#### Borylene Complexes

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# Molecular Structure and Cluster Formation of a *tert*-Butylborylene Complex\*\*

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In 1995 we reported on the first spectroscopically characterized borylene complexes  $[\mu$ -BX{ $(\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Mn(CO)<sub>2</sub>]<sub>2</sub>] (1:  $X = NMe_2$ , R = H; **2**: X = tBu,  $R = Me)^{[1]}$  and the molecular structure of 1. During the past decade, intense research efforts were focused on borylene complexes,<sup>[2]</sup> and many different coordination modes for ligands of the type B-R were described and include terminal,<sup>[3]</sup> hetero-dinuclear,<sup>[4]</sup> and semibridging<sup>[5]</sup> species, thus experimentally proving the predicted close relationship between borylene ligands and CO.<sup>[6,7]</sup> More recent studies focused on the reactivity of borylene complexes and revealed some interesting characteristics of these species, for example, i) the potential of terminal borylene ligands to be transferred to metallic<sup>[8]</sup> and nonmetallic<sup>[9]</sup> substrates, ii) the strong tendency of some terminal borylene ligands to add metal bases of the type  $[M(PR_3)_n]$ (M = Pd, Pt),<sup>[5,10]</sup> and iii) the exceptional stability of the central Mn<sub>2</sub>B framework in 1.<sup>[7]</sup> This stability allowed for elusive substitution reactions at the borylene center without cleavage of the metal-boron framework.<sup>[11]</sup> Given the pronounced thermodynamic stability of these compounds with respect to M-B dissociation,<sup>[6,7]</sup> the latter finding may appear surprising; DFT calculations revealed a build-up of positive charge at the boron center, and hence, the M-B bond is kinetically labile and susceptible to nucleophilic cleavage.<sup>[7]</sup>

Despite significant progress in this area, the choice of boron-bound substituents that sufficiently stabilize the metalcoordinated borylene ligand is very much restricted to mainly  $\pi$ -stabilizing heteroatoms such as N and O. Only very few substituents with little or no  $\pi$  stabilization were reported, such as sterically very demanding aryl<sup>[3b]</sup> or hypersilyl groups.<sup>[3c]</sup> The *tert*-butylborylene complex **2** is in a way a unique example, as it still represents the only alkylborylene complex and, accordingly, has attracted much interest.<sup>[12]</sup> Because of the highly unsaturated nature of the boron center in **2**, a reactivity pattern has to be expected that is

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significantly different from that of its amino-stabilized counterpart **1**. Herein we report the synthesis and crystal structure of  $[\mu$ -BtBu{ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>]<sub>2</sub>] (**3**), as well as the unprecedented reactivity of its methyl-substituted analogue  $[\mu$ -BtBu{ $(\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Mn(CO)<sub>2</sub>]<sub>2</sub>] (**2**) towards  $[Pd(PCy_3)_2]$  (Cy = cyclohexyl) to yield a novel heterometallic boron cluster.

Since attempts to obtain suitable single crystals of **2** failed, its unsubstituted counterpart  $[\mu$ -BtBu{ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>}] (**3**) was prepared by an analogous procedure<sup>[13]</sup> from K[{ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>}H] and B<sub>2</sub>tBu<sub>2</sub>Cl<sub>2</sub> and recrystallized from hexanes at -35 °C.

Compound **3** crystallizes in the space group  $P2_1/n$  and displays the expected central three-membered Mn<sub>2</sub>B ring with an exocyclic B1–C5 bond length of 1.610(2) Å,<sup>[14]</sup> which is in the normal range for *tert*-butylboranes (Figure 1).<sup>[15]</sup>



*Figure 1.* Molecular structure of **3** (thermal ellipsoids set at 50% probability). Bond lengths [Å] and angles [°]: B1–Mn1 2.0288(16), B1–Mn2 2.0309(16), Mn1–Mn2 2.7952(5), B1–C5 1.610(2); Mn1-B1-Mn2 87.03(7), B1-Mn2-Mn1 46.45(5).

Despite the absence of  $\pi$  stabilization from the boronbound substituent, the geometry of the central Mn<sub>2</sub>B moiety, with two nearly identical B–Mn bond lengths of 2.0288(16) Å (B1–Mn1) and 2.0309(16) Å (B1–Mn2) and a Mn–Mn bond length of 2.7952(5) Å, closely resembles that of the corresponding amino-<sup>[1]</sup> or chloroborylene<sup>[16]</sup> complexes.

