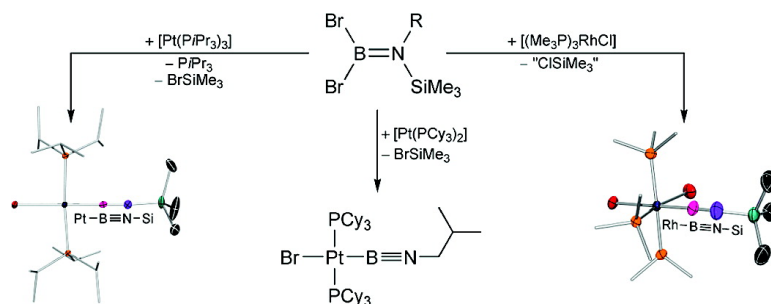


## Synthesis and Reactivity Studies of Iminoboryl Complexes

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*J. Am. Chem. Soc.*, **2008**, 130 (25), 7974-7983 • DOI: 10.1021/ja8016889 • Publication Date (Web): 30 May 2008

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### Synthesis and Reactivity Studies of Iminoboryl Complexes

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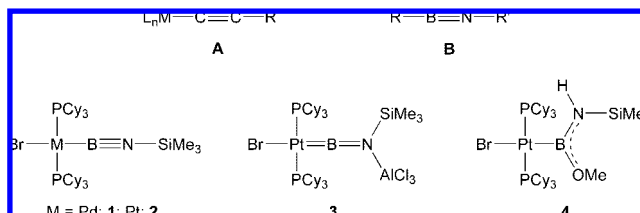
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**Abstract:** A range of new iminoboryl complexes of the type  $[L_nM-B\equiv N-R]$ , which are isoelectronic with  $\sigma$ -alkynyl complexes  $[L_nM-C\equiv C-R]$ , was obtained by systematically varying the metal M, the coligands L, and the nitrogen bound substituent R. Selected examples include, for example, *trans*- $[(C_3P)_2(Br)Pt(B\equiv N/Bu)]$ , which is characterized by a sterically less demanding N-R group or the unprecedented rhodium species *cis,mer*- $[(Br)_2(Me_3P)_3Rh(B\equiv NSiMe_3)]$ . All compounds were fully characterized in solution by multinuclear NMR spectroscopy and, where appropriate, in the solid state by X-ray crystallography. Subsequent reactivity studies revealed that particularly the combination of smaller N-R groups with Pt-B linkages of increased stability opens up opportunities for novel reactivity patterns of this class of compounds. Within the scope of these study, we inter alia succeeded in synthesizing the unusual bridged boryl species  $1,4\text{-trans-}[(C_3P)_2(Br)Pt(B\{NH/Bu\}NH)]_2C_6H_4$  and a complex bearing both an acetylide ligand and an iminoboryl ligand, respectively.

#### Introduction

During the past three decades, the interest in transition-metal  $\sigma$ -alkynyl complexes  $[L_nM-C\equiv C-R]$  (A, chart 1) has significantly increased, not least because of their potential applications, for example, as optoelectronic devices.<sup>1</sup> In addition, these complexes have also proven to be suitable building-blocks for rigid-rod polymers owing to the unsaturated character of the alkynyl moiety and its interaction with highly polarizable transition-metals. In several studies, polymeric alkynyl complexes demonstrated their relevance in areas of liquid crystallinity,<sup>2</sup> nonlinear optics,<sup>1c-f,i,l</sup> luminescence,<sup>1a,b,j</sup> and electrical semiconductivity.<sup>3</sup> Compared to their organic counterparts, such organometallic species provide additional opportunities to tune the electronic properties of the polymer by varying the transition-

**Chart 1.**  $\sigma$ -Alkynyl Complexes  $[L_nM-C\equiv C-R]$  (A), iminoboranes (B) as well as the first iminoboryl complexes (1, 2) and derivatives of 2 (3, 4)



metal itself as well as the bridging spacers and the coligands.<sup>1h</sup> Further improvement of the electronic features might be achieved by formal exchange of a CC-unit for an isoelectronic BN-unit.<sup>4</sup> This isoelectronic relationship initiated extensive experimental<sup>5,6</sup> and theoretical<sup>7</sup> investigations of the BN-analogues of alkynes, namely iminoboranes  $R-B\equiv N-R'$  (B, Chart 1). Because of the  $B\equiv N$  triple bond's intrinsic polarity,

- (1) For an overview on transition metal  $\sigma$ -alkynyl complexes see: (a) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165–176. (b) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227–1232. (c) Long, N. J. *Angew. Chem.* **1995**, *107*, 3756; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21–38. (d) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291–362. (e) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349–405. (f) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: Weinheim, Germany, 2002; 153–179. (g) Long, N. J.; Williams, C. K. *Angew. Chem.* **2003**, *115*, 26902722; *Angew. Chem., Int. Ed.* **2003**, *42*, 2586–2617. (h) Powell, C. E.; Humphrey, M. G. *Coord. Chem. Rev.* **2004**, *248*, 725–756. (i) Cifuentes, M. P.; Humphrey, M. G. *J. Organomet. Chem.* **2004**, *689*, 3968–3981. (j) Wong, W. Y.; Ho, C. L. *Coord. Chem. Rev.* **2006**, *250*, 2627–2690. (k) Wong, W.-Y. *J. Chem. Soc., Dalton Trans.* **2007**, 4495–4510. (l) Morrall, J. P.; Dalton, G. T.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **2008**, *55*, 61–136, and references therein.
- (2) (a) Takahashi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K.; Hagihara, N. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 139–143. (b) Takahashi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1984**, *3*, 5.

- (3) (a) Younus, M.; Köhler, A.; Cron, S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Khan, M. S.; Lewis, J.; Long, N. J.; Friend, R. H.; Raithby, P. R. *Angew. Chem.* **1998**, *110*, 3180–3183; *Angew. Chem. Int. Ed.* **1998**, *37*, 3036–3039. (b) Wong, W.-Y.; Wong, W.-K.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1998**, 2761–2766. (c) Ferri, A.; Polzonetti, G.; Licocchia, S.; Paollesse, R.; Favretto, D.; Traldi, P.; Russo, M. V. *J. Chem. Soc., Dalton Trans.* **1998**, 4063–4070. (d) Wong, W.-Y.; Choi, K.-H.; Lu, G.-L.; Shi, J.-X. *Macromol. Rapid Commun.* **2001**, *22*, 461–465.
- (4) (a) Côté, M.; Haynes, P. D.; Molteni, C. *Phys. Rev. B: Condens. Matter* **2001**, *63*, 125207. (b) Marder, T. B. *Angew. Chem.* **2008**, *120*, 248–250; *Angew. Chem. Int. Ed.* **2008**, *47*: 242–244.
- (5) (a) Nöth, H. *Angew. Chem.* **1988**, *100*, 1664–1684; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1603–1623. (b) Braun, U.; Böck, B.; Nöth, H.; Schwab, I.; Schwartz, M.; Weber, S.; Wietelmann, U. *Eur. J. Inorg. Chem.* **2004**, 3612–3628, and references therein.
- (6) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123–170.
- (7) (a) Baird, N. C.; Datta, R. K. *Inorg. Chem.* **1972**, *11*, 17–19. (b) Armstrong, D. R.; Clark, D. T. *Theor. Chim. Acta* **1972**, *24*, 307–316.

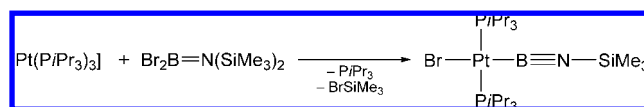
these compounds display increased reactivity, in particular, toward rapid oligomerization in the absence of kinetic stabilization. The size of the boron- and nitrogen-bound substituents not only strongly effects the rate of this oligomerization, but also subtly controls the nature of the stabilization products.<sup>5a,6</sup>

Despite the well examined chemistry of complexes with boron-centered ligands<sup>8</sup> on the one hand, and likewise, the large number of iminoboranes on the other hand,<sup>5,6</sup> the discovery of complexes containing corresponding  $\sigma$ -coordinated iminoboryl ligands was a long time coming, until in 2006, *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)M(B≡NSiMe<sub>3</sub>)] (M = Pd, **1**; Pt, **2**; Cy = cyclohexyl), the first two examples of this class of compounds, were prepared and fully characterized (Chart 1).<sup>9</sup> Access to these novel species was gained by reaction of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub> with zerovalent Pd and Pt precursors, respectively. The oxidative addition of B–Br bonds has recently developed into a highly useful synthetic protocol, which led to a variety of interesting palladium and platinum boryl species.<sup>9,10</sup> In contrast to these reactions, however, the addition of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub> to [M(P-Cy<sub>3</sub>)<sub>2</sub>] (M = Pd, Pt) is accompanied by spontaneous loss of BrSiMe<sub>3</sub> at ambient temperature, thus furnishing the final iminoboryl complexes **1** and **2**.

Preliminary findings<sup>9</sup> indicated that the B≡N triple bond is effectively stabilized in the coordination sphere of transition metals, thus leading to a remarkable stability of **1** and **2** toward oligomerization, much different from main-group-substituted iminoboranes. Examples of iminoboryl complexes are still very limited in number and likewise, knowledge concerning their reactivity is restricted to the interaction with Lewis and Brønsted acids, which led to the fully characterized derivatives *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{BN(SiMe<sub>3</sub>)(AlCl<sub>3</sub>)}] (**3**) and *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(OMe)(N(H)SiMe<sub>3</sub>)}] (**4**) (Chart 1).<sup>11</sup>

We report herein a study targeting new transition-metal iminoboryl complexes by systematically diversifying the substitution pattern of these substances with respect to (i) the central

**Scheme 1.** Synthesis of *trans*-[(iPr<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡NSiMe<sub>3</sub>)] (**7**)



metal; (ii) the metal-bound coligands; and (iii) the steric requirements of the N–R moiety. In particular, the combination of smaller iminogroups with Pt–B linkages of increased stability led to novel reactivity patterns of this class of compounds.

