## **ORGANOMETALLICS**

# Investigation of Steric Factors Involved in the Formation of Terminal Cationic Platinum Arylborylene Complexes

Nicole Arnold, Holger Braunschweig,\* Peter B. Brenner, Rian Dewhurst, Thomas Kramer, and Krzysztof Radacki

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

#### **Supporting Information**

**ABSTRACT:** The abstraction of halido ligands from  $Pt^{II}$  diphosphine boryl complexes has previously been shown to yield one of two isomeric products: either T-shaped cationic boryl complexes or square-planar cationic borylene complexes. However, the latter product has only been observed in one case, that of a mesitylboryl ligand, which converts to a mesitylborylene ligand upon halido abstraction. In an effort to test the efficacy of this reaction in the presence of different steric and electronic influences,  $Pt^{II}$  diphosphine boryl complexes were prepared with both 4-*tert*-butylphenyl and duryl (2,3,5,6-tetramethylphenyl) groups. Halide abstraction from the 4-*tert*-butylphenyl complex resulted in a T-shaped cationic boryl complex. However, subjecting the duryl-substituted complexes to the same conditions exclusively results in terminal cationic borylene complexes, a difference we attribute to the greater steric hindrance between the boron-bound bromide and the methyl groups at the 2- and 6-positions of the duryl group. This outcome indicates that the



electronic effect of alkylation at the para position is not a factor for this borylene formation reaction.

#### INTRODUCTION

Synthetically important boron-based catalytic functionalizations of organic substrates have greatly improved since the discovery of transition-metal-catalyzed hydroboration in 1985.<sup>1</sup> Common to all these synthetic protocols is the intermediacy of transition-metal-boron bonds.<sup>2</sup> In the last two decades the investigation of the bonding modes of boron-based ligands in transition-metal chemistry has developed immensely.<sup>3</sup> Boron-based ligands with only one substituent, such as borylene, iminoboryl  $(-B \equiv NR)$ , and oxoboryl  $(-B \equiv O)$  ligands, represent a particularly interesting class of compounds, because the boron atom in these ligands is in general both electronically and sterically unsaturated.

We have recently established a synthetic protocol for the stabilization of  $B \equiv N^{4,5}$  and  $B \equiv O^6$  triple bonds in the coordination sphere of the platinum fragment  $[Pt(PCy_3)_2]$  (Cy = cyclohexyl), allowing for the investigation of these systems at ambient temperature. A more common class of compounds with monosubstituted boron-centered ligands are terminal borylene complexes, the first of which were prepared through a double salt elimination reaction of Na<sub>2</sub>[M(CO)<sub>5</sub>] (M = Cr, Mo) and Cl<sub>2</sub>B{N(SiMe\_3)<sub>2</sub>},<sup>7-9</sup> in which the borylene moiety is stabilized by the electron-donating and sterically shielding amino substituent. Later, Aldridge et al. established a synthetic route to terminal borylene complexes via halide abstraction from the boron atom in the case of a resulting mesityl-substituted cationic borylene complex.<sup>10</sup>

In our group the chemistry of platinum boryl complexes of the general formula trans-[Pt{B(Br)R}Br(PCy\_3)\_2] (e.g., R =

tBu, Mes) has been studied extensively. The strong trans influence of these boryl complexes<sup>11,12</sup> allows for the easy abstraction of the bromo ligand with formation of cationic, Tshaped, in most cases non-agostic-free boryl complexes trans- $[Pt{B(Br)R}(PCy_3)_2]^+$  via reaction with a salt of a weakly coordinating anion (e.g.,  $Na[BAr_{4}^{f}]$  (Ar<sup>f</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),  $K[B(C_6F_5)_4]$ ,  $Na_2[B_{12}Cl_{12}]$ ,  $Ag[Al(Pftb)_4]$  (Pftb = OC-(CF<sub>3</sub>)<sub>3</sub>))<sup>6,13-15</sup> and formation of poorly soluble bromide salts in  $CH_2Cl_2$  reaction medium. In the case of R = Mes, the Tshaped boryl complex, which could be detected at -80 °C, is not the thermodynamic product. In this case the kinetic product of the halide abstraction reaction reacts further upon warming to yield the cationic terminal borylene complex trans- $[Pt(BMes)Br(PCy_3)_2]^+$  resulting from a formal 1,2-halide shift, whereas the both electronically and sterically related o-tolylsubstituted T-shaped cationic boryl complex does not react any further.14,16

This unexpected reactivity posed two questions. (1) Does the steric demand of 2,6-substitution at the boron-bound aryl substituent in T-shaped cationic complexes *trans*-[Pt{B(Br)-R}(PCy<sub>3</sub>)<sub>2</sub>]<sup>+</sup> induce the halide shift and borylene formation, or is the electron-donating effect of *para* alkyl groups responsible for this? (2) What is the influence of the steric interaction of the phosphine substituents? In order to answer these questions,

Special Issue: Mike Lappert Memorial Issue

Received: November 12, 2014

we synthesized the complexes *trans*-[Pt{B(Ar)Br}Br(PR<sub>3</sub>)<sub>2</sub>] (Ar = Dur = 2,3,5,6-tetramethylphenyl, R = Cy, *i*Pr; Ar = C<sub>6</sub>H<sub>4</sub>-4-*t*Bu, R = Cy) as precursors for the formation of cationic complexes. While the duryl-substituted derivatives both form new cationic terminal borylene complexes (regardless of the phosphine ligands), the C<sub>6</sub>H<sub>4</sub>-4-*t*Bu-substituted representative does not form such a compound.

