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Borylene Complexes

Synthesis and Electronic Structure of a Terminal Alkylborylene Complex**

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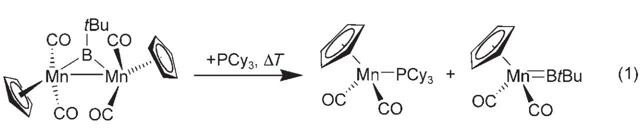
The chemistry of borylene complexes has significantly developed over the past few years,[1] and based on a more detailed understanding of the bonding situation of BR ligands, it is well-recognized that the presence of sterically demanding and electron-releasing substituents R is a requisite, particularly for the synthesis of terminal borylene complexes [$L_xM{=}B{-}R$]. This requirement is due to the fact that the coordination of BR to a metal center, although resembling the synergic bonding scheme of CO complexes, leads to a buildup of positive charge on the boron atom, and hence, the borylene center requires electronic and steric stabilization from R to effectively protect it against nucleophilic attack.[2] Consequently, bulky amino groups were established as particularly suitable groups for borylene complex synthesis,[3] while corresponding compounds with mesityl,[4] hypersilyl,[5] or metal substituents[6] represent exceptionally rare cases.

While NR_2 substituents are synthetically advantageous, they significantly moderate the reactivity of neutral complexes [$L_xM{=}B{=}NR_2$], and apart from very few exceptions,[7] the chemistry of such species is restricted to photochemically induced borylene-transfer reactions.[8] To fully exploit the potentially highly interesting reactivity of such species, it would be desirable to introduce less stabilizing substituents, preferably alkyl groups, to metal-bound borylenes. Knowledge on alkylborylene complexes, however, has so far been restricted to the dinuclear complex [μ-B*t*Bu{(η^5-C_5H_4R)Mn(CO)$_2$}$_2$] (**1a**, R = H; **1b**, R = Me).[9] Herein we report on the first terminal alkylborylene complex, which was obtained from a corresponding dinuclear precursor by an unprecedented phosphine-induced cleavage reaction.

An equimolar mixture of [μ-B*t*Bu{(η^5-C_5H_5)Mn(CO)$_2$}$_2$] (**1a**) and PCy_3 in benzene was heated at reflux, and the progress of the reaction was monitored by multinuclear NMR spectroscopy. A ^{31}P NMR resonance at $\delta = 92$ ppm indicated the formation of [(η^5-C_5H_5)Mn(CO)$_2$PCy$_3$] (**2**),[10] while a ^{11}B NMR signal at $\delta = 144$ ppm, which is shifted to higher field with respect to that of the dinuclear precursor ($\delta = 170$ ppm) but still significantly deshielded in comparison to terminal amino borylene complexes ($\delta \approx 100$),[3,8b] revealed the formation of the novel alkylborylene species [(η^5-C_5H_5)(OC)$_2$MnB*t*Bu] (**3**) [Eq. (1)]. The reaction was complete after 4 h, and no further products could be detected. Both compounds were separated by fractional crystallization from pentane at −35 °C, and **3** was isolated as an analytically pure, pale yellow solid, which turned out to be extremely sensitive toward air and moisture but could be stored under argon at room temperature for months without decomposition.



1a **2** **3**

The constitution of **3** was ascertained by an X-ray diffraction study on a suitable single crystal (Figure 1). The compound crystallizes in the monoclinic space group $P2_1/m$ with a mirror plane bisecting the molecule. Most notably, the structure of **3** is characterized by a B1−Mn1 bond length of only 1.809(9) Å,[11] which resembles the Fe−B bond length in the cationic species [(η^5-C_5Me_5)(OC)$_2$FeBMes][BAr$^F_4$][4] (1.792(8) Å; Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$), thus accounting for the shortest metal–boron separation in a neutral complex. Consequently, the Mn−B bond lengths in **1a**[9c] and in the boryl complex [(η^5-C_5H_4Me)(OC)$_2$(H)MnB(Cl)Si(SiMe$_3$)$_3$][12] are significantly greater (by 22 and 33 pm, respectively). The B1−C21 bond length of 1.531(11) Å is consistent with the reported value of 1.547(5) Å in *t*Bu−B=C(SiMe$_3$)$_2$,[13] which displays the same substitution pattern at a two-coordinate boron center.

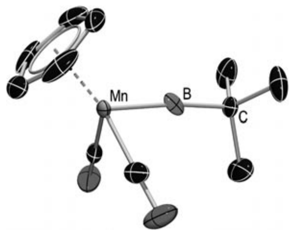


Figure 1. Molecular structure of **3**; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angle [°]: B1-Mn1 1.809(9), B1-C21 1.531(11); Mn1-B1-C21 174.3(7).