## Discussion

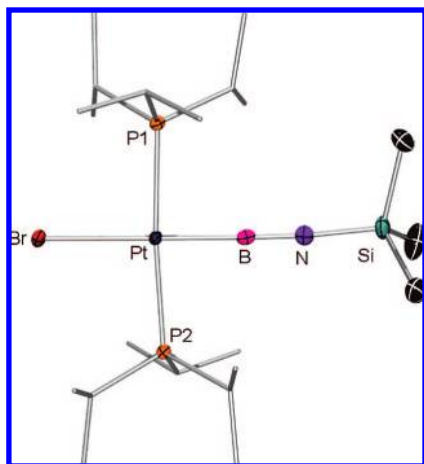
**Synthesis of New Iminoboryl Complexes.** As mentioned before, the iminoboryl complexes *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)M-(B≡NSiMe<sub>3</sub>)] (M = Pd, **1**; Pt, **2**) can be prepared by B–Br bond oxidative addition of dibromo(silylamino)boranes to coordinatively unsaturated metal fragments with concomitant liberation of bromosilane.<sup>9</sup> While the elimination of halosilanes from suitable aminoboranes is a very well established method of synthesis for iminoboranes R–B≡N–R (**B**),<sup>5,6</sup> it has to be noted that higher temperatures of about 350–500 °C are commonly required in these cases. The exceptionally mild conditions, that is ambient temperature, under which iminoboryl complexes were formed, is thus quite remarkable, and it may be assumed that the bulky PCy<sub>3</sub> ligands in **1** and **2** facilitate the BrSiMe<sub>3</sub> elimination so as to reduce intramolecular repulsion between the boron bound amino group and the cyclohexyl substituents. To examine the steric effects of the metal-bound coligands, we aimed to decrease the space requirement of the transition-metal fragment and the substituent linked to nitrogen, respectively. Therefore, we first adopted only minor modifications to the platinum system by employing [Pt(PiPr<sub>3</sub>)<sub>3</sub>] (**5**), which at ambient temperature in solution readily dissociates into [Pt(PiPr<sub>3</sub>)<sub>2</sub>] (**6**) and PiPr<sub>3</sub>.<sup>12</sup>

Monitoring the reaction of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub> with **5** by multinuclear NMR spectroscopy revealed the gradual consumption of both the bis(phosphine) platinum complex **6** and the borane. The <sup>1</sup>H NMR spectrum displays a new singlet at 0.30 ppm, indicating the formation of BrSiMe<sub>3</sub> and another one at 0.25 ppm, which can be assigned to the iminoboryl complex *trans*-[(iPr<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡NSiMe<sub>3</sub>)] (**7**). The <sup>11</sup>B NMR spectrum features one new broad signal at 16.9 ppm, which appears only slightly shifted to high field with respect to the starting material, whereas the changes in the <sup>31</sup>P NMR spectrum are much more pronounced and indicative. Both the chemical shift and the platinum–phosphorus coupling constant of the new singlet at 42.7 ppm (<sup>1</sup>J<sub>Pt–P</sub> = 2412 Hz) differ distinctly from the data for **6** (δ = 72.8 ppm; <sup>1</sup>J<sub>Pt–P</sub> = 4202 Hz).<sup>12a</sup> The spectroscopic properties are in good agreement with those of **2**, indicating the formation of the corresponding iminoboryl complex **7** (Scheme 1).

The constitution of the new compound was verified by an X-ray diffraction study performed on suitable single crystals obtained from hexane at –35 °C. The molecular structure is shown in Figure 1 (in the following, only the disordered component with higher occupancy is discussed). Compound **7** crystallizes in the triclinic space group *P* $\bar{1}$  and displays a slightly distorted square-planar geometry around the platinum center. The iminoboryl ligand is coordinated terminally to the metal

- (8) (a) 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. (b) Braunschweig, H. *Angew. Chem.* **1998**, *110*, 18821898; *Angew. Chem. Int. Ed.* **1998**, *17*, 1786–1801. (c) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1–51. (d) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535–559. (e) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem.* **2006**, *118*, 53805400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254–5274 and references therein. (9) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem.* **2006**, *118*, 169172; *Angew. Chem. Int. Ed.* **2006**, *45*, 162–165. (10) (a) Clegg, W. F.; Lawlor, J.; Lesley, G.; Marder, T. B.; Norman, N.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Scott, A. J.; Souza, F. E. S. *J. Organomet. Chem.* **1998**, *550*, 183–192. (b) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Organometallics* **2004**, *23*, 5545–5549. (c) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem.* **2005**, *117*, 1217–1219; *Angew. Chem. Int. Ed.* **2005**, *44*, 1192–1194. (d) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F.; Uttinger, K. *J. Am. Chem. Soc.* **2005**, *127*, 1386–1387. (e) Braunschweig, H.; Whittell, G. R. *Chem. Eur. J.* **2005**, *11*, 6128–6133. (f) Braunschweig, H.; Radacki, K.; Rais, D.; Scheschke, D. *Angew. Chem.* **2005**, *117*, 57965799; *Angew. Chem. Int. Ed.* **2005**, *44*, 5651–5654. (g) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem.* **2006**, *118*, 1087–1090; *Angew. Chem. Int. Ed.* **2006**, *45*, 1066–1069. (h) Braunschweig, H.; Radacki, K.; Uttinger, K. *Angew. Chem.* **2007**, *119*, 40544057; *Angew. Chem. Int. Ed.* **2007**, *46*, 3979–3982. (i) Braunschweig, H.; Brenner, P.; Müller, A.; Radacki, K.; Rais, D.; Uttinger, K. *Chem. Eur. J.* **2007**, *13*, 7171–7176. (j) Braunschweig, H.; Leech, R.; Rais, D.; Radacki, K.; Uttinger, K. *Organometallics* **2008**, *27*, 418–422. (k) Braunschweig, H.; Gruss, K.; Radacki, K.; Uttinger, K. *Eur. J. Inorg. Chem.* **2008**, 1462–1466. (11) Braunschweig, H.; Radacki, K.; Rais, D.; Schneider, A.; Seeler, F. *J. Am. Chem. Soc.* **2007**, *129*, 10350–10351.

- (12) (a) Mann, B. E.; Musco, A. J. *Chem. Soc., Dalton Trans.* **1980**, 776–785. (b) Haase, M.; Klingebiel, U.; Boese, R.; Polk, M. *Chem. Ber.* **1986**, *119*, 1117–1126.



**Figure 1.** Molecular structure of *trans*-[(*iPr*<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡NSiMe<sub>3</sub>)] (**7**). Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms and carbon atoms of the *iso*-propyl groups, as well as the disordered part of the molecule are omitted for clarity.

fragment (Pt–B–N: 177.9(6)°) and the B–N–Si angle (175.6(9)°) reveals a somewhat smaller deviation from linearity than its bis(tricyclohexylphosphine) analogues of palladium **1** (163.1(3)° and 166.1(2)°) and platinum **2** (173.3(3)°).<sup>9</sup> The B–N distance of 1.265(7) Å is statistically indistinguishable from those of the complexes **1** (1.251(4) Å and 1.262(3) Å) and **2** (1.260(4) Å) and only slightly longer than that of (Me<sub>3</sub>Si)<sub>3</sub>–Si–B≡N–*t*Bu (1.221(5) Å), which represents the only reliably structurally characterized main-group-substituted iminoborane.<sup>12b</sup> In addition to a wide range of platinum boryl complexes of the form *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(R)R'}], in which a three-coordinate boron center is linked to platinum, the first two platinum borylene complexes, namely *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt(BMes)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**8**; Mes = 2,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sup>10h</sup> and *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{BN(SiMe<sub>3</sub>)(AlCl<sub>3</sub>)}] (**3**),<sup>11</sup> with boron in coordination number two, were reported only very recently. A comparison of the Pt–B distances of **2** (1.960(3) Å) and **7** (1.959(3) Å) with those of Pt boryls and borylenes is rather instructive and reveals that the former two display significantly increased bond lengths compared with those observed for the borylene species **8** (1.859(3) Å) and **3** (1.904(3) Å), despite the fact that both classes of compounds display two coordinate boron centers, while boryl ligands are characterized by Pt–B separations in the range of 1.963(6)–2.090(3) Å.<sup>10a,i</sup> These observations can be explained by the electronic saturation of the low-coordinate boron center in **2** and **7** by the B≡N triple bond and therefore the Pt–B bond in iminoboryls can best be described by a single bond, while the electronically unsaturated borylene ligands receive significantly increased Pt–B  $\pi$ -back-donation, thus giving rise to a significant double bond character as indicated in the case of **8** by DFT calculations.<sup>10h</sup> The Pt–Br bond lengths of compounds **2** (2.5516(4) Å) and **7** (2.5439(2) Å) are almost identical and resemble those of the borylene complexes **3** (2.5418(6) Å) and **8** (2.5280(2) Å), but are smaller than those in platinum boryl complexes *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(R)R'}] (2.5617(10)–2.6454(4) Å).<sup>10i</sup> This finding underlines the fact that two-coordinate boron centered ligands commonly exert a smaller trans influence, due to weaker  $\sigma$ -donating ability, than boryl groups, which are coordinated via a three-coordinate boron atom and feature a very strong trans influence.<sup>10i,13</sup>

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

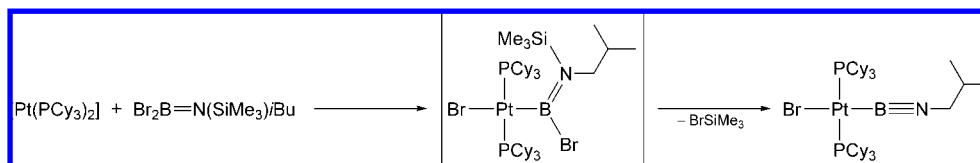
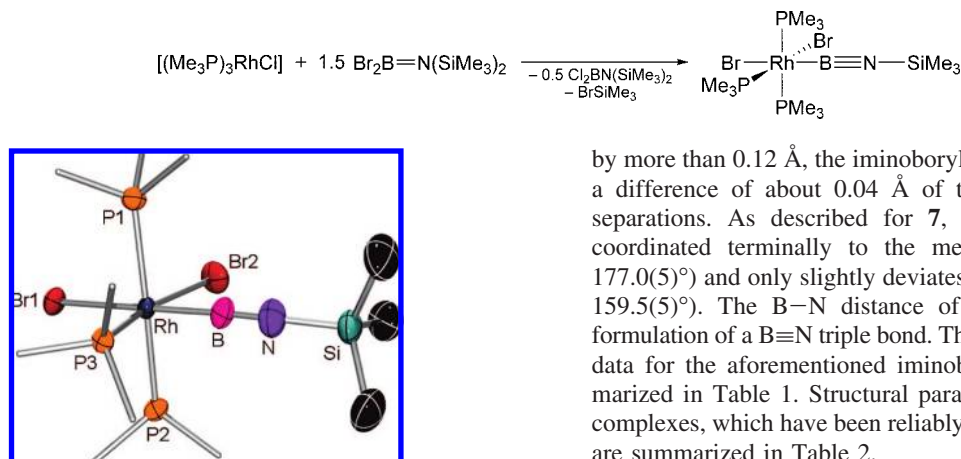
Since an albeit modest decrease in the steric demand of the metal fragment of **7** did not significantly influence the structural and spectroscopic properties, the reaction rate of its formation, nor its oligomerization tendency (similar to **2**, complex **7** remained inert over 8 h at 80 °C in benzene solution, and for 6 h at ambient temperature upon exposure to UV-irradiation with a Hg(Xe) lamp) we decided to significantly reduce the spacial requirement of the nitrogen linked substituent. Thus, Br<sub>2</sub>B=N(SiMe<sub>3</sub>)*i*Bu, was chosen as a precursor, particularly since iminoboranes with  $\alpha$ -unbranched substituents on nitrogen are known to display a significantly enhanced reactivity.