#### RESULTS AND DISCUSSION

**Syntheses of Platinum Boryl Complexes.** The platinum boryl complexes of the general formula *trans*-[Pt{B(Ar)Br}Br-(PR<sub>3</sub>)<sub>2</sub>] (**1a**, R = Cy, Ar = Dur; **1b**, R = Cy, Ar = C<sub>6</sub>H<sub>4</sub>-4-*t*Bu; **1c**, R = P*i*Pr<sub>3</sub>, Ar = Dur) were prepared by oxidative addition of the B–Br bond of the corresponding aryldibromoboranes Br<sub>2</sub>BAr to the corresponding low-valent platinum complexes [Pt(PR<sub>3</sub>)<sub>2</sub>] (Scheme 1).

#### Scheme 1. Synthesis of Platinum Boryl Complexes 1a-c



In a typical reaction, the aryldibromoborane was dissolved in hexanes or benzene and added dropwise to an equimolar yellow solution of the platinum complex. Because of its high reactivity, the addition of Br<sub>2</sub>B(C<sub>6</sub>H<sub>4</sub>-4-tBu) was perfomed at -78 °C. The reactions were monitored by multinuclear NMR spectroscopy at room temperature, revealing the consumption of the starting materials within 30 min. New high-field-shifted <sup>31</sup>P{<sup>1</sup>H} NMR signals flanked by <sup>195</sup>Pt satellites (1a,  $\delta$  21.3, <sup>1</sup>*J*<sub>PPt</sub> = 3033 Hz; 1b,  $\delta$  19.7, <sup>1</sup>*J*<sub>PPt</sub> = 2774 Hz; 1c,  $\delta$  28.5, <sup>1</sup>*J*<sub>PPt</sub> = 3050 Hz) and broad low-field-shifted <sup>11</sup>B{<sup>1</sup>H} NMR signals (1a,  $\delta$  73.7; 1b,  $\delta$  74.0; 1c,  $\delta$  74.1) in all cases indicated the formation of boryl complexes 1a–c.

Compounds 1a-c were isolated from the reaction mixtures as colorless powders upon cooling the solutions to -35 °C in good yields (59–74%). Crystals suitable for X-ray diffraction analysis of 1a,b could be obtained by crystallization from saturated solutions in methylene chloride at -35 °C.

The molecular structures of **1a,b** display *trans*-confiugured, slightly distorted square planar geometries around the platinum centers, respectively (Figure 1). In both complexes, the boryl



**Figure 1.** Molecular structures of **1***a*,**b** in the crystal. Phosphine substituents have been simplified. One molecule of cocrystallized methylene chloride in **1b** and the hydrogen atoms of both structures have been omitted for clarity. Thermal ellipsoids are displayed at the 50% probability level.

moieties are oriented nearly perpendicular to the PtP<sub>2</sub> axis. Long Pt-Br1 bond distances (1a, 2.618(1) Å; 1b, 2.610(1) Å) indicate the strong *trans* influence of the boryl moieties (Table 1). The dihedral angle Pt-B-C1-C2 in 1a (31.4(5)°) is significantly larger than those of *trans*-[Pt{B(Br)Mes}Br-(PCy<sub>3</sub>)<sub>2</sub>] (1d; 9.2(5)°) and 1b (4.3(7)°).

Table 1. Selected Bond Distances (Å) and Angles (deg) in 1a,b

	1a	1b
Pt-B	2.004(4)	1.977(6)
Pt-Br1	2.618(1)	2.610(2)
Pt-P1	2.336(1)	2.340(2)
Pt-P2	2.370(1)	2.340(2)
B-Br2	2.039(4)	1.989(6)
P1-Pt-P2	170.9(1)	170.4(1)
Pt-B-C1-C2	31.4(1)	4.3(7)

Synthesis of Cationic T-Shaped Boryl and Square-Planar Borylene Complexes. The boryl complexes 1a-cwere mixed with equimolar quantities of  $Na[BAr_{4}^{f}]$  ( $Ar^{f} = 3,5-(CF_{3})_{2}C_{6}H_{3}$ ) in  $CD_{2}Cl_{2}$  (Scheme 2). The reaction mixtures

