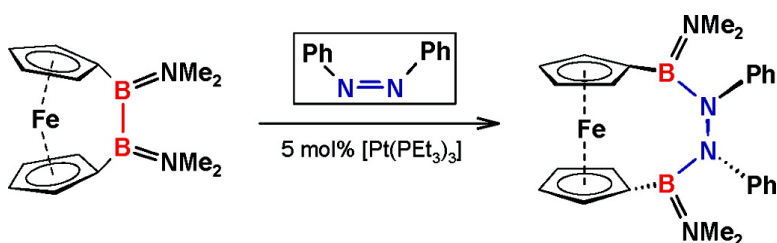


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## Stoichiometric and Homogeneous-Catalytic Diboration of the N=N Double Bond of Azobenzene

Holger Braunschweig\* and Thomas Kupfer

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

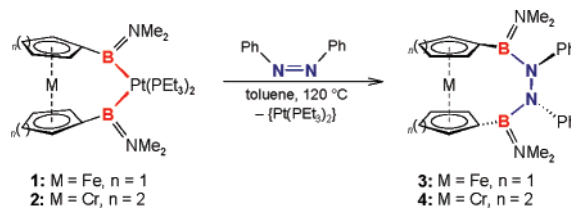
Received January 28, 2008; E-mail: h.braunschweig@mail.uni-wuerzburg.de

Hydroboration<sup>1</sup> and diboration<sup>2</sup> reactions are among the most valuable transformations in organic chemistry and have enabled convenient access to a variety of useful reagents.<sup>3</sup> However, the selective diboration of unsaturated organic substrates that contain elements other than carbon (i.e., substances other than alkenes, alkynes, 1,3-dienes, and  $\alpha,\beta$ -unsaturated ketones) still remains a challenging area of research.<sup>2a</sup> For example, the diboration of the N=N double bond of diimines to yield the well-known class of bis(boryl)hydrazines has only been reported twice and only in the case of species with a highly reactive B–B bond, namely the dichlorodiboranes(4) R(Cl)B–B(Cl)R (R = Mes, NMe<sub>2</sub>)<sup>4</sup> and the azadiboriridine NB<sub>2</sub>Bu<sub>3</sub>.<sup>5</sup> During the past decade, it was impressively demonstrated that the strained character of [n]metalloarenophanes is associated with an enhanced reactivity of either the bond between the carbocyclic ligands and the bridging element(s), that between the bridging elements, or those between the metal and one of the carbocyclic ligands, which facilitated a very interesting insertion and substitution chemistry.<sup>6</sup> Recently, we have shown that the molecular ring strain present in [2]borametalloarenophanes derived from ferrocene and bis(benzene)chromium can be exploited in the selective diboration of alkynes even in the absence of boron bound substituents, commonly increasing the reactivity of diborane(4) precursors. The strained character of these species also offered the possibility for an unprecedented heterogeneous-catalytic diboration reaction.<sup>7</sup> Herein we report on the extension of this reactivity to the diboration of the N=N double bond of azobenzene by [n]metalloarenophanes of iron and chromium. This diboration was accomplished both under stoichiometric and homogeneous catalysis conditions and represents, to the best of our knowledge, the first instance of a metal mediated diboration of a N=N double bond, thus employing less reactive non-halogenated diborane(4) precursors.

The diboration of the N=N double bond was achieved by reaction of the readily accessible [3]diboraplatinametalloarenophanes **1** and **2**<sup>7</sup> with azobenzene at elevated temperature. In a typical experiment, a Schlenk tube equipped with a resealable Teflon valve was charged with the *ansa*-complex and a 4-fold excess of azobenzene in toluene and was heated to 120 °C (Scheme 1). The progress of the reaction was monitored by multinuclear NMR spectroscopy, and the data confirmed the gradual consumption of the starting materials (**1**, **2**) and the almost quantitative formation (>90–95%) of the *ansa*-bis(boryl)hydrazines **3** and **4** over a period of 24 h (**3**) and 48 h (**4**), respectively. After workup and recrystallization from hexanes, the products (**3**, **4**) were isolated as analytically pure, red crystalline solids in yields of 52% and 54%.