The course of the reaction of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)*i*Bu with the platinum(0) complex [Pt(PCy<sub>3</sub>)<sub>2</sub>] is characterized by the formation of an intermediate, as indicated by a singlet in the <sup>31</sup>P NMR spectrum at 22.5 ppm (<sup>1</sup>J<sub>Pt–P</sub> = 2915 Hz). Both the chemical shift and the platinum–phosphorus coupling constant differ markedly from the values observed for the iminoboryl complexes **2** and **7**, but are characteristic of boryl complexes of the type *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(R)R'}] (18.7–29.0 ppm; 2587–3067 Hz).<sup>10a,i</sup> In addition, the <sup>1</sup>H NMR spectra exhibit two doublets at 3.83 (2H) and 1.05 ppm (6H), which can be assigned to the *iso*-butyl group and one singlet at 0.59 ppm (9H) for the trimethylsilyl group, which differs significantly from that of free BrSiMe<sub>3</sub> (0.30 ppm, vide supra). These spectroscopic data clearly indicate the formation of the intermediate boryl complex *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(Br)(N(*i*Bu)SiMe<sub>3</sub>)}]. During the further course of the reaction, the intensities of these signals associated with the intermediate gradually decrease, giving rise to a new set of signals. The <sup>31</sup>P NMR spectrum shows a new singlet at 31.5 ppm (<sup>1</sup>J<sub>Pt–P</sub> = 2427 Hz), which is almost identical to that of **2**, and additionally, a new singlet in the proton NMR spectra at 0.30 ppm indicates the liberation of BrSiMe<sub>3</sub>, thus giving reason to assume the reaction sequence illustrated in Scheme 2, finally leading to the product *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡N*i*Bu)] (**9**). Obviously, distinct reduction of the steric demand of the substituent linked to nitrogen causes a pronounced decrease of the elimination rate of BrSiMe<sub>3</sub>. Hence, an intermediate boryl complex, obtained by B–Br bond oxidative addition, which was postulated for the synthesis of the (trimethylsilyl)iminoboryl complexes (vide supra), was now spectroscopically observed for the first time.

To exploit further the facile formation of iminoboryl complexes, we last turned our attention to different transition metals. It is well documented that rhodium(III) boryl complexes are key intermediates in catalytic hydroboration and related processes,<sup>14a</sup> since rhodium(I) species are very susceptible to oxidative addition of various boron–element bonds.<sup>14b,c</sup> Furthermore, there have been several studies on rhodium acetylide complexes bearing PMe<sub>3</sub> as coligands.<sup>15</sup> Hence, we expected [(Me<sub>3</sub>P)<sub>3</sub>RhCl] (**10**) to be a suitable precursor for the synthesis of the first iminoboryl complex of a group 9 metal.

One hour after addition of 1.5 equiv of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub> to a solution of **10** in C<sub>6</sub>D<sub>6</sub>, the <sup>31</sup>P NMR spectrum of the reaction mixture shows predominant formation of one new product displaying two resonances at 1.6 (dt, <sup>1</sup>J<sub>P–Rh</sub> = 126 Hz, <sup>3</sup>J<sub>P–P</sub> = 27 Hz, P–Rh–Br) and –13.9 ppm (dd, <sup>1</sup>J<sub>P–Rh</sub> = 89 Hz, <sup>3</sup>J<sub>P–P</sub> = 27 Hz, P–Rh–P) indicating the presence of three phosphorus

(14) (a) Burgess, K.; Van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350–9359. (b) Dai, C.; Stringer, G.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Inorg. Chem.* **1997**, *36*, 272–273. (c) Souza, F. E. S.; Nguyen, P.; Marder, T. B.; Scott, A. J.; Clegg, W. *Inorg. Chim. Acta* **2005**, *358*, 1501–1509.

**Scheme 2.** Synthesis of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡N/Bu)] (9)**Scheme 3.** Synthesis of *cis,mer*-[(Br)<sub>2</sub>(Me<sub>3</sub>P)<sub>3</sub>Rh(B≡NSiMe<sub>3</sub>)] (11)**Figure 2.** Molecular structure of *cis,mer*-[(Br)<sub>2</sub>(Me<sub>3</sub>P)<sub>3</sub>Rh(B≡NSiMe<sub>3</sub>)] (11). Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms and carbon atoms of the methyl groups are omitted for clarity.

nuclei, which are distributed over two chemically nonequivalent sites. Apart from the signal of the starting material at 31.3 ppm, the <sup>11</sup>B NMR spectrum displays two new sharp signals at 36.6 and 34.5 ppm, the former being identified as Cl<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub>.<sup>16</sup> Obviously, a halogen exchange occurs between the rhodium chloro complex and the bromoborane, as observed in previous cases,<sup>14c</sup> and hence, the latter signal can be tentatively assigned to the mixed aminodihaloborane Cl(Br)B=N(SiMe<sub>3</sub>)<sub>2</sub>. Besides these three signals, the <sup>11</sup>B NMR spectrum also displays a broad resonance at 27.0 ppm. Those spectroscopic data indicate the formation of the rhodium iminoboryl complex *cis,mer*-[(Br)<sub>2</sub>(Me<sub>3</sub>P)<sub>3</sub>Rh(B≡NSiMe<sub>3</sub>)] (11) (Scheme 3).

The molecular structure obtained by an X-ray diffraction study on suitable single crystals, grown from a mixture of benzene and hexane at ambient temperature by allowing the solvent mixture to evaporate, unequivocally affirms the proposed constitution (Figure 2). Different from most rhodium(III) boryl complexes, which were prepared by B–B or B–H bond oxidative addition to the Wilkinson complex [(Ph<sub>3</sub>P)<sub>3</sub>RhCl],<sup>8a,14a</sup> oxidative addition of a B–Br bond to the rhodium fragment utilized here furnishes a six-coordinate complex, presumably due to the sterically less demanding trimethylphosphine ligands. A similar, slightly distorted octahedral geometry, however, was observed for the related boryl complexes *cis,mer*-[Cl<sub>2</sub>(Me<sub>3</sub>P)<sub>3</sub>Rh(Bcat)] (12; cat = O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) and *fac*-[(Me<sub>3</sub>P)<sub>3</sub>Rh(Bcat)<sub>3</sub>]<sup>14b,c</sup> which also contain sterically less demanding PMe<sub>3</sub> coligands. Both species 11 and 12 display a mutually trans disposition of the boron-centered ligand and the weak σ-donor halide, as expected due to the strong trans influence of the former.<sup>10i,13</sup> However, comparison of the rhodium-halogen bond lengths within the respective complexes again reveals the lesser trans influence of the iminoboryl ligand as opposed to boryl ligands with a three-coordinate boron atom. While the two different rhodium-chloride bonds in the catecholboryl complex 12 differ

by more than 0.12 Å, the iminoboryl complex 11 only displays a difference of about 0.04 Å of the corresponding Rh–Br separations. As described for 7, the iminoboryl ligand is coordinated terminally to the metal fragment (Rh–B–N: 177.0(5)°) and only slightly deviates from linearity (B–N–Si: 159.5(5)°). The B–N distance of 1.255(7) Å justifies the formulation of a B≡N triple bond. The most characteristic NMR data for the aforementioned iminoboryl complexes are summarized in Table 1. Structural parameters for the iminoboryl complexes, which have been reliably structurally characterized, are summarized in Table 2.

**Reactivity of Iminoboryl Complexes.** All aforementioned transition-metal iminoboryl complexes display a considerably increased stability against oligomerization. In contrast, most main group substituted iminoboranes tend to cyclooligomerize spontaneously even at ambient temperature giving either borazines,<sup>6,17</sup> or, somewhat less commonly, 1,3,2,4-diazadiboretidienes.<sup>18</sup> In some cases, oligomerization can be discouraged by side-on coordination of the B≡N triple bond to metal centers.<sup>19</sup> The dominating strategy to prevent oligomerization, however, is to employ sterically demanding substituents on either side of the triple bond. Furthermore, iminoboranes can

- (15) (a) Marder, T. B.; Zargarian, D.; Calabrese, J. C.; Herskovitz, T.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1484–1485. (b) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540–544. (c) Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1545–1547. (d) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187–188. (e) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188–190. (f) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1992**, 424, 87–97. (g) Rourke, J. P.; Bruce, D. W.; Marder, T. B. *J. Chem. Soc., Dalton Trans.* **1995**, 317–318. (h) Rourke, J. P.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **2001**, 2626–2627. (i) Rourke, J. P.; Stringer, G.; Chow, P.; Deeth, R. J.; Yufit, D. S.; Howard, J. A. K.; Marder, T. B. *Organometallics*, **2002**, 21, 429–437. (j) Zhu, X.; Ward, R. M.; Albesa-Jové, D.; Howard, J. A. K.; Porrès, L.; Beeby, A.; Low, P. J.; Wong, W.-K.; Marder, T. B. *Inorg. Chim. Acta* **2006**, 359, 2859–2863.
- (16) Haubold, W.; Kraatz, U. *Z. Anorg. Allg. Chem.* **1976**, 421, 105–110.
- (17) (a) Paetzold, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, 93–94, 39–50. (b) Münster, J.; Paetzold, P.; Schröder, E.; Schwan, H.; Bennigsen-Mackiewicz, T. *Z. Anorg. Allg. Chem.* **2004**, 630, 2641–2651.
- (18) (a) Delpy, K.; Schmitz, D.; Paetzold, P. *Chem. Ber.* **1983**, 116, 2994–2999. (b) Paetzold, P.; Delpy, K.; Boese, R. *Z. Naturforsch. B* **1988**, 43, 839–845.
- (19) (a) Männig, D.; Nöth, H.; Schwartz, M.; Weber, S.; Wietelmann, U. *Angew. Chem.* **1985**, 97, 979–980; *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 998–999. (b) Paetzold, P.; Delpy, K. *Chem. Ber.* **1985**, 118, 2552–2553. (c) Bulak, E.; Herberich, G. E.; Manners, I.; Mayer, H.; Paetzold, P. *Angew. Chem.* **1988**, 100, 964965; *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 958–959. (d) Bulak, E.; Paetzold, P. *Z. Anorg. Allg. Chem.* **2000**, 626, 1277–1278.