Scheme	2. Synthes	sis of Cation	nic Boryl	Complex	2b and
Cationic	: Borylene	Complexes	2a,c via	Bromide	Abstraction



both turned yellow, and colorless solids precipitated. The resulting suspensions were filtered, and the retained yellow reaction mixtures were monitored via multinuclear NMR spectroscopy. New downfield-shifted singlet resonances, with respect to the precursors 1a-c, flanked by <sup>195</sup>Pt satellites were detected in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the cationic complexes trans-[Pt(BDur)Br(PCy<sub>3</sub>)<sub>2</sub>][BAr<sup>f</sup><sub>4</sub>] (**2a**,  $\delta$  44.8, <sup>1</sup>J<sub>PPt</sub> = 2075 Hz), trans-[Pt{B(Br)(C<sub>6</sub>H<sub>4</sub>-4-tBu)}(PCy<sub>3</sub>)<sub>2</sub>][BAr<sup>f</sup><sub>4</sub>] (**2b**,  $\delta$ 41.8,  ${}^{1}J_{PPt} = 2833 \text{ Hz}$ , and trans- $[Pt\{B(Dur)\}Br(PiPr_{3})_{2}]$  $[BAr_4^f]$  (2c,  $\delta$  55.8,  ${}^1J_{PPt} = 2102$  Hz). The  ${}^1J_{PPt}$  coupling constants in 2b ( ${}^1J_{PPt} = 2833$  Hz) and 1b ( ${}^1J_{PPt} = 2812$  Hz) are very similar, indicating the formation of a T-shaped, cationic boryl platinum complex. The corresponding coupling constants in 2a,c display values that are about 1000 Hz smaller than those of the corresponding precursors, respectively, suggesting the presence of cationic borylene complexes. Notable is the detection of <sup>11</sup>B{<sup>1</sup>H} NMR resonances of **2a** at  $\delta$  101 (fwhm  $\approx$  2400 Hz) and 2c at  $\delta$  99.6 (fwhm  $\approx$  2400 Hz), the first <sup>11</sup>B{<sup>1</sup>H} NMR resonances to be reported for platinum-bound borylenes. Storing the reaction mixtures of 2a,c at -35 °C yielded colorless crystals within 2-4 days in moderate to good yields (69–74%). Unfortunately, 2b is too unstable in solution to be isolated, due to rehalogenation and reversion back to the starting material **1b**.

The X-ray-derived molecular structures of 2a,c display slightly distorted square-planar geometries around the platinum centers (Figure 2). The Pt–B bond distances in 2a (1.861(5)



**Figure 2.** Molecular structures of **2a,c**. Thermal ellipsoids of the phosphine substituents, counterions  $([BAr_4^r]^-)$ , cocrystallized molecules of methylene chloride (one in **2c**, two in **2a**), and all hydrogen atoms have been omitted for clarity. Thermal ellipsoids are displayed at the 50% probability level.

Å) and 2c (1.863(5) Å) are identical within experimental uncertainty (Table 2) and are similar to that in the only other

Table 2. Selected Bond Distances  $(\text{\AA})$  and Angles (deg) in 2a,c

	2a	2c
Pt-B	1.861(5)	1.863(5)
Pt-Br1	2.531(1)	2.531(1)
Pt-P1	2.362(2)	2.352(1)
Pt-P2	2.368(2)	2.355(1)
P1-Pt-P2	174.4(1)	171.5(1)

cationic borylene complex reported thus far, *trans*-[Pt(BMes)-Br(PCy<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (**2d**; 1.859(3) Å).<sup>14</sup> Both of these bond distances are ca. 7% shorter than in the precursor neutral boryl complex **1a** (2.004(4) Å). This indicates the multiple-bond character between the metal center and the boron atom, which was examined previously using a simplified model of **2d** through calculation of Kohn–Sham orbitals. Two orbitals with considerable Pt–B  $\sigma$ -bonding character and two orthogonal orbitals with  $\pi$ -bonding character were found therein. The Pt–Br bond distances of the borylene complexes **2a** (2.531(1) Å) and **2c** (2.531(1) Å) are similar to that of **2d** (2.542(1) Å).

In order to understand the driving force for the formation of either cationic T-shaped or square-planar borylene complexes by the abstraction of a bromido ligand, we found substantial differences in the spatial constitution of the corresponding precursors by comparison of their structural parameters. While the bond distances and angles around the platinum centers in the four complexes are very similar, the dihedral angles Pt–B–C1–C2 in **1b** ( $4.3(7)^{\circ}$ ) and *trans*-[Pt{B(Br)*o*-Tol}Br(PCy<sub>3</sub>)<sub>2</sub>] (**1e**,  $3.2(4)^{\circ}$ )<sup>16</sup> are significantly smaller than those in **1a** ( $31.4(1)^{\circ}$ ) and **1d** ( $9.2(5)^{\circ}$ )<sup>14</sup> (Table 3). The last two complexes indicate a greater steric hindrance due to the two

Table 3. Pt-B-C1-C2 Dihedral Angles in the Boryl Complexes 1a,b,d,e

	1a	1b	1d	1e
Pt-B-C1-C2	31.4(1)	4.3(7)	9.2(5)	3.2(4)

methyl groups in *ortho* positions of the aryl substituent. These results seem to indicate a propulsive force for the halide shift from the boron atom to the platinum center following the halide abstraction reaction, whereas evidence for the halide shift due to electronic effects of the phosphine substituent was not obtained.

