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$[(OC)_5Cr{=}BSi(SiMe_3)_3]$: A Terminal Borylene Complex with an Electronically Unsaturated Boron Atom**

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Dedicated to Professor Gerhard E. Herberich on the occasion of his 65th birthday

Stable molecules with both electronically and coordinatively unsaturated boron atoms are extremely rare and restricted to a few methyleneboranes of the type $(Me_3Si)_2C{=}BR$ (R = Me, *t*Bu, 2,3,5,6-tetramethylphenyl, 2,4,6-trimethylphenyl).[1a–e] The chemical and structural properties of such alkyl- and aryl(alkylidene)boranes are decisively determined by the low coordination number and the electron deficiency at the boron center.

A similar bonding situation for boron is found in terminal borylene complexes of the type $[L_xM{=}BR]$ (R = alkyl, aryl, silyl). Owing to their significance[2] for the understanding of metal – boron interactions, alkyl- and arylborylene complexes have been already subject to several theoretical studies.[3a–e] On the basis of ab initio calculations it appears to be generally accepted that these compounds exhibit a stronger metal-to-boron π-backbonding than corresponding borylene complexes $[L_xM{=}B{=}X]$ ($X = NR_2$, F)[4a,b] in which electron deficiency at the boron center is relieved by π interaction with X. Experimental evidence for a complex $[L_xM{=}B{-}R]$ in which R is not a π donor, however, has yet to be reported.

In the course of our investigations on both bridged and terminal borylene complexes,[5a–i] we recently reported on compounds of the type $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (**1a**, **b**; M = Cr, W). These aminoborylene complexes were obtained either by direct salt elimination reactions[6] or alternatively, in the case of **1a**, by photochemically induced borylene transfer,[7] and represent the only compounds of this type comprising two-coordinate and hence, coordinatively unsaturated boron centers. The boron atom, however, is electronically stabilized by a π-donating amino ligand. Apart from **1a**, **b** only two structurally authentic terminal borylene complexes have been reported, which comprise, however, saturated boron atoms in higher coordination numbers of three and six, respectively.[8, 9]

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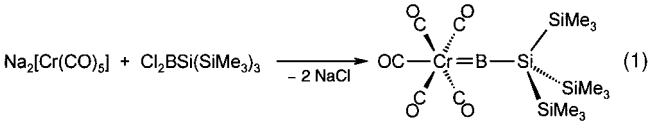
Herein we describe the synthesis and structural characterization of $[(OC)_5Cr{=}BSi(SiMe_3)_3]$ (**2**), which is the first borylene complex in which the boron center is both coordinatively and electronically unsaturated.

The title compound **2** was obtained by a salt elimination reaction according to Equation (1) and isolated as yellow crystals in 81% yield. The complex is very soluble in all



(1)

2

common aliphatic or aromatic hydrocarbons and only forms crystals from concentrated solutions at temperatures lower than $-50\,^{\circ}C$. In contrast to its rather stable amino analogue $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**1a**), the silylborylene complex **2** is extremely sensitive and shows significant decomposition in solution and even in the solid state after several hours at ambient temperature. The enhanced sensitivity of **2** is evidently due to the lack of a ligand-to-boron π interaction, as its steric shielding must be considered equal to or even larger than that in **1a**.

The most striking spectroscopic feature of **2** is the extremely low-field shifted ^{11}B NMR resonance signal at $\delta = 204.3$ in comparison to that for **1a** ($\delta = 92.3$), thus largely extending the known dispersion of the ^{11}B nucleus for classical boranes. Similarly low-field shifted resonances were reported for metal clusters comprising interstitial boron atoms, for example *cis*- and *trans*-$[Fe_4Rh_2(CO)_{16}B]^-$ ($\delta = 211$ and 205).[10a,b] The observed significant difference in the ^{11}B NMR spectroscopic data between **2** and **1a** could be expected for terminal borylene complexes in which the boron center is not part of a boron–ligand π system,[2] particularly if one compares the bridged amino- and alkylborylene complexes of the type $[(\mu\text{-BR})\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ ($R = NMe_2$, $\delta(^{11}B) = 103$; $R = t$Bu, $\delta(^{11}B) = 170$).[5a,b,f] ^1H and ^{13}C NMR spectra of **2** show single sets of signals for all Me and equatorial CO groups, which indicates free rotation about the boron–silicon single bond. Although the structural data support the assumption of a stronger Cr–B π-backbonding in the case of **2** (see below), the CO stretching frequencies are only slightly shifted to higher wavenumbers than those of **1a.**