**Table 1.** NMR Data of Iminoboryl Complexes and Their Derivatives, Respectively

compound	$\delta(^{11}\text{B})$ [ppm]	$\delta(^{31}\text{P})$ [ppm]	$^1J_{\text{M-P}}$ [Hz]
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pd(B≡NSiMe <sub>3</sub> )] (1)	22.0	34.3	-
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt(B≡NSiMe <sub>3</sub> )] (2)	25.9	31.2	2389
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{BN(SiMe <sub>3</sub> )(AlCl <sub>3</sub> )}] (3)	45.6	31.2	2135
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{B(OMe)(N(H)SiMe <sub>3</sub> )}] (4)	30.3	25.4	2923
<i>trans</i> -[(iPr <sub>3</sub> P) <sub>2</sub> (Br)Pt(B≡NSiMe <sub>3</sub> )] (7)	16.9	42.7	2412
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt(B≡NiBu)] (9)	not observed	31.5	2427
<i>cis,mer</i> -[(Br) <sub>2</sub> (Me <sub>3</sub> P) <sub>3</sub> Rh(B≡NSiMe <sub>3</sub> )] (11)	27.0	1.6, -13.9	126, 89
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{B(OH)(N(H)SiMe <sub>3</sub> )}] (13)	32.5	25.7	2894
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{B(N(H)Ph)(N(H)SiMe <sub>3</sub> )}] (14)	31.7	21.3	2907
1,4- <i>trans</i> -[[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{B(NH <i>i</i> Bu)NH}] <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] (15)	not observed	21.5	2957
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> Pt(B≡NSiMe <sub>3</sub> )(C≡CPh)] (16)	not observed	30.3	2397

**Table 2.** Selected Bond Lengths [Å] and Angles [deg] of the Iminoboryl Complexes

compound	B–N	M–B	M–Br	M–B–N	B–N–Si
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pd(B≡NSiMe <sub>3</sub> )] (1)	1.251(4), 1.262(3)	1.958(3), 1.967(3)	2.5531(5), 2.5224(5)	176.1(3), 178.3(2)	163.1(3), 166.1(2)
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt(B≡NSiMe <sub>3</sub> )] (2)	1.260(4)	1.960(3)	2.5516(4)	178.8(3)	173.3(3)
<i>trans</i> -[(iPr <sub>3</sub> P) <sub>2</sub> (Br)Pt(B≡NSiMe <sub>3</sub> )] (7)	1.265(7)	1.959(3)	2.5439(2)	177.9(6)	175.6(9)
<i>cis,mer</i> -[(Br) <sub>2</sub> (Me <sub>3</sub> P) <sub>3</sub> Rh(B≡NSiMe <sub>3</sub> )] (11)	1.255(7)	1.956(6)	2.6226(5), 2.5861(5)	177.0(5)	159.5(5)

be stabilized by a  $\pi$ -electron-donating amino group at boron, which provides an additional reactivity pattern. Thus, amino(imino)boranes react with heavier group 13 element halides by formation of Lewis acid–base adducts upon coordination of the imino nitrogen to the aluminum center.<sup>20</sup> Preliminary reactivity studies on iminoboryl complexes provided a corresponding AlCl<sub>3</sub> adduct, *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{BN(SiMe<sub>3</sub>)(AlCl<sub>3</sub>)}] (3), indicating a certain similarity of iminoboryl complexes and amino(imino)boranes.<sup>11</sup> However, usually reagents affect both sides of the B≡N triple bond, and [2 + *n*] cycloadditions<sup>5,6,21</sup> as well as 1,2-additions of dipolar reagents<sup>5,6</sup> represent the most common reactivity patterns of iminoboranes. Examples thereof are plentiful and the aforementioned reviews by Paetzold<sup>6</sup> and Nöth<sup>5</sup> provide a comprehensive overview of this chemistry.

Reactivity toward protic reagents claims an exceptionally large section in the chemistry of the B≡N triple bond. Hence, iminoboranes were reacted with a wide variety of Brønsted acids, affording the products of 1,2-dipolar addition of the element-hydrogen bond. In this way, both strong acids, such as hydrogen chloride,<sup>22a</sup> triflic acid<sup>22b</sup> as well as carbon acids,<sup>22c</sup> and weaker Brønsted acids such as alcohols and amines, were added to the B≡N triple bond.<sup>22a,c</sup> In the latter case, the relative rate of addition was found to be governed primarily by steric factors.<sup>22c</sup>

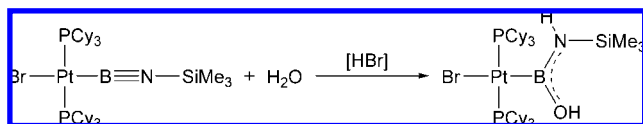
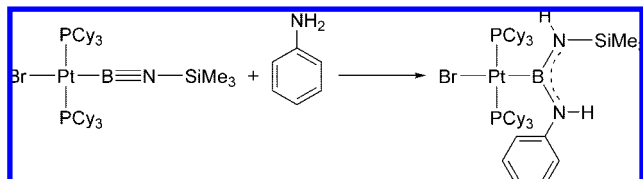
Transition metal complexes containing boron centered ligands are usually very sensitive under protic conditions and react with cleavage of the metal–boron bond. Noteworthy exceptions are the bridged chloroborylene complex [( $\mu$ -BCl){( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)-Mn(CO)<sub>2</sub>}]<sub>2</sub>, which by treatment with water and alcohols can be converted in the corresponding hydroxo- and alkoxoborylene complexes<sup>23a</sup> and the dichloroboryl complex [Os(BCl<sub>2</sub>)-Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] that additionally allows replacement of the chlorine substituents at boron by aminolysis.<sup>23b–d</sup> Given the pronounced reactivity of most metal–boron linkages toward protic reagents, platinum iminoboryl complexes, which in

comparison to their palladium and rhodium counterparts, are expected to show the least labile metal–boron bond,<sup>24</sup> were chosen for aminolysis studies. Interestingly though, neither the sterically considerably hindered amines HNR<sub>2</sub> (R = SiMe<sub>3</sub>, *i*Pr), nor the primary butylamine affected the B≡N triple bond of 2. The NMR spectra of equimolar solutions of 2 and the corresponding amine in toluene did not show any signals that might indicate the formation of a corresponding boryl complex, even after heating for 5 h at 80 °C.

Subsequently, reactivity of 2 toward water was studied, but neither addition of water to solid 2 nor to its benzene solution caused any reaction, as determined by multinuclear NMR spectroscopy. Addition of aqueous hydrogen bromide to a benzene solution of 2, however, gave rise to one new set of signals in the NMR spectra, which is in agreement with the formation of a platinum boryl complex. The <sup>31</sup>P NMR spectrum shows a singlet at 25.7 ppm, which together with the coupling constant <sup>1</sup>J<sub>Pt–P</sub> = 2894 Hz, is characteristic for trans platinum boryl complexes,<sup>10a,1</sup> and in excellent agreement with the signal observed for the methoxyboryl complex *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)-Pt{B(OMe)(N(H)SiMe<sub>3</sub>)}] (4) (25.4 ppm, <sup>1</sup>J<sub>Pt–P</sub> = 2923 Hz).<sup>11</sup> Likewise, the <sup>11</sup>B NMR signal of the new compound at 32.5 ppm closely resembles that of 4 (30.3 ppm), and is thus slightly downfield shifted with respect to the starting material 2 (25.9 ppm). Furthermore, the <sup>1</sup>H NMR spectrum displays a signal at 3.77 ppm with an integration of 1 with respect to the cyclohexyl (66) and the trimethylsilyl protons (9) and a <sup>4</sup>J-coupling of 3 Hz to the proton (also integrating to 1) observed at 2.60 ppm,

- (20) (a) Nöth, H.; Weber, S. *Chem. Ber.* **1985**, *118*, 2554–2556. (b) Böck, B.; Braun, U.; Habereeder, T.; Mayer, P.; Nöth, H. *Z. Naturforsch. B* **2004**, *59*, 681–684.  
 (21) (a) Paetzold, P.; Delpy, K.; Hughes, R. P.; Herrmann, W. A. *Chem. Ber.* **1985**, *118*, 1724–1725. (b) Paetzold, P.; Hahnfeld, D.; Englert, U.; Wojnowski, W.; Dreczewski, B.; Pawelec, Z.; Walz, L. *Chem. Ber.* **1992**, *125*, 1073–1078.

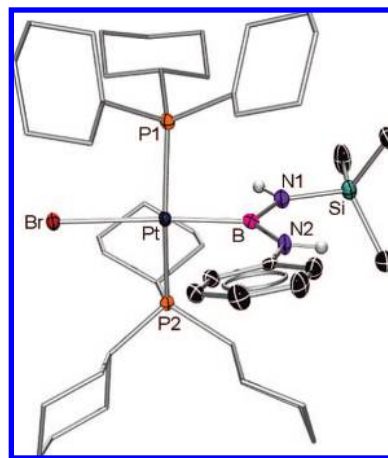
- (22) (a) Paetzold, P.; von Platho, C.; Schwan, H.; Meier, H. U. *Z. Naturforsch. B* **1984**, *39*, 610–614. (b) Nöth, H.; Weber, S. *Chem. Ber.* **1985**, *118*, 2144–2146. (c) Brandl, A.; Nöth, H. *Chem. Ber.* **1985**, *118*, 3759–3770.  
 (23) (a) Braunschweig, H.; Müller, M. *Chem. Ber.* **1997**, *130*, 1295–1298. (b) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem.* **2000**, *112*, 978980; *Angew. Chem., Int. Ed.* **2000**, *39*, 948–950. (c) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 4862–4872. (d) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2003**, *680*, 81–88.  
 (24) (a) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742–751. (b) Sakaki, S.; Kai, S.; Sugimoto, M. *Organometallics* **1999**, *18*, 4825–4837.  
 (25) (a) Ha, T. B. T.; Souchard, J. P.; Wimmer, F. L.; Johnson, N. P. *Polyhedron* **1990**, *9*, 2647–2649. (b) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434.