#### CONCLUSION

In order to investigate whether the *ortho* substitution pattern of the boron-bound aryl group is a prerequisite for the halide shift and borylene formation, platinum boryl complexes with alternative aryl substituents at the boron atom were treated with Na[BAr<sup>f</sup><sub>4</sub>]. The 4-*tert*-butylphenyl-substituted complex forms a T-shaped cationic boryl complex. In contrast, the two duryl complexes undergo formal boron-to-metal halide shifts and formation of the corresponding cationic borylene complexes. These results indicate that (1) the steric demand of the boron substituent is more important for the boron-toplatinum halide shift than the substituent's electron donation ability and (2) the influence of the phosphine coligand appears to play a minor role.

#### EXPERIMENTAL SECTION

General Considerations. All manipulations were performed in dried glassware under an atmosphere of dry argon using standard Schlenk-line or glovebox techniques. Solvents (benzene, hexane, and methylene chloride) were dried according to standard procedures and stored under argon over molecular sieves (4 Å). C<sub>6</sub>D<sub>6</sub>, d<sub>8</sub>-Tol, and CD<sub>2</sub>Cl<sub>2</sub> were degassed by three freeze-pump-thaw cycles and stored under argon over molecular sieves (4 Å). Routine NMR spectra were recorded on a Bruker Avance 400 spectrometer. The NMR spectra of the products were acquired on a Bruker Avance 500 ( $^{1}$ H, 500.13 MHz;  $^{11}$ B, 160.47 MHz;  $^{13}$ C, 125.76 MHz;  $^{31}$ P, 202.46 MHz) NMR spectrometer. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to external tetramethylsilane via the residual proton signal of the solvent (<sup>1</sup>H) or the solvent itself (<sup>13</sup>C). <sup>11</sup>B{<sup>1</sup>H}  $\hat{NMR}$  spectra were referenced to external BF<sub>3</sub>·OEt<sub>2</sub>, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to external 85%  $\rm H_3PO_4.$  The chemical shift  $\delta$  is reported in ppm. Microanalyses for C, H, and N were performed on either a LecoCHNS-932 or a Carlo Erba Model 1106 instrument. Br<sub>2</sub>BDur,<sup>17</sup> Br<sub>2</sub>B(C<sub>6</sub>H<sub>4</sub>-4-*t*Bu),<sup>18</sup> [Pt(PCy<sub>3</sub>)<sub>2</sub>],<sup>19–21</sup> and [Pt(PiPr<sub>3</sub>)<sub>3</sub>]<sup>22</sup> were prepared according to published procedures.

**Synthesis of** *trans*-[Pt{B(Br)Dur}Br(PCy<sub>3</sub>)<sub>2</sub>] (1a). A solution of Br<sub>2</sub>BDur (40.3 mg, 0.132 mmol) in hexane (5 mL) was added dropwise to a stirred solution of [Pt(PCy<sub>3</sub>)<sub>2</sub>] (100 mg, 0.132 mmol) in hexane (5 mL). Colorless crystals of 1a were isolated from the reaction mixture upon cooling to -65 °C for 1 day (yield 103 mg, 74%). <sup>1</sup>H NMR (500.13 MHz, *d*<sub>8</sub>-Tol, 70 °C):  $\delta$  6.92 (s, 1H, Dur), 3.19 (s, 6H, CH<sub>3</sub>-o, Dur), 3.01 (m, 6H, CH-*i* of Cy), 2.26-2.12 (m, 12H, Cy), 2.16 (s, 6H, CH<sub>3</sub>-*m* of Dur), 1.81-1.57 (m, 30H, Cy), 1.21-1.13 (m, 18H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz, *d*<sub>8</sub>-Tol, 70 °C):  $\delta$  150.1 (s, C<sup>q</sup> of Dur), 139.4 (s, CCH<sub>3</sub>-*o* of Dur), 134.5 (s, CCH<sub>3</sub>-*m* of Dur), 134.3 (s, CH, Dur), 36.4 (*vt*, N = |<sup>1</sup>J<sub>CP</sub> + <sup>3</sup>J<sub>CP</sub>| = 26.4 Hz, C<sup>1</sup>, Cy), 31.3 (m, C<sup>3,5</sup>, Cy), 28.0 (m, C<sup>2,6</sup>, Cy), 27.1 (s, CH<sub>3</sub>-*o* of Dur), 27.2 (m, C<sup>4</sup>, Cy), 20.8 (s, CH<sub>3</sub>-*m* of Dur).<sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, *d*<sub>8</sub>-Tol, 25 °C):  $\delta$  21.4 (s, <sup>1</sup>J<sub>PPt</sub> = 3036 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128.38 MHz, *d*<sub>8</sub>-Tol, 25 °C):  $\delta$  °C):  $\delta$  73.7 (br s, fwhm ≈ 2550 Hz). Anal. Calcd for C<sub>46</sub>H<sub>79</sub>BBr<sub>2</sub>P<sub>2</sub>Pt: C, 52.13; H, 7.51. Found: C, 52.70; H, 7.72.