In contrast to the similarities with respect to their molecular structures, **1** and **3** show markedly different reactivity, as already indicated by the extreme sensitivity of **3** in stark contrast to the stability of **1** even towards air and water. The aminoborylene species also proved unreactive towards  $[Pd(PCy_3)_2]$ , whereas **2** underwent a clean, albeit slow, reaction with  $[Pd(PCy_3)_2]$  to form the unprecedented trimetallic species  $[(\mu_3-BtBu)\{[(\eta^5-C_5H_4Me)Mn(CO)_2][Pd-(PCy_3)]_2]]$  (**4**).

A 1:2 mixture of **2** and  $[Pd(PCy_3)_2]$  in C<sub>6</sub>D<sub>6</sub> was monitored by multinuclear NMR spectroscopy at ambient temperature. After a few hours, a slowly increasing new <sup>11</sup>B NMR spectroscopic resonance at  $\delta = 150$  ppm was detected, which



is 20 ppm highfield-shifted with respect to that of 3, thus indicating the formation of 4. The <sup>31</sup>P NMR spectrum signals at  $\delta = 10$  (PCy<sub>3</sub>), 92 ([(η<sup>5</sup>revealed  $C_5H_4Me)Mn(CO)_2PCy_3]^{[17]}$  (5)), and 27 ppm (4), as well as the signal from  $[Pd(PCy_3)_2]$  at  $\delta = 39$  ppm. After three weeks the reaction was complete, and no additional signals indicative of further byproducts were detected. The new complex 4 was isolated as red crystals in 25% yield after repeated recrystallization from hexane. The formation of 4 requires the extrusion (and trapping by PCy<sub>3</sub>) of one  $\{(\eta^5 C_5H_4Me)Mn(CO)_2$  fragment from 2, thereby formally giving а terminal borylene complex "[(ŋ<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)(OC)<sub>2</sub>Mn=BtBu]",<sup>[18]</sup> which is subsequently stabilized by two {Pd(PCy<sub>3</sub>)} moieties. Neither the controlled degradation of the thermodynamically very stable Mn<sub>2</sub>B core under thermal conditions nor the multiple addition of metal bases to a boryl or borylene center has any precedence in metal-boron chemistry, and the occurrence of these transformations is here ascribed to the presence of the boronbound alkyl substituent. Complex 4 crystallizes in the space group  $P\bar{1}$  and consists of an MnPd<sub>2</sub> isosceles triangle (bond lengths: Mn1–Pd1 2.6426(10) Å, Mn1–Pd2 2.6458(10) Å, Pd1–Pd2 2.8423(7) Å) which is capped in a  $\mu_3$  fashion by the tert-butylborylene ligand (Figure 2).<sup>[14]</sup> The B1–Mn1 bond length of 1.987(7) Å is close to that of 1, while the B-Pd bond lengths (B1-Pd1 2.144(7) Å, B1-Pd2 2.128(8) Å) are comparable to those of  $[(\eta^5-C_5Me_5)Fe(\mu-CO)_2(\mu-BCl_2)Pd(PCy_3)]$ (2.062(4) Å),<sup>[19]</sup> thus indicating M–B single bonds in **4**.

Compound **4** can be viewed as the first example of a *hetero*metallic  $\mu_3$ -borylene complex. The class of  $\mu_3$ -borylene



*Figure 2.* Molecular structure of **4** (thermal ellipsoids set at 50% probability). Bond lengths [Å] and angles [°]: Mn1–Pd1 2.6426(10), Mn1–Pd2 2.6458(10), Pd1–Pd2 2.8423(7), B1–Mn1 1.987(7), B1–Pd1 2.144(7), B1–Pd2 2.128(8); O1-C1-Mn1 158.9(5), O2-C2-Mn1 160.1(5).

# Communications

compounds is restricted to very few examples that exclusively consist of homometallic frameworks of either Co<sup>[20]</sup> or, more commonly, Ru centers.<sup>[21]</sup> A formal electron count (each of  $\{Cy_3PPd\},^{[22]}$  $\{tBuB\},\$ the fragments and  $\{(\eta^{5} C_5H_4Me)Mn(CO)_2$  contributes two electrons to the cluster framework) is in agreement with a metallaborane that is two electrons short of a *closo* species (that is, *hypercloso*). DFT studies, however, suggest a more localized bonding picture.<sup>[23]</sup> Natural bond orbital (NBO) calculations indicate a rather strong covalent Mn–B bond (Wiberg bond index, WBI = 0.8) and somewhat weaker Pd-B interactions (WBI = 0.42 and 0.48). The Pd-Pd interaction (WBI=0.05), however, was calculated to be almost nonexistent. This description is reflected by electron localization function (ELF) computations (Figure 3), which revealed two fused basins between the



Figure 3. ELF = 0.6 plot for the model of complex 4. The ELF contributions of ligand atoms are omitted for clarity.

boron and manganese atoms that also affect both palladium centers, thus representing two (3c, 2e) Mn-B-Pd bonds. Furthermore, no basins indicative of a typical metallaborane cluster were found over any triangular face of the  $\{BMnPd_2\}$  core.