Single crystals of **2** suitable for an X-ray structure analysis (Figure 1) were grown from hexane at $-78\,^{\circ}C$. The compound crystallizes in the space group $P3_2$ and the molecule adopts C_1 symmetry in the crystal. The molecular structure of **2** reveals some significant differences to that of the aminoborylene complex **1a**, which provides strong evidence for an increased chromium-to-boron π-backbonding. The Cr–B bond in **2** (187.8(10) pm) is 12 pm shorter than that in **1a** (199.6(6) pm), while the axial $Cr{-}C_{ax}$ bond (193.9(10) pm) is 3 pm longer than that in **1a** (190.8(6) pm). This *trans*-effect also becomes evident from the different intramolecular $Cr{-}C_{ax}$ and $Cr{-}C_{eq}$ distances: the $Cr{-}C_{ax}$ distance in **2** is almost 5 pm longer than

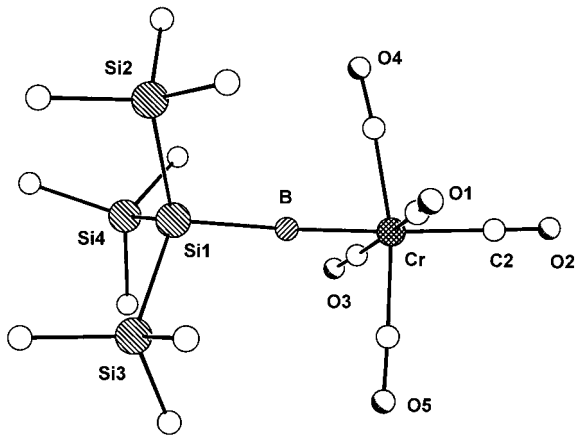


Figure 1. Structure of **2** in the crystal. Selected distances [Å] and angles [°]: Cr-B 1.878(10), B-Si(1) 1.998(10), Cr-B-Si(1) 176.9(5).

the average $Cr{-}C_{eq}$ value of 189.4 pm, while the $Cr{-}C_{ax}$ distance in **1a** resembles the average $Cr{-}C_{eq}$ value of 189.0 pm. A corresponding trend for M–B, $M{-}C_{ax}$, and $M{-}C_{eq}$ bonds was reported for the calculated structures of $[(OC)_4FeBMe]$ and $[(OC)_4FeB(\eta^5\text{-}C_5H_5)]$, which indicated stronger iron-to-boron backbonding in the case of the methylborylene complex.[3a] Additionally, the equatorial CO ligands in **2** show a somewhat stronger umbrella effect than those in **1a** which is indicated by the on average more acute $B{-}Cr{-}C_{eq}$ (**2**: 85°; **1a**: 88°) and $Cr{-}C_{eq}$-O angles (**2**: 176°; **1a**: 179°). Again, calculations on a series of compounds $[L_xM{-}ER]$ (E = B, Al, Ga, In, Tl) showed that a more pronounced umbrella effect indicates a stronger M–E bond.[3b] The aforementioned structural parameters for **2** strongly suggest that the electron deficiency of the boron center demands an enhanced Cr–B π-backbonding. The B–Si and Si–Si distances and the undistorted B-Si-Si angles provide no evidence for hyperconjugation, which is well known to relieve electron deficiency in (silylalkylidene)boranes $(Me_3Si)_2C{=}BR$ by formation of nonclassical $B{-}C{-}Si$ three-center, two-electron (3c–2e) bonds.[1e]

SCF calculations[12] on the parent molecule $[(OC)_5Cr{=}B\text{-}SiH_3]$ (**3**) and on its silane derivative $[(OC)_5Cr{=}BSi(SiH_3)_3]$ (**4**) were performed for staggered and eclipsed conformations of the $Cr(CO)_5$ moiety with respect to the SiR_3 group. For both molecules, the eclipsed form was found to be a minimum, and the staggered one to be a transition state through rotation of the SiR_3 group. The calculated geometries and chemical shifts (by GIAO) of **3** and **4** closely match the experimental data of **2**. The calculated bond lengths are generally slightly longer by 1–4 pm, and the carbonyl umbrella is more opened by 1–2° (Table 1). In particular, the extremely low-field

Table 1. Selected spectroscopic and structural data of **1a**, **2**, **3**, and **4**.

Compound	$\delta(^{11}B)$	$\delta(^{13}C_{ax})$	$\delta(^{13}C_{eq})$	Cr–B [Å]	B–Si/B–N [Å]	$Cr{-}C_{ax}$ [Å]	$Cr{-}C_{eq}$[a] [Å]
1a	92.3	218.0	217.6	1.996(6)	1.353(6)	1.908(6)	1.890
2	204.3	213.3	213.3	1.878(10)	1.998(10)	1.939(10)	1.894
3[b]	196.5	209.8	205.4[a]	1.875	2.026	1.978	1.919
4[b]	195.3	210.5	206.0[a]	1.875	2.026	1.978	1.919

[a] Average value. [b] Calculated values.