Synthesis of *trans*-[Pt{B(Br)( $C_6H_4$ -4-tBu)}Br(PCy\_3)<sub>2</sub>] (1b). A pale yellow solution of [Pt(PCy<sub>3</sub>)<sub>2</sub>] (80 mg, 0.11 mmol) and a solution of Br<sub>2</sub>B( $C_6H_4$ -4-tBu) (32.2 mg, 0.106 mmol) in 2 mL of hexanes were cooled to -78 °C. The solution of the borane was added dropwise to the platinum complex with continuous stirring. After the mixture was stored at ambient temperature and stirred over a period of 1 h, the volume was reduced by half and stored for 1 day at -35 °C for crystallization. The solvent was removed in vacuo, and the colorless solid was gently washed with hexanes to separate the phosphine–

borane adduct  $Cy_3P \cdot BBr_2(Ph-4-tBu)$ . *trans*-[Pt{B(Br)(Ph-4-tBu)}Br-(PCy\_3)\_2] was dried under vacuum (yield 66.2 mg, 59%). <sup>1</sup>H NMR (500.13 MHz,  $d_8$ -Tol, 70 °C):  $\delta$  8.80 (br s, 2H, H-*o* of C<sub>6</sub>H<sub>4</sub>-4-tBu), 7.32 (d, 2H, H-*m* of C<sub>6</sub>H<sub>4</sub>-4-tBu), 2.80 (m, 6H, CH-*i* of Cy), 2.42–2.31 (m, 6H, Cy), 1.95–1.88 (m, 6H, Cy), 1.81–1.51 (m, 30H, Cy), 1.37–0.97 (m, 18H, Cy), 1.21 (s, 9H, tBu). <sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz,  $d_8$ -Tol, 70 °C):  $\delta$  155.8 (s, C<sup>q</sup>, C-*ipso* of C<sub>6</sub>H<sub>4</sub>-4-tBu), 129.3 (s, C<sup>q</sup>, C(CH<sub>3</sub>)<sub>3</sub> of C<sub>6</sub>H<sub>4</sub>-4-tBu), 128.4 (s, C<sup>q</sup>, C(tBu) of C<sub>6</sub>H<sub>4</sub>-4-tBu), 125.5 (s, CH-o of C<sub>6</sub>H<sub>4</sub>-4-tBu), 124.5 (s, CH-m of C<sub>6</sub>H<sub>4</sub>-4-tBu), 36.4 (*vt*, N = |<sup>1</sup>J<sub>CP</sub> + <sup>3</sup>J<sub>CP</sub>| = 27.4 Hz, C<sup>1</sup>, Cy), 31.5 (m, C<sup>3,5</sup>, Cy), 28.0 (*vt*, N = |<sup>2</sup>J<sub>CP</sub> + <sup>4</sup>J<sub>CP</sub>| = 10.6 Hz, C<sup>2,6</sup>, Cy), 27.1 (m, C<sup>4</sup>, Cy), 31.3 (s, CH<sub>3</sub> of C<sub>6</sub>H<sub>4</sub>-4-tBu). <sup>13</sup>P{<sup>1</sup>H} NMR (128.38 MHz,  $d_8$ -Tol, 70 °C):  $\delta$  74.0 (br s, fwhm  $\approx$  1600 Hz). Anal. Calcd for C<sub>46</sub>H<sub>79</sub>BBr<sub>2</sub>P<sub>2</sub>Pt: C, 52.13; H, 7.51. Found: C, 52.27; H, 7.69.

Synthesis of trans-[Pt{B(Br)Dur}Br(PiPr<sub>3</sub>)<sub>2</sub>] (1c). Neat [Pt- $(PiPr_3)_3$ ] was heated under vacuum to 60 °C. The obtained yellow oil ([Pt(PiPr<sub>3</sub>)<sub>2</sub>]; 206 mg, 0.399 mmol) was dissolved in benzene. A solution of Br<sub>2</sub>BDur (121 mg, 0.399 mmol) in 2 mL of benzene was added dropwise with continuous stirring. After 1 h the solvent was removed under vacuum at 50 °C. The remaining colorless solid was crystallized from hexanes at -35 °C within 4 days (yield 206.3 mg, 63%). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 24 °C): δ 6.95 (s, 1H, CH of Dur), 3.16-3.08 (m, 6H, CH of iPr), 2.11 (s, 6H, CH<sub>3</sub>-m of Dur), 1.35-1.16 (m, 36H, CH<sub>3</sub> of *i*Pr, 6H, CH<sub>3</sub>-0 of Dur). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz, 24 °C): δ 150.6 (s, C<sup>q</sup> of Dur), 138.7 (s, CCH<sub>3</sub>-o of Dur), 134.5 (br s, CCH<sub>3</sub>-m of Dur), 134.2 (s, CH of Dur), 26.1 (t,  ${}^{1}J_{PC}$  = 28.2 Hz, CH of *i*Pr), 20.9 (s, CCH<sub>3</sub>-*m* of Dur), 20.4 (br s, CH<sub>3</sub> of iPr), 19.7 (s, CCH<sub>3</sub>-o of Dur). <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, C<sub>6</sub>D<sub>6</sub>, 24 °C):  $\delta$  28.5 (s, <sup>1</sup>J<sub>PPt</sub> = 3050 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128.38 MHz,  $C_6D_6$ , 24 °C):  $\delta$  ca. 74.1 (br s, fwhm  $\approx$  1990 Hz). Anal. Calcd for C<sub>28</sub>H<sub>56</sub>BBr<sub>2</sub>P<sub>2</sub>Pt: C, 40.99; H, 6.88. Found: C, 40.61; H, 7.07.

