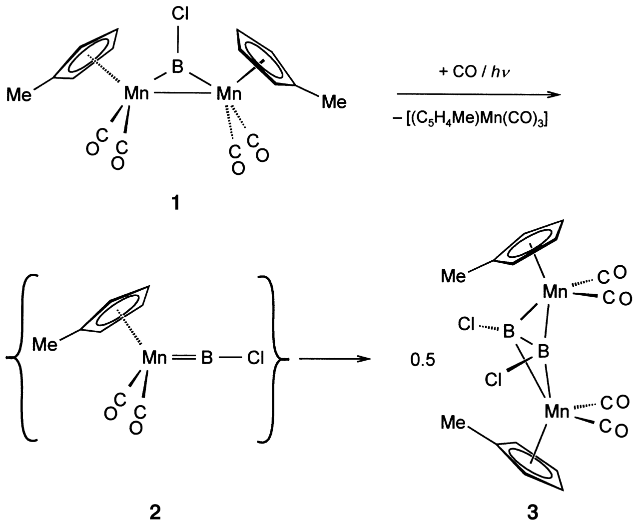
From Classical to Nonclassical Metal – Boron Bonds: Synthesis of a Novel Metallaborane**

Holger Braunschweig,* Miriam Colling, Chunhua Hu, and Krzysztof Radacki

Metallaboranes and borylene complexes are related to some extent as they both display direct metal – boron bonds—the nature of these interactions, however, is diverse. The borylene ligands BR are linked to one or two transition metal centers by classical, electron-precise, two-center two-electron (2c – 2e) bonds, whereas the cluster skeleton of a metallaborane is made up by nonclassical, electron-deficient, multicenter two-electron bonds.[1] While metallaboranes constitute a long known and well established class of transition metal – boron compounds comprising several hundreds of examples,[2] both bridged[1b] and terminal borylene complexes were realized only very recently and are still rare—in the case of the latter only five structurally authentic examples were reported since 1998.[1d, 3] Despite the enormous variety of metallaboranes, certain structural motifs, such as the four-vertex *nido*-deltahedron are still unknown. Our investigations on borylene complexes now provided the first synthetic link between these two classes of metal – boron compounds, and thus give access to an unprecedented "butterfly"-shaped *nido*-metallaborane.

Irradiation of the bridged chloroborylene complex [μ-BCl{(η^5-$C_5H_4CH_3$)Mn(CO)$_2$}$_2$] (**1**)[4] in hexane under an atmosphere of CO at −30 °C afforded complex **3** (yield 37 %, orange, crystalline, air sensitive solid) and [(η^5-$C_5H_4CH_3$)Mn(CO)$_3$] [Eq. (1)]. Although the detailed mechanism for the formation of **3** is unknown as yet, the terminal chloroborylene complex **2** appears to be a likely transient intermediate, formed by addition of CO to a [(η^5-$C_5H_4CH_3$)Mn(CO)$_2$] moiety of the starting material, and then dimerizes to the final product. This assumption is supported by the absence of further boron-containing products (by ^{11}B NMR spectroscopy) and the stoichiometric formation of methylcymantrene [(η^5-$C_5H_4CH_3$)Mn(CO)$_3$], which was identified by ^{1}H and ^{13}C NMR spectroscopy.



(1)

The photochemistry of **1** observed here is significantly different from that of terminal aminoborylene complexes of the type [(OC)$_5$M=B=NR$_2$], which at −30 °C undergo a photochemically induced transfer of the aminoborylene B=NR$_2$ to another metal center, for example chromium.[3d] Irradiation of **1** in the presence of [(OC)$_5$ML] (M = Cr, Mo, W; L = CO, NMe$_3$) under identical conditions gave no evidence for a transmetallation of chloroborylene B−Cl, but the Group 6 carbonyl complexes were found to act as a source for CO, thus affording **3** as the only boron-containing species, however, in significantly lower yields.