This description is reminiscent of the bonding situation found in metal-base-stabilized amino-<sup>[5]</sup> and metallobory-lene<sup>[10]</sup> complexes. In sharp contrast to these { $(Me_3Si)_2N$ }- and { $Cp^*Fe(CO)_2$ }-substituted borylenes, however, the presence of the non- $\pi$ -stabilizing *tert*-butyl group in **4** allows for the unprecedented addition of two metal bases to the boron center.

## **Experimental Section**

All manipulations were conducted in an atmosphere of dry argon by employing either standard Schlenk techniques or a glovebox.

**4**: [Pd(PCy<sub>3</sub>)<sub>2</sub>] (0.200 g, 0.300 mmol) was added to a solution of **2** (0.060 g, 0.134 mmol) in C<sub>6</sub>D<sub>6</sub> (0.8 mL) at room temperature. The course of the reaction was monitored by multinuclear NMR spectroscopy. After three weeks the reaction was judged to be complete. The solvent was removed in vacuo, and hexane was added to the residue. Compound **4** was separated by fractional crystallization and recrystallization from hexanes at -35 °C as red crystals (0.035 g, 25 % yield). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS):  $\delta$  = 4.59(m, 2H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 4.54 (m, 2H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 2.04 (s, 3H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 1.65 (s, 9H, *t*Bu), 2.15–1.15 ppm (m, 66H, Cy); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 98.3 (*ipso*-C, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>),

83.4, 79.4 ( $C_5H_4Me$ ), 35.2 (d,  ${}^{1}J_{CP}$  = 10.5 Hz, Cy), 32.1, 31.8 (brs, Cy), 30.7 (s, *t*Bu), 28.6, 28.5, 27.3 (s, Cy), 12.7 ppm (s,  $C_5H_4CH_3$ ), the signal for the semibridging CO ligand was not observed;  ${}^{11}B{}^{1}H{}$  NMR (64 MHz,  $C_6D_6$ , 25 °C): 150 ppm (brs);  ${}^{31}P{}^{1}H{}$  NMR (202 MHz,  $C_6D_6$ , 25 °C): 27.1 ppm; IR (benzene):  $\tilde{\nu} = 1811$ , 1770 cm<sup>-1</sup>

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atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in the structure-factor calculations. CCDC-602961 (3) and CCDC-602990 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Crystal data for **3**:  $C_{18}H_{19}BMn_2O_4$ ,  $M_r = 420.02$ , dark red polyhedra,  $0.5 \times 0.5 \times 0.4$  mm<sup>3</sup>, monoclinic, space group  $P2_1/$ *n*, a = 8.5604(9), b = 13.3225(10), c = 15.7316(17) Å,  $\beta =$ 95.861(13)°, V = 1784.7(3) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.563$  g cm<sup>-3</sup>,  $\mu = 1.433$  mm<sup>-1</sup>, F(000) = 856, T = 173(2) K, R(all data):  $R_1 =$  $0.0267, wR_2 = 0.0641, 2.60^{\circ} < \theta < 28.01^{\circ}, 20339/4062$  reflections collected/unique,  $R_{int} = 0.0340$ , 229 parameters. Crystal data for 4:  $C_{48}H_{82}BMnO_2P_2Pd_2$ ,  $M_r = 1031.63$ , red prisms,  $0.2 \times 0.2 \times$ 0.1 mm<sup>3</sup>, triclinic, space group  $P\overline{1}$ , a = 10.7449(9), b =21.7062(16), c = 33.376(3) Å,  $\alpha = 72.686(9)$ ,  $\beta = 82.471(10)$ ,  $\gamma =$ 77.668(9)°,  $V = 7241.2(10) \text{ Å}^3$ , Z = 6,  $\rho_{\text{calcd}} = 1.419 \text{ g cm}^{-3}$ ,  $\mu =$ 1.097 mm<sup>-1</sup>, F(000) = 3228, T = 173(2) K,  $R(I > 2\sigma(I))$ :  $R_1 =$  $0.0535, wR_2 = 0.1218, 2.48^{\circ} < \theta < 26.55^{\circ}, 58283/27614$  reflections collected/unique,  $R_{int} = 0.0741$ , 1536 parameters. Three molecules were found in the independent part of the cell and differ essentially only by rotation of the PCy3 groups; all bond lengths and angles given in the text are for the same molecule.

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