Synthesis of trans-[Pt(BDur)Br(PCy<sub>3</sub>)<sub>2</sub>][BAr<sup>f</sup><sub>4</sub>] (2a). trans-[Pt- $\{B(Br)(Dur)\}Br(PCy_3)_2\}$  (1a; 20 mg, 19  $\mu$ mol) and Na $[BAr_4^f]$  (16.7 mg, 18.9  $\mu$ mol) were mixed in CD<sub>2</sub>Cl<sub>2</sub>. The colorless reaction mixture turned yellow, and a colorless solid precipitated. After filtration and storage at -35 °C for 3 days, colorless crystals of trans-[Pt(BDur)-Br(PCy<sub>3</sub>)<sub>2</sub>][BAr<sup>f</sup><sub>4</sub>] were isolated (yield 25.7 mg, 74%). <sup>1</sup>H NMR (500.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): δ 7.99 (m, 8H, BAr<sup>f</sup><sub>4</sub>), 7.75 (br s, 4H, BAr<sup>f</sup><sub>4</sub>), 7.49 (br s, 1H, CH-p of Dur), 2.88 (m, 6H, CH-i of Cy), 2.79 (s, 6H, CH<sub>3</sub>-o of Dur), 2.31 (s, 6H, CH<sub>3</sub>-m, Dur), 2.21-2.01 (m, 12H, Cy), 1.95–1.71 (m, 30H, Cy), 1.26–1.09 (m, 18H, Cy).  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (125.76 MHz,  $CD_2Cl_2$ , 23 °C):  $\delta$  162.4 (q,  ${}^{1}J_{CB}$  = 49.9 Hz, CHipso of BAr<sup>f</sup><sub>4</sub>), 142.4 (s, CCH<sub>3</sub>-o of Dur), 141.9 (s, CH, Dur), 137.3 (s, CCH<sub>3</sub>-*m* of Dur), 135.4 (br s, C-*o* of BAr<sup>f</sup><sub>4</sub>), 129.5 (qq,  ${}^{2}J_{CF}$  = 31.5 Hz, C-m of BAr<sup>f</sup><sub>4</sub>), 125.2 (q,  ${}^{1}J_{CF} = 272$  Hz, CF<sub>3</sub>, BAr<sup>f</sup><sub>4</sub>), 118.0 (sep,  ${}^{3}J_{CF} = 4.0$  Hz, C-p of BAr<sup>f</sup><sub>4</sub>), 37.6 (vt, N =  ${}^{1}J_{CP} + {}^{3}J_{CP} = 26.6$  Hz, C<sup>1</sup>, Cy), 30.7 (s, C<sup>3,5</sup>, Cy), 27.5 (vt, N =  ${}^{1}J_{CP} + {}^{4}J_{CP} = 11.4$  Hz, C<sup>2,6</sup>, Cy), 26.2 (s, C<sup>4</sup>, Cy), 21.5 (s, CH<sub>3</sub>-o of Dur), 18.6 (s, CH<sub>3</sub>-m of Dur).  ${}^{31}P{}^{1}H{}$ NMR (202.46 MHz,  $CD_2Cl_2$ , 23 °C):  $\delta$  44.8 (s,  ${}^{1}J_{PPt}$  = 2075 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 23 °C):  $\delta$  101 (br s, fwhm  $\approx$ 2100 Hz), -7.3 (s, BAr<sup>f</sup><sub>4</sub>). Anal. Calcd for C<sub>78</sub>H<sub>91</sub>B<sub>2</sub>BrF<sub>24</sub>P<sub>2</sub>Pt: C, 50.83; H, 4.98. Found: C, 50.30; H, 4.93.

Synthesis of *trans*-[Pt{B(Br)( $C_6H_6$ -4-tBu)}(PCy<sub>3</sub>)<sub>2</sub>] [BAr<sup>f</sup><sub>4</sub>] (2b). Equimolar amounts of 1b (50 mg, 43  $\mu$ mol) and Na[BAr<sup>f</sup><sub>4</sub>] (41.8 mg, 42.7  $\mu$ mol) were mixed in CD<sub>2</sub>Cl<sub>2</sub>. The colorless reaction mixture turned yellow, and a colorless solid precipitated. Although fitting <sup>31</sup>P and <sup>11</sup>B NMR data were obtained, it was not possible to isolate the resulting unstable product due to facile rehalogenation and reformation of the precursor 1b. <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 24 °C):  $\delta$  41.8 (s, <sup>1</sup>J<sub>PPt</sub> = 2833 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128.38 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 24 °C):  $\delta$  24.3 (br s), -7.4 (s, BAr<sup>f</sup><sub>4</sub>).