Compound **3** readily dissolves in all common aliphatic or aromatic hydrocarbons. In solution, the ^{1}H and ^{13}C NMR spectra display single sets of signals for the two [(η^5-$C_5H_4CH_3$)Mn(CO)$_2$] moieties and a strongly deshielded resonance signal at $\delta = 142.2$ is observed in the ^{11}B NMR spectrum which resembles that of the borylene precursor **1** at $\delta = 133.5$. It should be noted though, that unbridged B_2X_2 moieties, which are only known from very few metal-rich metallaboranes with X = H, are also characterized by considerably downfield shifted ^{11}B NMR signals in the range of $\delta = 104 - 114$.[5]

X-ray structure analyses were carried out for both **3** and **1** (Figure 1),[6, 7] since the latter was previously only character-

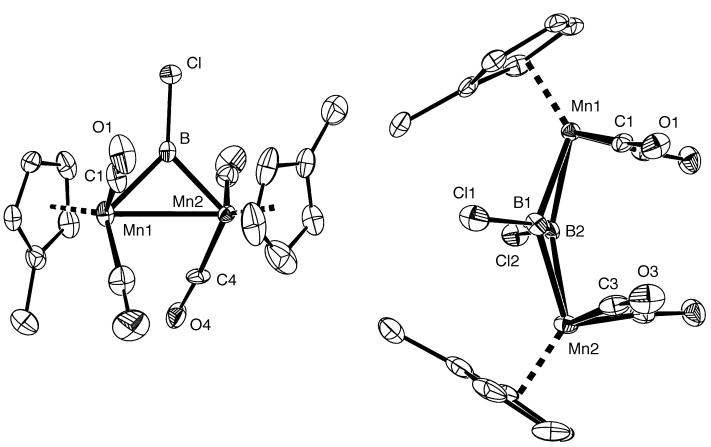


Figure 1. Structures of **1** (left) and **3** (right) in the crystal. Selected distances [Å] and angles [°]; **1**: Mn1-B 2.039(11), Mn2-B 1.976(9), Mn1-Mn2 2.8236(15), Mn1-B-Mn2 89.4(4); **3**: Mn1-B1 2.071(6), Mn1-B2 2.072(5), Mn2-B1 2.079(6), Mn2-B2 2.084(6), B1-B2 1.695(7), B1-Cl1 1.804(6), B2-Cl2 1.788(6); Mn1-B1-Mn2 124.3(3), Cl1-B1-B2 148.8(5).

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ized in solution.[4] The chloroborylene complex **1** crystallizes in the orthorhombic space group $P2_12_12_1$ and exhibits a disorder of one Mn atom, one CO group, and the BCl moiety over two positions with equal occupancy, which accounts for slightly higher standard deviations. The central three-membered ring of **1** has B–Mn bonds of 2.039(11) and 1.976(9) Å, and a Mn–Mn bond of 2.8236(15) Å, thus matching the geometries of the related complexes [μ-BOEt{(η^5-$C_5H_4CH_3$)Mn(CO)$_2$}$_2$] and [μ-BNMe$_2${(η^5-C_5H_5)Mn(CO)$_2$}$_2$].[4, 8]

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ and has approximate C_{2v} symmetry. The central Mn_2B_2 skeleton displays a bicyclobutane or "butterfly" geometry with a dihedral angle of 150.9° between the two MnB_2 triangles. This particular geometry together with a rather short B–B bond of 1.695(7) Å[9] and the two boron-bound Cl ligands in *exo*-position supports the description of **3** as a dimetalla-*nido*-tetraborane derived from the corresponding trigonal-bipyramidal *closo*-species by formal elimination of an equatorial vertex—and indeed, **3** fulfills the electron counting rules for a *nido*-compound.[10] A tetrahedral arrangement of the Mn_2B_2 skeleton, which is adopted by certain four-vertex *nido*-clusters as an alternative to the bicyclobutane structure,[11] can be ruled out from the large Mn–Mn separation of 3.670 Å.[12] The Mn–B separations of 2.079(6) and 2.084(6) Å are slightly larger than those in **1** (2.039(11) and 1.976(9) Å), thus accounting for the increased coordination numbers of the boron and manganese atoms. While related four-vertex metalla-*nido*-boranes are unknown, the structures of various aza-*nido*-tetraboranes of the type NB_3R_6 (R = H, alkyl) were reported over the past decade, all being characterized by the same "butterfly" geometry.[13]

Self-consistent field (SCF) calculations[14] on **3** converged for a C_{2v} symmetrical geometry, which frequency analysis confirmed to be a minimum. The calculated structural parameters of **3** are in good agreement with the experimental data (Table 1), and show only slightly larger interatomic distances (0.001–0.015 Å) than those reported for calculations on other transition metal–boron compounds.[3e, 15] An exception, however, is the B–B bond, which was calculated to be 0.02 Å shorter than in the crystal structure. The Mn1-B1-B2-Mn2 dihedral angle was found to be 149.0°, thus being 1.1° more acute than in the crystal, which together with slightly longer B–Mn distances results in almost the same Mn–Mn separation.