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shifted ^{11}B NMR resonance signal, the short Cr–B distance, and the *trans*-effect of the silylborylene ligand are reproduced by the calculations. The bonding situation in terms of frontier orbitals follows the known pattern for terminal borylene complexes:[3] the σ donation occurs through the interaction of the HOMO of the $BSiR_3$ ligand with the A_1-symmetric LUMO of the $Cr(CO)_5$ fragment, and the π-backdonation through the corresponding interaction of the doubly degenerate HOMOs of $Cr(CO)_5$ with the LUMO of the borylene unit. Inspection of the MOs in **4** gives no indication for a nonclassical B–Si–Si 3c–2e bond (hyperconjugation), which could relieve the electron deficiency of the boron center. Also, the Wiberg bond indices (WBI) for all three pairs of boron and terminal silicon atoms are close to zero. The WBI for the B–Cr bond (ca. 1) in conjunction with relatively high Mullikan charges on both atoms (B: 0.80; Cr: −1.73) corroborates, as known from other examples, the strongly ionic character of the B–Cr bond.[3]

Experimental Section

2: In analogy to the known synthesis of $Na_2[Cr(CO)_5]$,[13] a solution of $[Me_3NCr(CO)_5]$[14] (0.97 g, 3.86 mmol) in THF (25 mL) was cooled to −78 °C, and a solution of $NaC_{10}H_8$ (46.2 mL, 0.2 M in THF) was added dropwise over a period of 20 min. When the addition was completed all volatile materials were removed under high vacuum (0 °C/0.001 Torr). The remaining yellow solid was treated with Et_2O (50 mL) at 0 °C, filtered, and washed with Et_2O (2 × 10 mL). The light yellow product was dried briefly under high vacuum and subsequently suspended in toluene (30 mL) at −78 °C. A solution of $Cl_2BSi(SiMe_3)_3$[15] (1.05 g, 3.20 mmol) in toluene (5 mL) was added dropwise by a syringe. Within 30 min the suspension was allowed to come to ambient temperature and the color of the reaction mixture turned from orange to dark brown. After the reaction mixture had been stirred for 10 min at ambient temperature, all volatile materials were removed under high vacuum (0.001 Torr). The dark brown residue was treated with hexane (30 mL), filtered, and the remaining solid was washed with hexane (2 × 5 mL). The filtrate was concentrated under vacuum to 10 mL and stored at −80 °C. After 48 h $[(OC)_5Cr{=}BSi(SiMe_3)_3]$ (1.51 g, 2.59 mmol, 80.9 %) was obtained as yellow crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.34$ (s; $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 204.3$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.6$ ($SiMe_3$), 213.3 (CO); IR (toluene): $\tilde{\nu} = 2066$, 2014, 1982, 1952 cm^{-1} (CO); elemental analysis (%) calcd for $C_{14}H_{27}BCrO_5Si_4$: C 37.32, H 6.04; found: C 36.77, H 5.90.

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[11] Crystal structure determination of **2**: $C_{14}H_{27}BCrO_5Si_4$, $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å, graphite monochromator), $T = 203(2)$ K, $0.2 \times 0.1 \times 0.1$ mm, trigonal, space group $P3_2$; $a = 9.659(3)$, $b = 9.659(3)$, $c = 23.235(11)$ Å, $V = 1877.5(12)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.195$ g cm^{-1}, $\mu(Mo_{K\alpha}) = 6.66$ cm^{-1}, $F(000) = 708$, 9777 measured reflections ($2.43 < \theta < 25.09$), 4406 independent reflections with $I > \sigma(I)$, 226 variables. Transmission factors: T_{max}: 1.00000, T_{min}: 0.744666. The intensities were measured with a Bruker-axs-SMART diffractometer. The structure was solved by direct methods (SHELXS 97). Refinements were carried out with the SHELXL-97 package. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined isotropically in riding mode (C–H = 98 pm, $U_{iso}(H) = 1.3\ U_{iso}(C)$). All refinements were made by full-matrix least-squares on F^2. $R1$ ($I > 2\sigma(I)$) = 0.0627, $wR2$ (all data) = 0.1596; $GOF = 0.985$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163495. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] SCF Calculations: The GAUSSIAN 98 package, run on a cluster of workstations was applied for all SCF calculations. The total energies E_h and the ZPVE (in Hartrees, in parentheses) all calculated on B3LYP level with 6-31G(d,p) basis set for nonmetal atoms and CEP-31G for chromium are as follows: $(CO)_5CrBSiH_3$: eclipsed −969.371737 (0.07050), staggered −969.371677 (0.07047); $(CO)_5CrB$-$Si(SiH_3)_3$: eclipsed −1841.480006 (0.122903), staggered −1841.479976 (0.122852); 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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