Synthesis of trans-[Pt(BDur)Br(PiPr<sub>3</sub>)<sub>2</sub>][BAr<sup>f</sup><sub>4</sub>] (2c). trans-[Pt-{B(Br)Dur}Br(PiPr<sub>3</sub>)<sub>2</sub>] (30 mg, 37  $\mu$ mol) and Na[BAr<sup>f</sup><sub>4</sub>] (32.4 mg, 33.6  $\mu$ mol) were mixed in CD<sub>2</sub>Cl<sub>2</sub> (4 mL). The solution turned yellow, and a colorless solid precipitated. After the solids were filtered off and the solution was stored at -35 °C over 3 days, colorless crystals of trans-[Pt(BDur)Br(PiPr<sub>3</sub>)<sub>2</sub>][BAr<sup>f</sup><sub>4</sub>] were isolated (yield 40.5 mg, 69%). <sup>1</sup>H NMR (500.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 24 °C):  $\delta$  7.72 (m, 8H, BAr<sup>f</sup><sub>4</sub>), 7.56 (br s, 4H, BAr<sup>f</sup><sub>4</sub>), 7.41 (br s, 1H, CH-*p* of Dur), 3.05 (m, 6H, CH of *i*Pr), 2.69 (s, 6H, CH<sub>3</sub>-*o* of Dur), 2.20 (s, 6 H, CH<sub>3</sub>-*m* of Dur), 1.36 (q, 36 H, CH<sub>3</sub> of *i*Pr). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100.61 MHz, 24 °C): δ 162.1 (q, <sup>1</sup>J<sub>CB</sub> = 49.8 Hz, C-*ipso*, BAr<sup>f</sup><sub>4</sub>), 142.4 (s, CCH<sub>3</sub>-*o* of Dur), 142.2 (s, CH, Dur), 137.3 (s, CCH<sub>3</sub>-*o* of Dur), 135.2 (s, C-*o*, BAr<sup>f</sup><sub>4</sub>), 129.2 (qq, <sup>2</sup>J<sub>CF</sub> = 30.9 Hz, C-*m* of BAr<sup>f</sup><sub>4</sub>), 124.9 (q, <sup>1</sup>J<sub>CF</sub> = 273 Hz, CF<sub>3</sub>, BAr<sup>f</sup><sub>4</sub>), 117.8 (sep, <sup>3</sup>J<sub>CF</sub> = 3.8 Hz, C-*p*, BAr<sup>f</sup><sub>4</sub>), 27.8 (br s, C, *i*Pr), 21.9 (s, CH<sub>3</sub>-*o* of Dur), 20.2 (s, CH<sub>3</sub> of *i*Pr), 18.6 (s, CH<sub>3</sub>-*m* of Dur). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202.46 MHz, 24 °C): δ 55.8 (s, <sup>1</sup>J<sub>PPt</sub> = 2102 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 160.46 MHz, 24 °C): δ 99.6 (br s, fwhm ≈ 2400 Hz), -7.6 (s, BAr<sup>f</sup><sub>4</sub>). Anal. Calcd for C<sub>60</sub>H<sub>68</sub>B<sub>2</sub>BrF<sub>24</sub>P<sub>2</sub>Pt: C, 44.98; H, 4.27. Found: C, 45.35; H, 4.26.

**Crystallographic Data.** The crystal data of **1a**,**b** and **2a**,**c** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multilayer mirror monochromated Mo K $\alpha$  radiation. The structures were solved using direct methods, refined with the Shelx software package, and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for **1a**: C<sub>46</sub>H<sub>79</sub>BBr<sub>2</sub>P<sub>2</sub>Pt,  $M_r$  = 1059.75, colorless block, 0.774 × 0.656 × 0.466 mm<sup>3</sup>, orthorhombic space group  $P2_12_12_1$ , a = 14.3925(8) Å, b = 17.5114(11) Å, c = 18.3676(11) Å, V =4629.2(5) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.521$  g cm<sup>-3</sup>,  $\mu = 4.857$  mm<sup>-1</sup>, F(000) =2152, T = 100(2) K, R1 = 0.0265, wR2 = 0.0428, 9867 independent reflections ( $2\theta \le 53.64^{\circ}$ ), and 473 parameters.

*Crystal data for 1b*: C<sub>46</sub>H<sub>79</sub>BBr<sub>2</sub>P<sub>2</sub>Pt, *M*<sub>r</sub> = 1059.75, colorless block, 0.24 × 0.19 × 0.15 mm<sup>3</sup>, triclinic space group *P*I, *a* = 13.0435(17) Å, *b* = 14.2865(18) Å, *c* = 14.9344(18) Å, *α* = 80.703(4)°, *β* = 89.627(4)°, *γ* = 72.306(4)°, *V* = 2613.8(6) Å<sup>3</sup>, *Z* = 2,  $\rho_{calcd} = 1.347$  g cm<sup>-3</sup>,  $\mu = 4.301$  mm<sup>-1</sup>, *F*(000) = 1076, *T* = 100(2) K, R1 = 0.0611, wR2 = 0.0907, 11241 independent reflections (2 $\theta \leq 53.84^{\circ}$ ), and 472 parameters.