The NMR spectroscopic data are in agreement with the anticipated constitution of **3** and **4** in solution and suggest the presence of C<sub>2</sub> symmetric species. Accordingly, two resonances are observed for the aminomethyl groups (**3**:  $\delta$  = 2.49, 2.50; **4**:  $\delta$  = 2.45, 2.46) that feature a noticeable highfield shift in comparison to the starting

**Scheme 1.** Stoichiometric Diboration of Azobenzene To Yield the *ansa*-Bis(boryl)hydrazines **3** and **4**

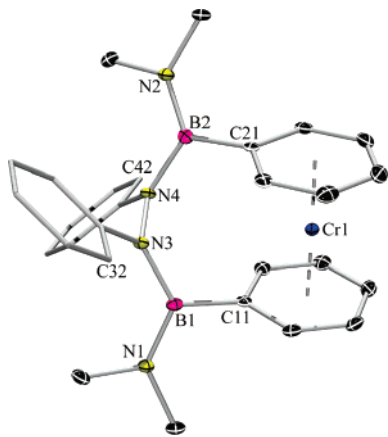


materials (**1**:  $\delta$  = 3.03, 3.27; **2**:  $\delta$  = 3.08, 3.31).<sup>7</sup> The <sup>1</sup>H NMR resonances of the  $\eta^5$ - and  $\eta^6$ -coordinated carbocyclic ligands show splitting patterns, which are characteristic for substituted metalloarenophanes and strongly resemble those reported for the analogous *ansa*-bis(boryl)alkenes of ferrocene and bis(benzene)-chromium.<sup>7</sup>

As expected for the substitution of a boron bound platinum center by an additional nitrogen atom, the resonances of the boron nuclei in the <sup>11</sup>B NMR spectrum of **3** ( $\delta$  = 33.0) and **4** ( $\delta$  = 33.8) are significantly shielded with respect to the corresponding signal of the starting materials (**3**:  $\delta$  = 62.2; **4**:  $\delta$  = 61.6).<sup>7</sup> According to <sup>31</sup>P NMR spectroscopy, the reductive elimination of the [Pt(PEt<sub>3</sub>)<sub>2</sub>] fragment is accompanied by the formation of the azobenzene complex [(PhN=NPh)Pt(PEt<sub>3</sub>)<sub>2</sub>] ( $\delta$  = 5.90; <sup>1</sup>J<sub>P,Pt</sub> = 4067 Hz).<sup>8</sup>

To authenticate the formation of the bis-borylated product, the molecular structure of **4** was determined by X-ray diffraction (Figure 1). As expected, the formation of a B–N–N–B bridge in **4** is accompanied by the decrease of molecular ring strain in comparison to the starting material **2**, which is manifested in the almost coplanar arrangement of the  $\eta^6$ -coordinated ligands with a tilt-angle of  $\alpha$  = 1.98(2)° and a deformation angle of  $\delta$  = 178.4° [**2**:  $\alpha$  = 4.12(15)°;  $\delta$  = 176.6°].<sup>7</sup> In agreement with the unstrained character, the boron atoms are found to be almost ideally sp<sup>2</sup>-hybridized, thus featuring a regular trigonal-planar geometry [119.1(2)–120.7(2)°; B1, B2:  $\Sigma$  = 360°]. The B–N bond lengths are in the typical range found for the aminoboranes R<sub>2</sub>BNR<sub>2</sub> and are indicative of multiple B–N bonding, whereby the distances to the NMe<sub>2</sub>-moieties [both 1.402(3) Å] are significantly shorter than those to the nitrogens of the hydrazine bridge [1.471(3) Å and 1.476(3) Å]. Hence, the double bond character of the former appears to be much more pronounced. The structural features of the hydrazine moiety, i.e., the N–N bond length [1.425(2) Å] and the distorted trigonal-planar environment of the nitrogen atoms [114.7(2)–128.5(2)°; N1, N2:  $\Sigma$  = 360°] as well as the torsion angle B1–N3–N4–B2 = –107.0(2)°, are comparable to those found in the related species [–B(NMe<sub>2</sub>)N(Me)N(Me)–]<sub>2</sub><sup>9</sup> or Mes<sub>2</sub>B(Ph)N–NH(Ph)<sup>10</sup> and have been discussed in detail by Power and Nöth.<sup>4,10</sup>