**Scheme 4.** Synthesis of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(OH)(N(H)SiMe<sub>3</sub>)}] (**13**)**Scheme 5.** Synthesis of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(N(H)Ph)(N(H)-SiMe<sub>3</sub>)}] (**14**)

which by <sup>15</sup>N, <sup>1</sup>H NMR correlation spectroscopy was proven to be bound to nitrogen. Additionally, these two signals display platinum satellites with coupling constants of 40 and 38 Hz, respectively, similar to those observed for bis(pyridine) platinum(II) complexes (29–43 Hz) and hence, indicate a <sup>3</sup>J<sub>Pt–H</sub> coupling.<sup>25a</sup> The NMR spectroscopic data for the product are consistent with the formation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(OH)(N(H)SiMe<sub>3</sub>)}] (**13**) obtained by acid-catalyzed 1,2-dipolar addition of water to the B≡N triple bond (Scheme 4).<sup>26</sup> The product could be isolated in almost quantitative yields, once more demonstrating the clean reactivity of iminoboryl complex **2**, even toward strong protic reagents. At this point, it should be explicitly noted that, in benzene solution, compound **13** is actually stable in the presence of dilute hydrobromic acid.

In contrast to the above-mentioned aliphatic amines, aniline easily adds to the B≡N triple bond of **2**. After 5 hours at ambient temperature, multinuclear NMR spectroscopy revealed the complete consumption of **2** and clean formation of the bis(amino)boryl complex *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(N(H)Ph)(N(H)-SiMe<sub>3</sub>)}] (**14**, Scheme 5). Again, the <sup>31</sup>P NMR (21.3 ppm, <sup>1</sup>J<sub>Pt–P</sub> = 2907 Hz) and the <sup>11</sup>B NMR spectra (31.7 ppm) show signals typical of boryl complexes. The <sup>1</sup>H NMR spectrum exhibits five signals for the aromatic protons, revealing their inequivalence in solution and hence the hindered rotation of the phenyl group. The signals at 5.38 and 2.91 ppm could be assigned to protons being linked to two chemically nonequivalent nitrogen atoms by <sup>15</sup>N, <sup>1</sup>H correlation NMR spectroscopy. The latter exhibits not only a chemical shift, but also a <sup>3</sup>J<sub>Pt–H</sub> coupling constant (38 Hz) very similar to **13** and thereby, considerably distinguishes itself from the former signal, which therefore was ascribed to the proton in the immediate vicinity of the phenyl group. This signal appears at a pronounced downfield shift with respect to “classical” amines, but is almost identical to the one observed for borazine [HB–NH]<sub>3</sub>, whose aminic proton gives rise to a signal at 5.54 ppm.<sup>25b</sup> At first glance, the platinum–proton coupling constant of 54 Hz, too, appears to be quite large. This observation, however, might be explained by a *trans* orientation of the corresponding proton with respect to the platinum atom, which was verified in the solid-state structure.

Single crystals suitable for an X-ray study were grown from a mixture of dichloromethane and hexane via diffusion at room temperature. The molecular structure of **14** is displayed in Figure 3. As observed for the methoxyboryl complex **4**, addition of the element–hydrogen bond causes an elongation of the boron–nitrogen distance from 1.260(4) (**2**)<sup>9</sup> to 1.444(5) Å, indicating the decrease in the bond order. Both boron–nitrogen



**Figure 3.** Molecular structure of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(N(H)Ph)(N(H)-SiMe<sub>3</sub>)}] (**14**)·CH<sub>2</sub>Cl<sub>2</sub>. Thermal ellipsoids are displayed at the 50% probability level. Solvent molecule, nonaminic hydrogen atoms, and carbon atoms of the cyclohexyl groups are omitted for clarity.

bond lengths are statistically indistinguishable (B–N2, 1.435(6) Å) and therefore the nitrogen atoms should contribute in equal measure to the compensation of electron deficiency at boron,<sup>27</sup> which is enabled by an almost planar geometry of the boryl moiety (Si–N1–B–N2, 0.0(6)°; C–N2–B–N1, 171.1(4)°). As usual for this type of complexes, the boryl ligand is oriented almost perpendicular to the phosphorus–platinum–phosphorus axis and the platinum–boron bond length of 2.048(4) Å, is indeed typical for platinum(II) boryl complexes (1.963(6)–2.090(3) Å).<sup>10a,i</sup> However, compound **14** displays a platinum–bromine distance of 2.6579(4) Å, which, to our knowledge, is the longest platinum–bromine bond reported for a boryl complex (2.5617(10)–2.6454(4) Å).<sup>10i</sup> This particular boryl ligand obviously excels by a markedly strong *trans* influence.

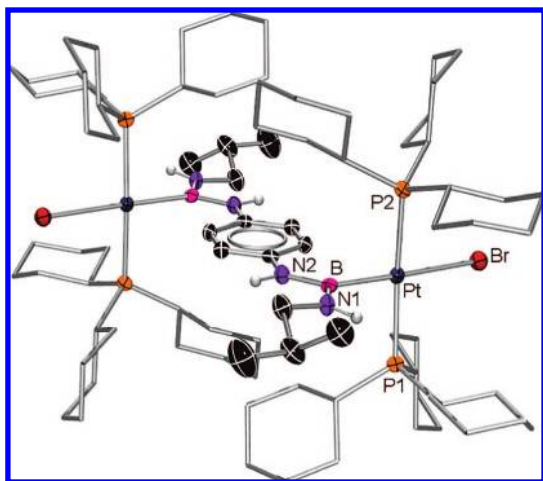
Addition of protic reagents to iminoboryl ligands provides facile access to transition metal complexes bearing a mixed boryl ligand, which are rare and otherwise demand significant experimental effort. Employment of bifunctional Brønsted acids additionally allows the synthesis of dinuclear transition-metal complexes bridged by a bidentate boryl ligand. This ligand type was previously almost unknown, although corresponding dinuclear boryl complexes provide an interesting case for analyzing the metal–boryl linkage and might serve as model substances for transition-metal containing  $\pi$ -conjugated polymers, as was claimed in case of the boryl-bridged iron complexes [( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>BO<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>] and *spiro*-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>BO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>C.<sup>28</sup>

As was determined by multinuclear NMR spectroscopy, reaction of **2** with *p*-phenylenediamine not only proceeds very slowly and cannot be accelerated notably by heating the reaction mixture, but also yields a mixture of products, which could not be separated by fractional crystallization. Using the sterically less hindered complex *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B≡NiBu}] (**9**) in

(26) It should be noted that electrophilic attack at the beta carbon of metal acetylides is well known (analogous to the attack by electrophiles at the nitrogen atom of the iminoboryls) as discussed in detail in the following: Kostnic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974–982.

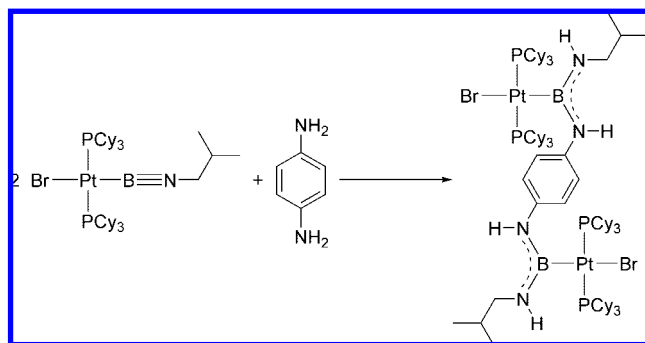
(27) Kroner, J.; Nöth, H.; Polborn, K.; Stolpmann, H.; Tacke, M.; Thomann, M. *Chem. Ber* **1993**, *126*, 1995–2002.

(28) 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. *J. Chem. Soc., Dalton Trans.* **2002**, 2020–2026.



**Figure 4.** Molecular structure of 1,4-*trans*-[ $\{(\text{C}_6\text{H}_{11})_3\text{P}\}_2(\text{Br})\text{Pt}(\text{B}\{\text{NH}i\text{Bu}\}\text{NH})\}_2\text{C}_6\text{H}_4]$  (**15**)·6CH<sub>2</sub>Cl<sub>2</sub>. Thermal ellipsoids are displayed at the 50% probability level. Solvent molecules, nonaminic hydrogen atoms, and carbon atoms of the cyclohexyl groups are omitted for clarity.

**Scheme 6.** Synthesis of 1,4-*trans*-[ $\{(\text{C}_6\text{H}_{11})_3\text{P}\}_2(\text{Br})\text{Pt}(\text{B}\{\text{NH}i\text{Bu}\}\text{NH})\}_2\text{C}_6\text{H}_4]$  (**15**)



place of iminoboryl complex **2** leads both to an appreciably increased reaction rate and almost clean formation of a single product. Addition of *p*-phenylenediamine to a solution of **9** in dichloromethane thus causes slow precipitation of a colorless, highly crystalline solid which, by X-ray diffraction, was identified as 1,4-*trans*-[ $\{(\text{C}_6\text{H}_{11})_3\text{P}\}_2(\text{Br})\text{Pt}(\text{B}\{\text{NH}i\text{Bu}\}\text{NH})\}_2\text{C}_6\text{H}_4]$  (**15**), whose centrosymmetric molecular structure is displayed in Figure 4. The relevant geometric parameters for **15** are statistically identical to those of **14**, except for the platinum–bromine distance, which in **15** amounts to 2.6306(6) Å and, therefore, is slightly shorter than that in **14**. Compound **15** possesses a markedly low solubility in most organic solvents as well as in water. Only in tetrahydrofuran-*d*<sub>8</sub> could a concentration sufficient for NMR spectroscopy be achieved. Owing to the low solubility of dinuclear **15**, few spectroscopic features, observable for the mononuclear complex **14**, could not be detected. Nevertheless, excellent agreement of the spectral data with those of **14**, leaves no doubt in almost clean formation of **15** stemming from 1,2-dipolar addition of *p*-phenylenediamine to the B≡N triple bond of **9** (Scheme 6).

NMR data for the derivatives of complexes **2** and **9**, respectively, are compared to those of the iminoboryl complexes in Table 1. Structural parameters of derivatives are summarized in Table 3.

