reflections [$2\theta \leq 65.68°$] and 1201 parameters.

Crystal data for **15**: $C_{82}H_{101}B_2BrF_{24}N_2P_2Pt$, M_r = 1929.21, colorless plate, 0.18 × 0.16 × 0.095 mm^3, monoclinic space group $P2_1/n$, a = 15.5886(4) Å, b = 14.4814(3) Å, c = 38.1580(10) Å, β = 92.9160(10)°, V = 8602.8(4) Å^3, Z = 4, ρ_{calcd} = 1.490 g·cm^{-3}, μ = 2.228 mm^{-1}, $F(000)$ = 3904, T = 100(2) K, R_1 = 0.0511, wR_2 = 0.1197, 17 000 independent reflections [$2\theta \leq 52.18°$] and 1228 parameters.

Crystal data for **17**: $C_{42}H_{74}BBr_2Cl_6P_2Pt$, M_r = 1219.37, yellow block, 0.32 × 0.21 × 0.19 mm^3, monoclinic space group $P2_1/c$, a = 12.7827(4) Å, b = 24.4857(7) Å, c = 16.2173(5) Å, β = 90.412(2)°, V = 5075.8(3)Å^3, Z = 4, ρ_{calcd} = 1.596 g·cm^{-3}, μ = 4.746 mm^{-1}, $F(000)$ = 2444, T = 100(2) K, R_1 = 0.0493, wR_2 = 0.0711, 16 084 independent reflections [$2\theta \leq 64.18°$] and 509 parameters.

Crystal data for **18**: $C_{78}H_{125}B_2Br_4P_3Pt$, M_r = 1692.04, yellow plate, 0.190 × 0.120 × 0.04 mm^3, monoclinic space group $P2_1/n$, a = 14.9389(5) Å, b = 24.4311(9) Å, c = 21.7945(6) Å, β = 90.9880(10)°, V = 7953.2(5) Å^3, Z = 4, ρ_{calcd} = 1.413 g·cm^{-3}, μ = 3.874 mm^{-1}, $F(000)$ = 3464, T = 100(2) K, R_1 = 0.0814, wR_2 = 0.1168, 22 237 independent reflections [$2\theta \leq 59.62°$] and 766 parameters.

Crystal data for **19**: $C_{64}H_{70}B_2BrCl_2F_{20}P_2Pt$, M_r = 1648.66, yellow block, 0.235 × 0.135 × 0.120 mm^3, triclinic space group $P\bar{1}$, a = 14.1057(3) Å, b = 14.7139(3) Å, c = 18.4361(5) Å, α = 66.9520(10)°, β = 68.6530(10)°, γ = 78.7260(10)°, V = 3273.14(13) Å^3, Z = 2, ρ_{calcd} = 1.673 g·cm^{-3}, μ = 2.982 mm^{-1}, $F(000)$ = 1642, T = 293(2) K, R_1 = 0.0242, wR_2 = 0.0547, 16 124 independent reflections [$2\theta \leq 56.62°$] and 829 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 695416−695421. 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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Supporting Information Available: Crystallographic data of compounds **7**, **11** and **14**−**16** (cif). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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