In order to develop a transition-metal-catalyzed protocol, the [2]boraferrocenophane **5**<sup>11</sup> and [Cr( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>)B<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>] (**6**)<sup>12</sup> were treated in subsequent experiments with azobenzene and catalytic amounts of [Pt(PEt<sub>3</sub>)<sub>3</sub>]. The thermal lability of the chromium



**Figure 1.** Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Cr1–C<sub>Ph</sub> between 2.126(2) and 2.158(2), C11–B1 1.585(3), C21–B2 1.583(3), B1–N1 1.402(3), B2–N2 1.402(3), B1–N3 1.471(3), B2–N4 1.476(3), N3–N4 1.425(2), Cr1–X<sub>Ph1</sub> 1.603, Cr1–X<sub>Ph2</sub> 1.611; C11–B1–N3 119.8(2), C21–B2–N4 119.1(2), B1–N3–N4 117.2(2), B2–N4–N3 116.9(2), C31–N3–N4 114.7(2), C41–N4–N3 114.7(2), X<sub>Ph1</sub>–Cr1–X<sub>Ph2</sub> 178.4, B1–N3–N4–C41 72.6(2), B1–N3–N4–B2 –107.0(2), B2–N4–N3–C31 71.9(2), C31–N3–N4–C41 –108.5(1), X<sub>Ph1</sub>–C11–C21–X<sub>Ph2</sub> –36.1,  $\alpha$  1.98(2) (X<sub>Ph1</sub> = centroid of C11–C16, X<sub>Ph2</sub> = centroid of C21–C26).

**Scheme 2.** Homogeneous-Catalytic Diboration of Azobenzene by [2]Boraferrocenophane **5**



derivative **6** prevented its utilization in a catalytic process, since the reaction conditions (120 °C) entailed quantitative degradation of **6** into chromium metal and the free ligand NMe<sub>2</sub>(Ph)B–B(Ph)–NMe<sub>2</sub>. The identity of the latter was unambiguously confirmed by its <sup>1</sup>H and <sup>11</sup>B NMR spectra, which are in agreement with the presence of both two noncoordinated phenyl ligands [ $\delta$  = 2.56 (6H), 2.82 (6H), 7.25–7.39 (10H)] and a diarylaminoborane ( $\delta$  = 48.8), respectively. However, the [2]boraferrocenophane **5** proved to be thermally much more robust and was successfully converted into **3** under homogeneous catalysis conditions (Scheme 2). The reaction of **5** with a 4-fold excess of azobenzene and 5 mol % [Pt(PEt<sub>3</sub>)<sub>3</sub>] proceeded smoothly in toluene at 120 °C, and <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy of the reaction mixture confirmed the quantitative consumption of the starting *ansa*-complex and the formation of the *ansa*-bis(boryl)hydrazine **3** over a period of 6 d. The conversion into **3** as judged by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy reached 85% and was accompanied only by minor amounts of several unidentified side and degradation products. **3** was isolated analytically pure from the reaction mixture after workup and recrystallization from hexanes in good yields of up to 79%.