The fact that Lewis basic solvents (e.g., tertiary amines and tetrahydrofuran) do not influence the <sup>11</sup>B NMR shifts of iminoboranes suggests that most additions to the B≡N triple

bond proceed via electrophilic attack at the imino nitrogen or incorporate a cyclic transition state.<sup>6</sup> An example, where nucleophilic attack at boron should be the initiating step, is the addition of highly nucleophilic organyl anions. In the case of main group substituted iminoboranes, this attack can neither be prevented by sterically demanding *tert*-butyl groups nor by the electronically stabilizing *tert*-butyl(trimethylsilyl)amino substituent linked to boron.<sup>29</sup> Therefore, we decided to investigate, whether the stabilization of the B≡N triple bond in the platinum iminoboryl complex **2** is sufficient to substitute the bromide by an acetylide ligand without attacking the boron center, thus leading to an interesting platinum complex, exhibiting both a C≡C and an isoelectronic B≡N moiety terminally coordinated to the metal center.<sup>30</sup>

Addition of equimolar amounts of sodium(phenylacetylide) to a solution of **2** in tetrahydrofuran causes only minor changes in the phosphorus NMR spectrum. The new singlet at 30.3 ppm appears slightly shifted to highfield with respect to the starting material (31.2 ppm). The platinum–phosphorus coupling constant of 2397 Hz, being almost identical to the one observed for **2** (2389 Hz), indicates the iminoboryl ligand to be unchanged. Further NMR spectroscopic data, also, are in full agreement with the formation of the platinum complex *trans*-[ $\{(\text{C}_6\text{H}_{11})_3\text{P}\}_2\text{Pt}(\text{B}\equiv\text{NSiMe}_3)(\text{C}\equiv\text{CPh})]$  (**16**) obtained via bromide substitution by the phenylacetylide (Scheme 7), even though no signals could be observed for the boron and the carbon atoms linked directly to the platinum center. This phenomenon has already been observed and probably is due to unresolved coupling to the platinum and phosphorus nuclei.<sup>10h,31</sup>

The crystallographic investigation of **16** was quite challenging. Crystals were grown from different solvents and solvent mixtures (hexane, pentane, DCM, and toluene). The crystals obtained adopted two different space groups, and the crystals contain solvent accessible voids of ~190 Å<sup>3</sup>, with ranges of slightly varying unit cell parameters. None of the data sets showed indication of twinning. In all cases there were no difficulties with solving the structures; however, all of them showed high residual peaks in close proximity (~0.7–0.9 Å) to a C≡C bond (+5 e<sup>-</sup> in comparison to -1.4 e<sup>-</sup> for the deepest hole), and the bond itself was found to be too short (~1 Å). It appeared that all crystals contained small amounts of a second component, where the main domain (86–92%) was that of compound **16** and the remaining part was compound **2**. Inclusion of the Br-atom in refinement improved the residual electron density (±1.2 e<sup>-</sup>), but the close proximity of a heavy element to the C≡C bond makes the description of this part of the structure imprecise. Therefore, the connectivity of compound **16** can be confirmed (Figure 5) but a detailed analysis of the structural parameters of **16** would be misleading.

## Conclusion

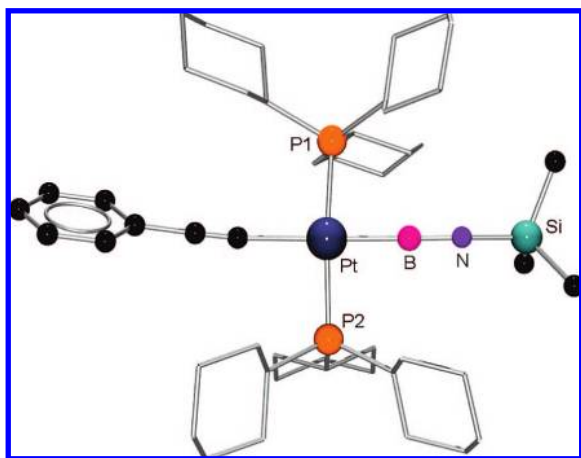
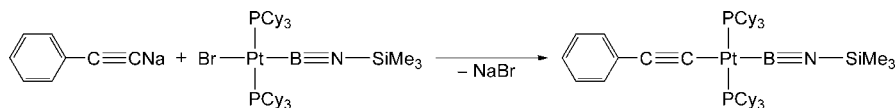
In the present paper we reported an experimental study on iminoboryl complexes targeting, in particular, a systematic variation of these compounds with respect to (i) the central metal, (ii) the metal-bound coligands, and (iii) the steric requirements of the N-R moiety. Thus, a variety of unprecedented species was obtained and fully characterized, including

- (29) Paetzold, P.; Pelzer, C.; Boese, R. *Chem. Ber.* **1988**, *121*, 51–59.  
 (30) For unsymmetric platinum bis(acetylide)s see: Nguyen, P.; Lesley, G.; Marder, T. B.; Ledoux, I.; Zyss, J. *Chem. Mater.* **1997**, *9*, 406–408.  
 (31) Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **1995**, *117*, 4403–4404.



**Table 3.** Selected Bond Lengths [Å] of the Derivatives of **2** and **9**, Respectively

Compound	B–N1	B–N2	Pt–B	Pt–Br
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{BN(SiMe <sub>3</sub> )(AlCl <sub>3</sub> )}] ( <b>3</b> )	1.330(3)		1.904(3)	2.5280(2)
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{B(OMe)(N(H)SiMe <sub>3</sub> )}] ( <b>4</b> )	1.432(3)		2.053(2)	2.6351(2)
<i>trans</i> -[(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt{B(N(H)Ph)(N(H)SiMe <sub>3</sub> )}] ( <b>14</b> )	1.444(5)	1.435(6)	2.048(4)	2.6579(4)
1,4- <i>trans</i> -[{(Cy <sub>3</sub> P) <sub>2</sub> (Br)Pt(B{NH <i>i</i> Bu}NH)} <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] ( <b>15</b> )	1.429(7)	1.436(7)	2.048 (6)	2.6306(6)

**Scheme 7.** Synthesis of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt(B≡NSiMe<sub>3</sub>)(C≡CPh)] (**16**).**Figure 5.** Molecular structure of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt(B≡NSiMe<sub>3</sub>)(C≡CPh)] (**16**)·0.5C<sub>6</sub>H<sub>14</sub>. Solvent molecule, hydrogen atoms, and carbon atoms of the cyclohexyl groups are omitted for clarity.

for example, the first rhodium iminoboryl complex *cis,mer*-[(Br)<sub>2</sub>(Me<sub>3</sub>P)<sub>3</sub>Rh(B≡NSiMe<sub>3</sub>)] (**11**), which was fully characterized in solution and in the crystalline state. Subsequent reactivity studies were undertaken, revealing that novel reactivity patterns for these species are enabled by the combination of sterically less demanding iminogroups with Pt–B linkages of increased stability, thus yielding, for example, the unusual dinuclear species 1,4-*trans*-[{(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt(B{NH*i*Bu}NH)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (**15**) and the complex *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt(B≡NSiMe<sub>3</sub>)(C≡CPh)] (**16**), in which, for the first time, the two isoelectronic ligand species RN≡B and RC≡C are bound to the same metal center.

## Experimental Details

**General Considerations.** All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk-line or glovebox techniques. Benzene and tetrahydrofuran were dried by distillation over potassium and sodium/potassium alloy, respectively, and were stored then under argon over activated molecular sieves. Dichloromethane and hexane were purified and dried using an M. Braun Solvent Purification System and then stored over activated molecular sieves. C<sub>6</sub>D<sub>6</sub>, tetrahydrofuran-D<sub>8</sub> and CD<sub>2</sub>Cl<sub>2</sub> were dried over molecular sieves and degassed by three freeze–pump–thaw cycles before use. Photolysis experiments were performed with a LOT-Oriel photolysis apparatus with a 500 W Hg(Xe) lamp. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer. <sup>15</sup>N, <sup>1</sup>H COSY spectra were recorded on a DRX 300 spectrometer. Routine NMR spectra were recorded on a Bruker Avance 200 spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to external tetramethylsilane via the residual protio solvent (<sup>1</sup>H) or the solvent itself (<sup>13</sup>C). <sup>11</sup>B{<sup>1</sup>H} 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 to 85%

H<sub>3</sub>PO<sub>4</sub>. Microanalyses were performed either on a Leco CHNS-932 or an Elemental vario MICRO-cube elemental analyzer. [Pt(P*i*Pr<sub>3</sub>)<sub>3</sub>] (**5**),<sup>32</sup> [Pt(PCy<sub>3</sub>)<sub>2</sub>],<sup>33</sup> [(Me<sub>3</sub>P)<sub>3</sub>RhCl] (**10**),<sup>34</sup> *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡NSiMe<sub>3</sub>)] (**2**),<sup>9</sup> Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub>,<sup>16</sup> Br<sub>2</sub>B=N(*i*Bu)(SiMe<sub>3</sub>)<sup>35</sup> and NaC≡CPh<sup>36</sup> were prepared according to published literature procedures. All other compounds were purchased from commercial sources and used as supplied.