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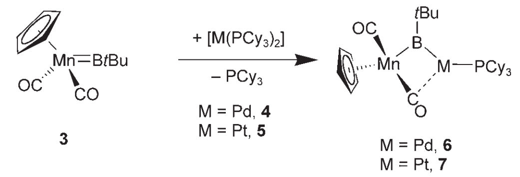

To provide initial information about the reactivity of the new species, **3** was treated with the complexes [M(PCy$_3$)$_2$] (M = Pd, **4**; M = Pt, **5**), which recently have proven their pronounced propensity to act as Lewis bases toward metal-coordinated boron-centered ligands.[7a,14–16] Treatment of **3** with **4** and **5** yielded the novel heterodinuclear species [(η^5-C$_5$H$_5$)(CO)Mn(μ-CO)(μ-B*t*Bu)MPCy$_3$] (M = Pd, **6**; M = Pt, **7**) [Eq. (2)], as indicated by ^{11}B NMR signals at δ = 151 ppm (**6**) and δ = 143 ppm (**7**), in 70% yield as bright yellow crystals.

X-ray diffraction studies revealed **6** and **7** to be isostructural and to crystallize in the space group $P\bar{1}$. Owing to the increased coordination number of the boron atoms, the B1–Mn1 bond lengths of 1.9237(18) Å (**6**) and 1.953(2) Å (**7**) are significantly greater than those in **3**, while the B1–Pd1 and B1–Pt1 bond lengths of 2.0359(18) Å (**6**) and 1.998(2) Å (**7**) fall in the expected range of corresponding heterodinuclear borylene species. The overall geometry of the central {Mn(μ-CO)(μ-B*t*Bu)M} fragment, in particular the relevant bond angles (Mn-C-O, Mn-B-C$_{t\text{Bu}}$, M-Mn-B, and M-Mn-C; see Figure 2), indicates that in both compounds CO and B*t*Bu constitute a set of two semibridging ligands—a pattern previously observed in metal–base adducts of terminal borylene complexes.[7a,16]

To elucidate the particular bonding situation in the first terminal alkylborylene complex, density functional theory (DFT) calculations were performed.[17] The Mn–B bond in **3** comprises three orbital interactions: Firstly the σ-type donation (HOMO−5) is characterized by interaction of the electron lone pair of B*t*Bu with the LUMO of the {CpMn(CO)$_2$} moiety (predominantly d$_{z^2}$), and secondly the π-symmetric LUMO and LUMO+1 of the borylene ligand interact with the HOMO−1 and HOMO−2 of the metal fragment, resulting in a set of two orbitals that demonstrate π back-bonding (see Figure 3). Previous computations of electron localization function (ELF) for borylene complexes[18] revealed the presence of a ring-type attractor for the metal–boron bond, thus emphasizing the significance of orthogonal π components in the bonding pattern. For **3** two adjacent disynaptic V(B,Mn) basins can be identified, whose attractors are localized on the Cp side of the metal–boron bond (Figure 4). These two mutually bound basins create a ring-type attractor, typical for multiple-bond character. The computed instantaneous interaction energy ($-\Delta E_{\text{int}}$) of the B–Mn bond (93.2 kcal mol^{-1}) is significantly higher than that found for [(OC)$_5$CrBN(SiMe$_3$)$_2$] (67.7 kcal mol^{-1}) and still greater than that of the silylborylene complex [(OC)$_5$CrBSi(SiMe$_3$)$_3$] (89.4 kcal mol^{-1}).[18]

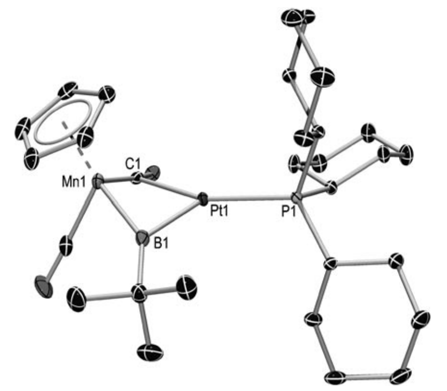

Figure 2. Molecular structure of **7**; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **6**: B1-Mn1 1.9237(18), B1-Pd1 2.0359(18); Mn1-C1-O1 169.23(13), Mn1-B1-C$_{t\text{Bu}}$ 146.05(13), Pd1-Mn1-B1 51.08(5), Pd1-Mn1-C1 58.14(5); **7**: B1-Mn1 1.953(2), B1-Pt1 1.998(2); Mn1-C1-O1 168.81(16), Mn1-B1-C$_{t\text{Bu}}$ 143.46(15), Pt1-Mn1-B1 49.96(6), Pt1-Mn1-C1 59.46(6).

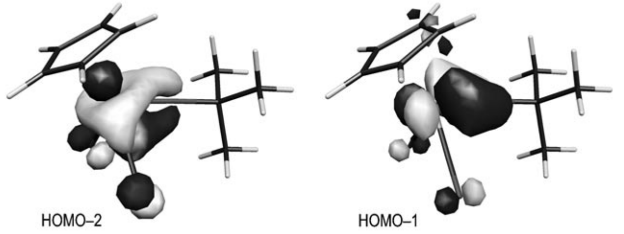

Figure 3. Kohn–Sham orbitals of π components of the B–Mn bond in **3**.