Crystal data for **2a**:  $C_{78}H_{91}B_2BrF_{24}P_2Pt$ ,  $M_r = 1843.07$ , colorless block,  $0.24 \times 0.18 \times 0.09 \text{ mm}^3$ , triclinic space group  $P\overline{1}$ , a = 13.0971(9) Å, b = 17.3259(14) Å, c = 20.8371(15) Å,  $\alpha = 71.694(4)^\circ$ ,  $\beta = 75.300(4)^\circ$ ,  $\gamma = 85.345(4)^\circ$ , V = 4342.1(6) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.410$  g cm<sup>-3</sup>,  $\mu = 2.203$  mm<sup>-1</sup>, F(000) = 1856, T = 100(2) K, R1 = 0.0567, wR2 = 0.1335, 17726 independent reflections ( $2\theta \le 52.74^\circ$ ), and 977 parameters.

Crystal data for **2c**: C<sub>61</sub>H<sub>69</sub>B<sub>2</sub>BrCl<sub>2</sub>F<sub>24</sub>P<sub>2</sub>Pt,  $M_r$  = 1687.62, colorless block, 0.35 × 0.27 × 0.22 mm<sup>3</sup>, monoclinic space group  $P2_1/n$ , a = 14.935(6) Å, b = 24.927(13) Å, c = 18.515(8) Å,  $\beta$  = 97.572(9)°, V = 6833(5) Å<sup>3</sup>, Z = 4,  $\rho_{calcd}$  = 1.640 g cm<sup>-3</sup>,  $\mu$  = 2.867 mm<sup>-1</sup>, F(000) = 3352, T = 100(2) K, R1 = 0.0621, wR2 = 0.0727, 14513 independent reflections ( $2\theta \le 53.54^{\circ}$ ), and 873 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1032889–1032892. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

CIF file giving crystallographic data for **1a,b** and **2a,c**. This material is available free of charge via the Internet at http:// pubs.acs.org.

#### AUTHOR INFORMATION

### **Corresponding Author**

\*E-mail for H.B.: h.braunschweig@uni-wuerzburg.de.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported by an ERC Advanced Grant to H.B.

#### **Organometallics**

#### REFERENCES

- (1) Männig, D.; Nöth, H. Angew. Chem., Int. Ed. 1985, 24, 878–879.
- (2) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice,

C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. Chem. Rev. 1998, 98, 2685-2722.

(3) Braunschweig, H.; Dewhurst, R. D.; Schneider, A. Chem. Rev. 2010, 110, 3924–3957.

(4) Braunschweig, H.; Kupfer, T.; Radacki, K.; Schneider, A.; Seeler, F.; Uttinger, K.; Wu, H. J. Am. Chem. Soc. **2008**, 130, 7974–7983.

(5) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. Angew. Chem., Int. Ed. 2006, 45, 162–165.

(6) Braunschweig, H.; Schneider, A.; Radacki, K. Science 2010, 328, 345-347.

(7) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H. G.; Neumann, B. Angew. Chem., Int. Ed. 2001, 40, 2298–2300.

(8) Blank, B.; Colling-Hendelkens, M.; Kollann, C.; Radacki, K.; Rais, D.; Uttinger, K.; Whittell, G. R.; Braunschweig, H. *Chem. Eur. J.* **2007**, 13, 4770–4781.

(9) Braunschweig, H.; Kollann, C.; Englert, U. Angew. Chem., Int. Ed. 1998, 37, 3179-3180.

(10) Aldridge, S.; Calder, R. J.; Rossin, A.; Dickinson, A. A.; Willock, D. J.; Jones, C.; Evans, D. J.; Steed, J. W.; Light, M. E.; Coles, S. J.; Hursthouse, M. B. *Dalton Trans.* **2002**, 2020.

(11) Zhu, J.; Lin, Z. Y.; Marder, T. B. Inorg. Chem. 2005, 44, 9384–9390.

(12) Braunschweig, H.; Brenner, P.; Müller, A.; Radacki, K.; Rais, D.; Uttinger, K. Chem. Eur. J. 2007, 13, 7171–7176.

(13) Braunschweig, H.; Herbst, T.; Rais, D.; Seeler, F. Angew. Chem., Int. Ed. 2005, 44, 7461-7463.

(14) Braunschweig, H.; Radacki, K.; Uttinger, K. Angew. Chem., Int. Ed. 2007, 46, 3979–3982.

(15) Arnold, N.; Braunschweig, H.; Brenner, P.; Jimenez-Halla, J. O. C.; Kupfer, T.; Radacki, K. *Organometallics* **2012**, *31*, 1897–1907.

(16) Braunschweig, H.; Radački, K.; Uttinger, K. Chem. Eur. J. 2008, 14, 7858–7866.

(17) Braunschweig, H.; Ye, Q.; Radacki, K. Chem. Commun. 2012, 48, 2701–2001.

(18) Paetzold, P.; Hoffmann, J. Chem. Ber. 1980, 113, 3724-3733.

- (19) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. J. Am. Chem. Soc. 1976, 98, 5850-5858.
- (20) Mann, B. E.; Musco, A. J. Chem. Soc., Dalton Trans. 1980, 5, 776-785.
- (21) Yoshida, T.; Otsuka, S. Inorg. Synth. 1990, 28, 113-119.
- (22) Matsuda, T.; Otsuka, S.; Yoshida, T. Inorg. Synth. 1979, 28, 122-123.