Gauge independent atomic orbitals (GIAO) chemical shifts for ^{1}H and ^{13}C nuclei match the experimental data (Table 1), however, the calculated ^{11}B NMR resonance signal is deshielded by 26 ppm. Both this discrepancy and the shorter B–B distance is probably a consequence of the smaller CEP-31 basis used for manganese.

The Wiberg bond index (WBI) for Mn–Mn is close to zero and indicates no interaction between the two metal centers. The WBI for B–B, however, was calculated to be 0.8 and thus suggests a strong boron–boron interaction. The natural bond orbital (NBO) analysis[16] gives no evidence for 2c–2e bonds between any of the four central atoms, but rather a 3c–2e Mn–B–B bond with a 27%:37%:37% composition.

Experimental Section

3: **1**[4] (0.44 g, 1.03 mmol) was dissolved in hexane (130 mL) under an atmosphere of CO. The mixture was irradiated with a high-pressure Hg lamp (Hereaus TQ 150) at −30°C for 6 h while gaseous CO was continuously conducted through the solution, the color of which gradually turned from red to orange. The orange reaction mixture was allowed to come to ambient temperature and filtered under a nitrogen atmosphere. The filtrate was concentrated in high vacuum (0°C/0.001 Torr) to 20 mL and stored at −30°C. After 3 days **3** (0.09 g, 0.19 mmol, 36.8%) was obtained as small orange crystals.

All NMR spectra were recorded in [D$_6$]benzene at 25°C. ^{1}H NMR (500 MHz, TMS): $\delta = 1.44$ (s, 6H, $C_5H_4C\mathit{H}_3$), 4.16, 4.22 (2m, 8H, $C_5\mathit{H}_4CH_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 142.4$; ^{13}C NMR (126 MHz, TMS): $\delta = 13.1$ ($C_5H_4\mathit{C}H_3$), 90.5, 90.8 ($\mathit{C}_5H_4CH_3$), 106.2 (ipso-C, $\mathit{C}_5H_4CH_3$), 220.6 (CO); IR (toluene): $\tilde{\nu} = 2000$, 1951 cm^{-1} (CO); MS $m/z = 472$ [M^+], 444 [$M^+ - CO$], 416 [$M^+ - 2CO$], 388 [$M^+ - 3CO$], 309 [$M^+ - 3CO - C_5H_4CH_3$], 263 [$M^+ - 3CO - C_5H_4CH_3 - BCl$], 180 [($C_5H_4CH_3$)MnBCl], 134 [($C_5H_4CH_3$)Mn], 79 [$C_5H_4CH_3$], 55 [Mn]; elemental analysis (%) calcd for $C_{16}H_{14}B_2Cl_2Mn_2O_4$: C 40.66, H 2.99; found: C 40.35, H 2.80.

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Table 1. Selected experimental and calculated spectroscopic and structural data for **3**.

	δ(^{1}H)[a]	δ (^{11}B)	δ (^{13}C)	B–B [Å]	Mn–B [Å]	B–Cl [Å]	B-B-Cl [°]	Mn-B-B-Mn [°]
exp	1.44, 4.16, 4.22[a]	142.4	13.1, 90.5, 90.8, 106.2,[a] 220.6[b]	1.695(7)	2.071(6), 2.072(5), 2.079(6), 2.084(6)	1.804(6), 1.788(6)	148.8(5), 148.1(4)	150.1
calcd	1.28, 3.91, 4.23[a]	168.9	11.9, 80.9, 86.0, 108.5[a], 223.3[b]	1.676	2.084	1.809	147.6	149.0

[a] Values for $C_5H_4CH_3$. [b] Values for CO.

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[6] Crystal data for **1**: $C_{16}H_{14}BClMn_2O_4$, $M_r = 426.41$, crystal dimensions $0.44 \times 0.36 \times 0.22$ mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.1914(14)$, $b = 12.347(3)$, $c = 14.856(3)$ Å, $V = 1685.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.680$ g cm^{-3}, $2\theta_{max} = 52°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\omega/2\theta$ scans, $T = 213(2)$ K, $\mu = 1.672$ mm^{-1}. Of 3660 collected reflections, 3298 were unique ($R_{int} = 0.0320$). LP and empirical (psi scans) absorption corrections were applied. The structure was solved by direct methods and refined using SHELXTL.[17] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions (C–H = 0.98 Å and included as riding with $U_{iso}(H) = 1.3\,U_{eq}$ (non-H). In the structure, a Mn atom, one CO group and the BCl moiety are disordered over two positions with equal occupancy; the $C_5H_4CH_3$ ligands are not affected by the disorder. $R = 0.0451$ ($I > 2\sigma(I)$), $R_w = 0.1065$ (F^2, all data), 262 parameters, final difference map extremes 0.345 and -0.501 e Å^{-3}.