In addition, control experiments were carried out for the reaction of **5** with azobenzene in the absence of the platinum catalyst [Pt(PEt<sub>3</sub>)<sub>3</sub>]. At 120 °C and over an extended period of 10 d <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy indicated very slow formation of the *ansa*-

bis(boryl)hydrazine **3**, however, only as a minor component <25% and in combination with significant amounts of side and degradation products. Moreover, the signals corresponding to **3** disappeared over the extended course of the reaction and devolved into a new set of signals [<sup>1</sup>H:  $\delta$  = 2.24 (NMe<sub>2</sub>); <sup>11</sup>B:  $\delta$  = 32.1], whereby the identity of this compound has not been clarified to date. It is noteworthy that the same resonances were observed, when the reaction of **5** with azobenzene was performed in the presence of 10 mol % Pd/C. In this case, only a static concentration of **3** was formed, which was converted into the unknown compound within 10 d at 120 °C. The isolation and full characterization of this species, which is hampered by the unselective nature of these transformations and the significant amounts of side and degradation products, is the purpose of current research efforts.

In this communication we provided our preliminary results on the selective diboration of the N=N double bond of azobenzene by [*n*]metalloarenophanes under stoichiometric and homogeneous catalysis conditions to yield the *ansa*-bis(boryl)hydrazines **3** and **4**. Due to the thermal lability of the chromium derivative **6**, a transition-metal-catalyzed diboration was only achieved with the [2]boraferrocenophane **5**.

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**Supporting Information Available:** Details of the syntheses and spectroscopic characterization of compounds **3** and **4**, experimental details on the X-ray diffraction of **4**, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (a) Brown, H. C. *Hydroboration*; Wiley-Interscience: New York, 1962. (b) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, 1972. (c) Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975. (d) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957–5026.
- (a) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63–73. (b) Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395–402. (c) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2000**, *611*, 392–402.
- (a) Cragg, G. M. L. *Organoboranes in Organic Synthesis*; Dekker: New York, 1972. (b) Suzuki, A.; Miyaura, N. *Chem. Rev.* **1995**, *95*, 2457–2483. (c) Kaufmann, D. E.; Matteson, D. S. *Science of Synthesis, Boron Compounds*; Thieme: Stuttgart, 2005.
- Hommer, H.; Nöth, H.; Sachdev, H.; Schmidt, M.; Schwenk, H. *Chem. Ber.* **1995**, *128*, 1187–1194.
- Luckert, S.; Eversheim, E.; Englert, U.; Wagner, T.; Paetzold, P. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1815–1823.
- E.g., (a) Sheridan, J. B.; Lough, A. J.; Manners, I. *Organometallics* **1996**, *15*, 2195–2197. (b) Tamm, M.; Kunst, A.; Herdtweck, E. *Chem. Commun.* **2005**, 1729–1731. (c) Braunschweig, H.; Lutz, M.; Radacki, K. *Angew. Chem.* **2005**, *117*, 5792–5796; *Angew. Chem., Int. Ed.* **2005**, *44*, 5647–5651. (d) Braunschweig, H.; Dirk, R.; Englert, U.; Berenbaum, A.; Green, J. C.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765–5774. (e) Mizuta, T.; Imamura, Y.; Miyoshi, K. *J. Am. Chem. Soc.* **2003**, *125*, 2068–2069.
- Braunschweig, H.; Kupfer, T.; Lutz, M.; Radacki, K.; Seeler, F.; Sigritz, R. *Angew. Chem.* **2006**, *118*, 8217–8220; *Angew. Chem., Int. Ed.* **2006**, *45*, 8048–8051.
- Cowan, R. L.; Troglor, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750–4761.
- Huffman, J. C.; Fustetter, H.; Nöth, H. *Z. Naturforsch., B: Chem. Sci.* **1976**, *31b*, 289–293.
- Pestana, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528–535.
- Braunschweig, H.; Seeler, F.; Sigritz, R. *J. Organomet. Chem.* **2007**, *692*, 2354–2356.
- Braunschweig, H.; Homberger, M.; Hu, C.; Zheng, X.; Gullo, E.; Clentsmith, G.; Lutz, M. *Organometallics* **2004**, *23*, 1968–1970.

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