**Preparation of *trans*-[(*i*Pr<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡NSiMe<sub>3</sub>)] (**7**).** A solution of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub> (64.4 mg, 0.195 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added to [Pt(P*i*Pr<sub>3</sub>)<sub>3</sub>] (**5**) (130.8 mg, 0.194 mmol). After 2 d at ambient temperature, all volatile components were removed in vacuo, and the residue was dissolved in hexane. The pale yellow solution was stored at –35 °C. During 4 d a pale-yellow crystalline solid precipitated, and was isolated via decantation of the supernatant solution (99.0 mg, 73%). Analogous recrystallization gave single crystals suitable for an X-ray diffraction study. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): δ = 3.04 (m, 6H, H1, *iPr*), 1.27 (dvt, <sup>3</sup>J<sub>H–H</sub> = 7.3 Hz, N = <sup>1</sup>J<sub>P–H</sub> + <sup>5</sup>J<sub>P–H</sub> = 14.4 Hz, 36H, H2, *iPr*), 0.25 (s, 9H, SiMe<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): δ = 16.9 (br s); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): δ = 25.4 (vt, N = <sup>1</sup>J<sub>P–C</sub> + <sup>3</sup>J<sub>P–C</sub> = 30 Hz, <sup>2</sup>J<sub>P–C</sub> = 37 Hz, C1, *iPr*), 20.1 (s, <sup>3</sup>J<sub>P–C</sub> = 22 Hz, C2, *iPr*), 2.7 (s, SiMe<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): δ = 42.7 (s, <sup>1</sup>J<sub>Pt–P</sub> = 2412 Hz). Anal. Calcd for C<sub>21</sub>H<sub>51</sub>BBrNP<sub>2</sub>PtSi: C, 36.37; H, 7.41; N, 2.02. Found: C, 36.23; H, 7.13; N, 2.02.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt(B≡N*i*Bu)] (**9**).** A solution of Br<sub>2</sub>B=N(*i*Bu)(SiMe<sub>3</sub>) (97.7 mg, 0.272 mmol) in C<sub>6</sub>D<sub>6</sub> (2 mL) was added to [Pt(PCy<sub>3</sub>)<sub>2</sub>] (200.9 mg, 0.266 mmol). After 4 d at ambient temperature all volatile components were removed in vacuo, and the yellow residue was washed with hexane (3 × 0.2 mL) to obtain a pale yellow, spectroscopically pure powder (133.9 mg, 55%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K): δ = 3.38 (d, <sup>3</sup>J<sub>H–H</sub> = 6.3 Hz, 2H, H<sub>1</sub>, *iBu*), 3.04 (br m, 6H, Cy), 2.21 (br m, 12H, Cy), 1.88 (m, 1H, H<sub>2</sub>, *iBu*), 1.79–1.65 (m, 48H, Cy), 1.10 (d, <sup>3</sup>J<sub>H–H</sub> = 6.7 Hz, 6H, H<sub>3</sub>, *iBu*). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 33.6 (br s); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K): δ = 52.9 (s, C<sub>1</sub>, *iBu*), 35.5 (vt, N = <sup>1</sup>J<sub>P–C</sub> + <sup>3</sup>J<sub>P–C</sub> = 29 Hz, C<sub>1</sub>, Cy), 32.9 (s, C<sub>2</sub>, *iBu*), 31.3 (s, C<sub>3,5</sub>, Cy), 28.5 (vt, N = <sup>1</sup>J<sub>P–C</sub> + <sup>4</sup>J<sub>P–C</sub> = 11 Hz, C<sub>2,6</sub>, Cy), 27.6 (s, C<sub>4</sub>, Cy), 21.3 (s, C<sub>3</sub>, *iBu*). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K): δ = 31.5 (s, <sup>1</sup>J<sub>Pt–P</sub> = 2427 Hz). Anal. Calcd for C<sub>40</sub>H<sub>75</sub>BBrNP<sub>2</sub>Pt: C, 52.35; H, 8.24; N, 1.53. Found: C, 51.99; H, 7.88; N, 1.50.

**Preparation of *cis,mer*-[(Br)<sub>2</sub>(Me<sub>3</sub>P)<sub>3</sub>Rh(B≡NSiMe<sub>3</sub>)] (**11**).** A solution of Br<sub>2</sub>B=N(SiMe<sub>3</sub>)<sub>2</sub> (36.0 mg, 0.110 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL) was added to a solution of [(Me<sub>3</sub>P)<sub>3</sub>RhCl] (**10**) (27.0 mg, 0.074 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL). The red-orange color of

(32) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 107–110.

(33) Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 101–107.

(34) Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1989**, *376*, 407–417.

(35) Synthesis analogous to ref 16, employing HN(*i*Bu)(SiMe<sub>3</sub>) instead of HN(SiMe<sub>3</sub>)<sub>2</sub>.

(36) Teuben, J. H.; Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87–93.

the reaction mixture slowly got more intense. After 1 d the solid components were removed via filtration, and the filtrate was layered with hexane (0.6 mL) immediately causing formation of a powdery precipitate. The supernatant solution was removed by decantation to obtain a beige-colored solid (22.0 mg, 50%). Single crystals were grown from a benzene/hexane mixture by allowing the solvent mixture to evaporate slowly.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 296 K):  $\delta = 1.54$  (vtd,  $N = |^2J_{\text{P-H}} + ^4J_{\text{P-H}} = 7.3$  Hz,  $^3J_{\text{Rh-H}} = 0.7$  Hz, 18H,  $\text{PMe}_3$ ), 1.18 (ddt,  $^2J_{\text{P-H}} = 10.3$  Hz,  $^3J_{\text{Rh-H}} = ^4J_{\text{P-H}} = 0.6$  Hz, 9H,  $\text{PMe}_3$ ), 0.31 (s, 9H,  $\text{SiMe}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ , 296 K):  $\delta = 27.0$  (br s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 20.4$  (dtd,  $^1J_{\text{P-C}} = 35.8$  Hz,  $^4J_{\text{P-C}} = 2.9$  Hz,  $^3J_{\text{Rh-C}} = 1.4$  Hz,  $\text{PMe}_3$ ), 18.1 (vt,  $N = |^1J_{\text{P-C}} + ^3J_{\text{P-C}} = 35.5$  Hz,  $\text{PMe}_3$ ), 3.3 (s,  $\text{SiMe}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 296 K):  $\delta = 1.6$  (dt,  $^1J_{\text{Rh-P}} = 126$  Hz,  $^3J_{\text{P-P}} = 27$  Hz),  $-13.9$  (dd,  $^1J_{\text{Rh-P}} = 89$  Hz,  $^3J_{\text{P-P}} = 27$  Hz). Anal. Calcd for  $\text{C}_{12}\text{H}_{36}\text{NBBr}_2\text{P}_3\text{RhSi}$ : C, 24.47; H, 6.16; N, 2.38. Found: C, 24.38; H, 5.85; N, 2.08.

**Preparation of *trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(OH)(N(H)SiMe $_3$ )}]** (13). Dilute hydrobromic acid (0.05 mL, 0.1M) was added to a solution of *trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(=NSiMe $_3$ )}] (2) (60.0 mg, 0.064 mmol) in benzene (0.6 mL), and the mixture was shook several times within 4 h. Multinuclear NMR control confirmed the complete reaction, and all volatile components were removed in vacuo to obtain a pale-yellow powder (59.1 mg, 97%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 3.77$  (d,  $^4J_{\text{H-H}} = 3$  Hz,  $^3J_{\text{Pt-H}} = 40$  Hz, 1H, OH), 2.87 (br m, 6H, Cy), 2.60 (br d,  $^4J_{\text{H-H}} = 3$  Hz,  $^3J_{\text{Pt-H}} = 38$  Hz, 1H, NH), 2.24–1.23 (m, 60H, Cy), 0.34 (s, 9H,  $\text{SiMe}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 32.5$  (br s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = 35.7$  (vt,  $N = |^1J_{\text{P-C}} + ^3J_{\text{P-C}} = 27$  Hz, C $_1$ , Cy), 31.4 (s, C $_{3,5}$ , Cy), 30.9 (s, C $_{3,5}$ , Cy), 27.9 (vt,  $N = |^2J_{\text{P-C}} + ^4J_{\text{P-C}} = 10$  Hz, C $_{2,6}$ , Cy), 27.2 (s, C $_4$ , Cy), 2.4 (s,  $\text{SiMe}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 25.7$  (s,  $^1J_{\text{Pt-P}} = 2894$  Hz).  $^{15}\text{N}$ ,  $^1\text{H}$  COSY ( $^{15}\text{N}$ : 30 MHz,  $^1\text{H}$ : 300 MHz,  $\text{C}_6\text{D}_6$ , 296 K): cross-peak between  $-291.7$  ( $^{15}\text{N}$ ) and 2.60 ( $^1\text{H}$ ). Anal. Calcd for  $\text{C}_{39}\text{H}_{77}\text{BBrNOPt}_2\text{Si}$ : C, 49.21; H, 8.15; N, 1.47. Found: C, 49.56; H, 8.25; N, 1.57.

**Preparation of *trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(N(H)Ph)(N(H)SiMe $_3$ )}]** (14). A solution of aniline (31.4 mg, 0.3372 mmol) in benzene (1 mL) was added to *trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(=NSiMe $_3$ )}] (2) (100.3 mg, 0.1074 mmol). The reaction mixture was layered with hexane (2 mL) after 6 h, and the solvent mixture was allowed to evaporate slowly. Within 3 d a yellow powder precipitated, which after decanting off the solution was washed twice with hexane (0.2 mL each portion) to obtain a colorless solid (76.2 mg, 69%). Recrystallization from dichloromethane/hexane via diffusion gave single crystals suitable for X-ray diffraction experiments.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 9.78$  (br s, 1H, *ortho*-H, Ph), 7.52 (br s, 1H, *meta*-H, Ph), 7.10 (br s, 1H, *meta*-H, Ph), 6.89 (t,  $^3J_{\text{H-H}} = 7.3$  Hz, 1H, *para*-H, Ph), 6.48 (br s, 1H, *ortho*-H, Ph), 5.38 (s,  $^3J_{\text{Pt-H}} = 53.8$  Hz, 1H, NHPH), 2.91 (s,  $^3J_{\text{Pt-H}} = 37.7$  Hz, 1H, NH( $\text{SiMe}_3$ )), 3.16–1.16 (m, 66H, Cy), 0.28 (s, 9H,  $\text{SiMe}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 31.7$  (br s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 297 K):  $\delta = 147.3$  (s, *ipso*-C, Ph), 128.6 (s, *meta*-C, Ph), 128.4 (s, *meta*-C, Ph), 120.0 (s, *para*-C, Ph), 119.6 (br s, *ortho*-C, Ph), 117.7 (br s, *ortho*-C, Ph), 35.6 (br vt,  $N = |^1J_{\text{P-C}} + ^3J_{\text{P-C}} = 28$  Hz, C $_1$ , Cy), 31.3 (s, C $_{3,5}$ , Cy), 30.1 (s, C $_{3,5}$ , Cy), 28.1 and 28.0 (two overlapping vt,  $N = |^2J_{\text{P-C}} + ^4J_{\text{P-C}} = 9$  Hz, C $_{2,6}$ , Cy), 27.2 (s, C $_4$ , Cy), 2.7 (s,  $\text{SiMe}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = 21.3$  (s,  $^1J_{\text{Pt-P}} = 2907$  Hz).  $^{15}\text{N}$ ,  $^1\text{H}$  COSY ( $^{15}\text{N}$ : 30 MHz,  $^1\text{H}$ : 300 MHz,  $\text{C}_6\text{D}_6$ , 296 K): cross-peaks between 5.38 ( $^1\text{H}$ ) and  $-329.8$  ( $^{15}\text{N}$ ) as well as between 2.91 ( $^1\text{H}$ ) and  $-355.1$  ( $^{15}\text{N}$ ). Anal. Calcd for  $\text{C}_{45}\text{H}_{82}\text{BBrN}_2\text{P}_2\text{Si}$ : C, 52.63; H, 8.05; N, 2.73. Found: C, 52.59; H, 8.10; N, 2.81.