[7] Crystal data for **3**: $C_{16}H_{14}B_2Cl_2Mn_2O_4$, $M_r = 472.67$, crystal dimensions $0.32 \times 0.20 \times 0.02$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.5756(18)$, $b = 7.9087(9)$, $c = 15.034(3)$ Å, $\beta = 102.045(13)°$, $V = 1811.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.733$ g cm^{-3}, $2\theta_{max} = 52°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\omega/2\theta$ scans, $T = 213(2)$ K, $\mu = 1.708$ mm^{-1}. Of 4338 collected reflections, 3556 were unique ($R_{int} = 0.0455$). LP and empirical (psi scans) absorption corrections were applied. The structure was solved by direct methods and refined using SHELXTL.[17] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions (C–H = 0.98 Å and included as riding with $U_{iso}(H) = 1.3\,U_{eq}$ (non-H). $R = 0.0526$ ($I > 2\sigma(I)$), $R_w = 0.0983$ (F^2, all data), 235 parameters, final difference map extremes 0.509 and -0.480 e Å^{-3}. CCDC-173229 (**1**) and -173230 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[9] The unbridged B_2H_2 moieties in 2-Ph-1,3,6,7,2,[(η^5-C_5H_5)Co$_4$]PB$_2$H$_2$[5a] and (μ_3-H)$_2$[(η^5-C_5H_5)Co]$_4$B$_2$H$_2$[5b] show very similar B–B distances of about 1.80 Å.

[10] Considering the t_{2g} orbital set the d^6ML_5 fragment (η^5-$C_5H_4CH_3$)Mn(CO)$_2$ is isolobal to CH_2 and the four vertex *nido*-cluster **3** shows the required total of six electron pairs in its skeleton. For isolobal analogy see: R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 725.

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[12] A Mn–Mn separation of 3.2 Å is regarded as the upper limit for a Mn–Mn bond, see: W. A. Herrmann, B. Koumboris, T. Zahn, M. L. Ziegler, *Angew. Chem.* **1984**, *96*, 802; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 812; in addition, it should be noted that in the case of **3** all intermolecular Mn–Mn distances are greater than 6 Å.

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[14] SCF Calculations: The GAUSSIAN 98 package, run on a cluster of workstations was applied for all SCF calculations. The total energy E_h and the ZPVE (in Hartree, in parentheses) calculated on B3LYP-level with 6-31G(d,p) basis set for non-metal atoms and CEP-31G for manganese is -2097.012890 (0.274282). Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

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Enantioselective C–C Bond Formation with Titanium(IV) Alkoxides—an Unusual Alkylation**

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Recently we described an enantioselective aldol reaction of aldehydes with unactivated ketones mediated by titanium(IV) alkoxide ligand exchange.[1] In attempts to optimize this reaction further by catalytic control, metal salts, among other things, have been used as additives in the aldol reactions. In particular the use of lithium salts has been described by a number of authors in different C–C bond formation processes,[2] and the use of lithium perchlorate in the Mukaiyama reaction has been known for some time.[3] Lithium perchlorate is also used in enantioselective aldol reactions. Here a weakening or a cleavage of the metal alkoxide–aldolate bond is assumed. The aldols formed are thus continuously released from the catalyst,[4] and in this way catalytic control of the reaction is achieved in many cases.[5]

In our investigations on catalytic aldol addition we observed an activation of the aldehyde in the absence of the ene component (ketone): under the reaction conditions described ($LiClO_4$, Ti(O*t*Bu)$_4$, α-hydroxy acids, RT) the aldehydes themselves react with the ligands of the Ti(O*t*Bu)$_4$ in an alkylation-type reaction. After the initial conversion of benzaldehyde and Ti(O*t*Bu)$_4$ the *meso* compound **1a**, the *anti* triol **2a**, and the monoaddition product **3a** (Scheme 1) were isolated. The structure of the compounds was determined by nuclear Overhauser enhancement (NOE) difference measurements.[6] By the addition of D-mandelic acid in this experiment the *anti*-triol **2a** was obtained in enantiomeric excesses of >85%,[7] whereas in contrast the diol **3a** was isolated as the racemate. (The *meso* compound **1a** is optically inactive.)

The formation of compounds **1a**, **2a**, and **3a** is dependent upon the amount of D-mandelic acid used. With one

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