In comparison to the aforementioned Group 6 complexes, **3** is characterized by a smaller difference in natural charges of the metal (−0.63) and the boron center (+0.86). In particular, the charge of the Mn atom is significantly reduced, presumably owing to the presence of the negatively charged cyclopentadienyl ligand. These findings suggest a somewhat reduced polar character of the Mn–B linkage, which is also reflected by an increased Wiberg bond index (WBI) of 1.10 in comparison to the values computed for the Cr–B bonds in [(OC)$_5$CrBN(SiMe$_3$)$_2$] (0.74) and [(OC)$_5$CrBSi(SiMe$_3$)$_3$] (0.97).

In conclusion, the first terminal alkylborylene complex was obtained by an unprecedented phosphine-induced cleavage of a homodinuclear manganese precursor. As elucidated by DFT computations, the Mn–B*t*Bu linkage is characterized by strong metal-to-boron π back-bonding of pronounced multiple-bond character, thus imposing a remarkably short

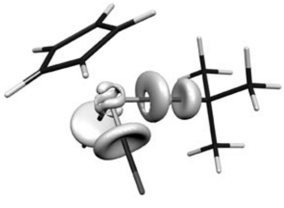

Figure 4. Isosurfaces with ELF = 0.8 for **3**. The envelopes around the remote parts of the ligands are omitted for clarity.

metal–boron separation in the crystal. Most notably, the title compound proved to be thermally stable enough for further reactions, despite the lack of π stabilization provided by the boron-bound alkyl substituent and the coordinatively unsaturated character of the boron center.

Experimental Section

All manipulations were conducted under an atmosphere of dry argon, employing either standard Schlenk techniques or a glove box.

3: A solution of **1a** (0.500 g, 1.19 mmol) and PCy_3 (0.333 g, 1.19 mmol) in C_6H_6 (10 mL) was heated for 4 h at reflux. The solvent was removed in vacuo, and pentane was added to the residue. Compound **3** was separated by fractional crystallization and recrystallization from pentane at −35 °C as pale yellow crystals (0.116 g, 40 % yield). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.26$ (s, 5H, C_5H_5), 0.95 ppm (s, 9H, *t*Bu); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 223.6$ (s, CO), 82.4 (s, C_5H_5), 24.0 ppm (s, *t*Bu); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 25 °C): $\delta = 144$ ppm; IR (benzene): $\tilde{\nu} = 1968$, 1912 cm^{-1}; EI-MS (70 eV): *m*/*z* (%): 244 (3) [M^{+}], 216 (2) [M−CO]$^{+}$, 188 (15) [M−2 CO]$^{+}$, 120 (100) [CpMn]$^{+}$, 55 (84) [Mn^{+}]. Elemental analysis (%) calcd for $C_{11}H_{14}BMnO_2$: C 54.14, H 5.97; found C 53.76, H 5.97.

6: Compound **4** (0.027 g, 0.04 mmol) was added to a solution of **3** (0.01 g, 0.04 mmol) in 0.3 mL C_6D_6. The color of the solution immediately changed from pale yellow to bright yellow. The solvent was removed in vacuo, and hexanes was added. The solution was then stored at −35 °C, yielding yellow crystals (0.018 g, 70 % yield). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.49$(s, 5H, C_5H_5), 1.34 (s, 9H, *t*Bu), 2.30–1.05 ppm (m, 33H, Cy); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 232.6$ (s, CO); 82.1 (s, C_5H_5), 33.7 (d, $^{1}J_{C,P} = 12.7$ Hz, C^{1}, Cy), 31.9 (d, $^{3}J_{C,P} = 5.1$ Hz, $C^{3,5}$, Cy), 27.2 (d, $^{2}J_{C,P} = 11.1$ Hz, $C^{2,6}$, Cy), 27.1 (s, *t*Bu), 26.0 ppm (s, C^{4}, Cy); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 25 °C): $\delta = 151$ ppm (br s); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C): $\delta = 31.0$ ppm; IR (benzene): $\nu = 1906$, 1818 cm^{-1}. Elemental analysis (%) calcd for $C_{29}H_{47}BMnO_2PPd$: C 55.21, H 7.51; found C 55.46, H 7.23.

7: As described above for the synthesis of **6**, compound **3** (0.01 g, 0.04 mmol) was treated with **5** (0.031 g, 0.04 mmol), yielding yellow crystals (0.02 g, 70 % yield). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.52$(s, 5H, C_5H_5), 1.37 (s, 9H, *t*Bu), 2.30–1.05 ppm (m, 33H, Cy); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 232.5$ (s, CO); 82.7 (s, C_5H_5), 36.2 (d, $^{1}J_{C,P} = 23.3$ Hz, C^{1}, Cy), 31.9 (s, $C^{3,5}$, Cy), 28.1 (s, *t*Bu), 28.1 (d, $^{2}J_{C,P} = 11.2$ Hz, $C^{2,6}$, Cy), 26.9 ppm (s, C^{4}, Cy); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 25 °C): $\delta = 143$ ppm (br s); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C): $\delta = 68.6$ ppm (s, $^{1}J_{Pt,P} = 4443$ Hz); IR (benzene): $\tilde{\nu} = 1904$, 1805 cm^{-1}. Elemental analysis (%) calcd for $C_{29}H_{47}BMnO_2PPt$: C 48.41, H 6.58; found C 48.45, H 6.40.

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