**Preparation of 1,4-*trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(NH*i*Bu)NH)}]- $\text{C}_6\text{H}_4$**  (15). A solution of *p*-phenylenediamine (1.5 mg, 0.014 mmol) in dichloromethane (1.5 mL) was added to *trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(=N*i*Bu)}] (9) (31.9 mg, 0.035 mmol). Within 2

weeks a highly crystalline solid precipitated and was isolated by decanting of the supernatant solution (25.3 mg, 94%).  $^1\text{H}$  NMR (500 MHz, THF- $\text{D}_8$ , 298 K):  $\delta = 9.23$  (d,  $^3J_{\text{H-H}} = 7$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 6.45 (d,  $^3J_{\text{H-H}} = 7$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 5.32 (s, 2H, NHPH), 2.89 (dd,  $^3J_{\text{H-H}} = 6$  Hz,  $^3J_{\text{H-H}} = 6$  Hz, 4H, H $_1$ , *i*Bu), 2.67 (t,  $^3J_{\text{H-H}} = 6$  Hz, 2H, NHPH), 2.70–1.23 (m, 66H, Cy), 1.00 (d,  $^3J_{\text{H-H}} = 7$  Hz, 12H, H $_3$ , *i*Bu), H $_2$  of *i*Bu could not be observed due to the overlapping cyclohexyl signals.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, THF- $\text{d}_8$ , 298 K): no signal observable due to the poor solubility of the compound.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, THF- $\text{d}_8$ , 298 K):  $\delta = 120.0$  (s,  $\text{C}_6\text{H}_4$ , from 2D HSQC), 117.1 (s,  $\text{C}_6\text{H}_4$ , from 2D HSQC), 51.1 (s, C $_1$ , *i*Bu), 36.2 (br s, C $_1$ , Cy), 31.5 (s, C $_2$ , *i*Bu), 30.7 (s, C $_{3,5}$ , Cy), 30.3 (s, C $_{3,5}$ , Cy), 28.7 (vt,  $N = |^2J_{\text{P-C}} + ^4J_{\text{P-C}} = 11$  Hz, C $_{2,6}$ , Cy), 28.5 (vt,  $N = |^2J_{\text{P-C}} + ^4J_{\text{P-C}} = 11$  Hz, C $_{2,6}$ , Cy), 27.8 (s, C $_4$ , Cy), 21.1 (s, C $_3$ , *i*Bu), *ipso*-C of  $\text{C}_6\text{H}_4$  could not be observed due to the poor solubility of the compound.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, THF- $\text{d}_8$ , 298 K):  $\delta = 21.5$  (s,  $^1J_{\text{Pt-P}} = 2957$  Hz). Anal. Calcd for  $\text{C}_{86}\text{H}_{158}\text{B}_2\text{Br}_2\text{N}_4\text{P}_4\text{Pt}_2$ : C, 53.14; H, 8.19; N, 2.88. Found: C, 52.35; H 8.10, N 2.82.

**Preparation of *trans*-[( $\text{C}_3\text{P}$ ) $_2$ Pt{B(=NSiMe $_3$ )(C=CPh)}]** (16). A solution of  $\text{NaC}\equiv\text{CPh}$  (14.0 mg, 0.1128 mmol) in tetrahydrofuran (0.5 mL) was added to a solution of *trans*-[( $\text{C}_3\text{P}$ ) $_2$ (Br)Pt{B(=NSiMe $_3$ )}] (2) (75.0 mg, 0.0803 mmol) in tetrahydrofuran (1 mL) affording a violet precipitate. The reaction mixture was filtered after 16 h and the yellow solution layered with hexane (3 mL). The solvent mixture was allowed to evaporate slowly affording a pale-yellow crystalline solid (40.3 mg, 53%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K):  $\delta = 7.65$  (m, 2H, *ortho*-H, Ph), 7.17 (m, 2H, *meta*-H, Ph), 6.98 (m, 1H, *para*-H, Ph), 2.98 (br m, 6H, Cy), 2.26–1.21 (m, 60H, Cy), 0.42 (s, 9H,  $\text{SiMe}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K) could not be observed due to the unresolved coupling to the platinum and phosphorus nuclei.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta = 130.9$  (s, *ortho*-C, Ph), 128.5 (s, *ipso*-C, Ph), 128.4 (s, *meta*-C, Ph), 125.1 (s, *para*-C, Ph), 114.5 (s, PtC=CPh), 36.2 (vt,  $N = |^1J_{\text{P-C}} + ^3J_{\text{P-C}} = 30$  Hz, C $_1$ , Cy), 30.9 (s, C $_{3,5}$ , Cy), 28.0 (vt,  $N = |^2J_{\text{P-C}} + ^4J_{\text{P-C}} = 11$  Hz, C $_{2,6}$ , Cy), 27.2 (s, C $_4$ , Cy), 3.8 (s,  $\text{SiMe}_3$ ), PtC=CPh could not be observed due to the low solubility and the unresolved coupling to the platinum, phosphorus and boron nuclei.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K):  $\delta = 30.3$  (s,  $^1J_{\text{Pt-P}} = 2397$  Hz). Anal. Calcd for  $\text{C}_{47}\text{H}_{80}\text{BNP}_2\text{PtSi}$ : C, 59.11; H, 8.44; N, 1.47. Found: C, 59.32; H, 8.55; N, 1.47.

**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 K $\alpha$  radiation (7, 14, 15, 16) or on a Bruker D8 APEX I with graphite monochromator (11). The structures were solved using direct methods, refined with the Shelx software package<sup>37</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

**Crystal data for *trans*-[( $\text{iPrP}$ ) $_2$ (Br)Pt{B(=NSiMe $_3$ )}]** (7).  $\text{C}_{21}\text{H}_{51}\text{BBrNP}_2\text{PtSi}$ ,  $M_r = 693.47$ , colorless plate,  $0.25 \times 0.06 \times 0.03$  mm $^3$ , triclinic space group  $P\bar{1}$ ,  $a = 7.9758(3)$  Å,  $b = 10.8093(4)$  Å,  $c = 17.2840(6)$  Å,  $\alpha = 94.350(2)^\circ$ ,  $\beta = 92.124(2)^\circ$ ,  $\gamma = 92.617(2)^\circ$ ,  $V = 1483.03(9)$  Å $^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.553$  g·cm $^{-3}$ ,  $\mu = 6.234$  mm $^{-1}$ ,  $F(000) = 692$ ,  $T = 98(2)$  K,  $R_1 = 0.0183$ ,  $wR_2^2 = 0.0440$ , 5801 independent reflections [ $2\theta \leq 52.12^\circ$ ] and 253 parameters.

**Crystal Data for *cis,mer*-[(Br) $_2$ (Me $_3$ P) $_3$ Rh{B(=NSiMe $_3$ )}]** (11).  $\text{C}_{12}\text{H}_{36}\text{BBR}_2\text{NP}_3\text{RhSi}$ ,  $M_r = 588.96$ , yellow plate,  $0.30 \times 0.20 \times 0.05$  mm $^3$ , monoclinic space group  $P2_1/n$ ,  $a = 9.0559(7)$  Å,  $b = 13.5250(10)$  Å,  $c = 19.8772(15)$  Å,  $\beta = 94.388(2)^\circ$ ,  $V = 2427.4(3)$  Å $^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.612$  g·cm $^{-3}$ ,  $\mu = 4.238$  mm $^{-1}$ ,  $F(000) = 1176$ ,  $T = 193(2)$  K,  $R_1 = 0.0448$ ,  $wR_2^2 = 0.0887$ , 4788 independent reflections [ $2\theta \leq 52.16^\circ$ ] and 190 parameters.

(37) Sheldrick, G. *Acta Crystallogr.* **2008**, *A64*, 112–122.

**Crystal Data for *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B(N(H)Ph)(N(H)-SiMe<sub>3</sub>)}] (14).** C<sub>46</sub>H<sub>84</sub>BBrCl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>PtSi, *M<sub>r</sub>* = 1111.89, colorless plate, 0.30 × 0.20 × 0.03 mm<sup>3</sup>, monoclinic space group *P*2<sub>1</sub>/*n*, *a* = 14.0147(15) Å, *b* = 21.578(2) Å, *c* = 16.6106(18) Å, β = 97.802(6)°, *V* = 4976.7(9) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.484 g·cm<sup>-3</sup>, μ = 3.851 mm<sup>-1</sup>, *F*(000) = 2280, *T* = 100(2) K, *R*<sub>1</sub> = 0.0435, *wR*<sup>2</sup> = 0.0803, 10234 independent reflections [2θ ≤ 52.98°] and 505 parameters.

**Crystal Data for 1,4-*trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(Br)Pt{B{NH*i*Bu}NH)}]<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>] (15).** C<sub>92</sub>H<sub>170</sub>B<sub>2</sub>Br<sub>2</sub>Cl<sub>12</sub>N<sub>4</sub>P<sub>4</sub>Pt<sub>2</sub>, *M<sub>r</sub>* = 2453.22, colorless block, 0.18 × 0.16 × 0.12 mm<sup>3</sup>, monoclinic space group *P*2<sub>1</sub>/*c*, *a* = 18.3001(12) Å, *b* = 17.1048(12) Å, *c* = 19.0262(13) Å, β = 110.753(3)°, *V* = 5569.2(7) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.463 g·cm<sup>-3</sup>, μ = 3.614 mm<sup>-1</sup>, *F*(000) = 2500, *T* = 100(2) K, *R*<sub>1</sub> = 0.0649, *wR*<sup>2</sup> = 0.1143, 13800 independent reflections [2θ ≤ 56.98°] and 590 parameters.

**Crystal Data for *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt{B≡NSiMe<sub>3</sub>}(C≡CPh)] (16).** C<sub>49.84</sub>H<sub>87</sub>BBr<sub>0.08</sub>NP<sub>2</sub>PtSi, *M<sub>r</sub>* = 1002.61, colorless plate, 0.19 × 0.09 × 0.05 mm<sup>3</sup>, triclinic space group *P*1̄, *a* = 10.1668(4) Å, *b* = 10.6685(4) Å, *c* = 22.9023(8) Å, α = 89.324(2)°, β = 89.453(2)°, γ = 83.333(2)°, *V* = 2467.03(16) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.350 g·cm<sup>-3</sup>,

μ = 3.031 mm<sup>-1</sup>, *F*(000) = 1046, *T* = 100(2) K, *R*<sub>1</sub> = 0.0260, *wR*<sup>2</sup> = 0.0604, 10167 independent reflections [2θ ≤ 53.22°] and 515 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 679830–679834. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Acknowledgment.** This work is dedicated to the memory of Dr. Daniela Rais. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. A.S. is grateful to the Fonds der Chemischen Industrie for a Ph.D. fellowship.

**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>.

JA8016889