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Borylene Reduction

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Reductive Borylene–CO Coupling with a Bulky Arylborylene Complex**

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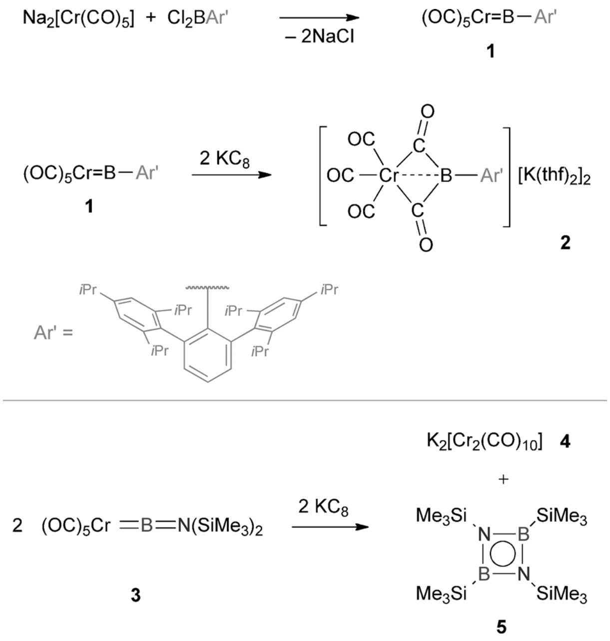
Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

Walter Hieber's seminal work on metal carbonyl compounds not only established these complexes as one of the most important classes of organometallics, but also disclosed important reactivity patterns, most notably the Hieber base reaction, which gives access to anionic carbonyl complexes.[1] Such carbonylates, for example, $[Fe(CO)_4]^{2-}$ (Collman's reagent)[2] or $[Cr(CO)_5]^{2-}$,[3] have found widespread application in organic and organometallic synthesis, especially for the formation of transition-metal–element bonds, yielding for example, silylene ($L_xM{=}SiR_2$),[4] gallylene ($L_xM{\equiv}GaR$),[5] or borylene complexes.[6] The latter have attracted considerable interest in the past decade owing to their isoelectronic relationship to carbonyls[7] and their importance for borylene-based functionalizations, such as transmetallation,[8] transfer to unsaturated organic substrates,[9] coupling reactions,[10] or metathesis.[11] Despite the increasing number of reactivity patterns emerging from borylene complexes, and the significance of the aforementioned carbonylates, it is surprising that no attempts have been made towards corresponding anionic borylene complexes. Herein we report the generation of a unique bulky terminal arylborylene $[(OC)_5Cr(BAr')]$ ($Ar' = 2,6\text{-}(2,4,6\text{-}i\mathrm{Pr}_3C_6H_2)_2C_6H_3$) and compare aspects of its bonding and unprecedented reduction chemistry with the better-known aminoborylene $[(OC)_5Cr\{BN(SiMe_3)_2\}]$.[6a]



Scheme 1. Top: synthesis and reduction of borylene complex **1**; bottom: reduction of borylene complex **3**.

Reaction of $Na_2[Cr(CO)_5]$ with Cl_2BAr' in a facile salt elimination reaction led to the formation and subsequent isolation of $[(OC)_5Cr(BAr')]$ as a yellow crystalline solid in 75 % yield (Scheme 1). The route was also successful with Br_2BAr' but led to lower yields of isolated product (23 %). The ^{11}B NMR shift of the compound was identified at $\delta_B = 150$ ppm, falling between values acquired for chromium amino- ($\delta_B = 92$ ppm)[6a] and hypersilylborylenes ($\delta_B = 204$ ppm).[12] It is also very close to the shifts reported for *trans*-$[(Me_3P)(OC)_3Fe(BDur)]$ ($\delta_B = 146$ ppm)[13] and $[\eta^5\text{-}C_5Me_5Fe(CO)_2(BMes)]^+[BAr^f_4]^-$ ($\delta_B = 145$ ppm)[6c] complexes (Dur = 2,3,4,5-Me_4C_6H, Mes = mesityl; $Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$. To confirm the identity of **1**, its molecular structure was determined by single-crystal X-ray diffraction (Figure 1).[23] Complex **1** adopts C_{2v} symmetry in the crystal. The Cr1–B1 distance is 190.4(5) pm, and the Cr1-B1-C1 angle of 175.9(4)° shows that there is a very slight deviation from a linear arrangement for these three atoms.

The susceptibility of the boron center in borylene complexes to nucleophilic attack is well-documented and can result in the cleavage of the M–B bond.[10a,11a,b,14] Similar reactivity has been observed in isoelectronic metal carbyne chemistry, with the other possibility being an initial attack at the metal center.[15] With this in mind, we decided to investigate the reactivity of the title compound toward the addition of electrons and compare its reduction chemistry with the aminoborylene $[(OC)_5Cr\{BN(SiMe_3)_2\}]$. Reaction of **1** with 2 equiv of KC_8 in THF gave a vibrant red compound upon work-up and isolation in quantitative yield with no identified side products (Scheme 1). This compound was found to be extremely air- and moisture-sensitive and only stable in the presence of THF. ^{11}B NMR spectroscopy gave a single signal at $\delta_B = 23$ ppm, which is in the typical range for 3/4 coordinate boron and the ^1H NMR spectrum indicated

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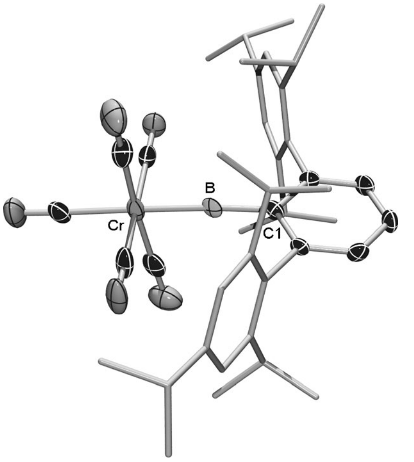

Figure 1. Molecular structure of $[(OC)_5Cr(BAr')]$ **1**. Ellipsoids are set at 50% probability. All hydrogen atoms have been omitted and some groups have been simplified for clarity. The atom labels differ from those reported in the CIF file, and only one of two independent units is shown here. Selected distances [pm] and angles [°]: Cr1–B1 190.4(5), B1–C1 153.7(6); Cr1-B1-C1 175.9(4).

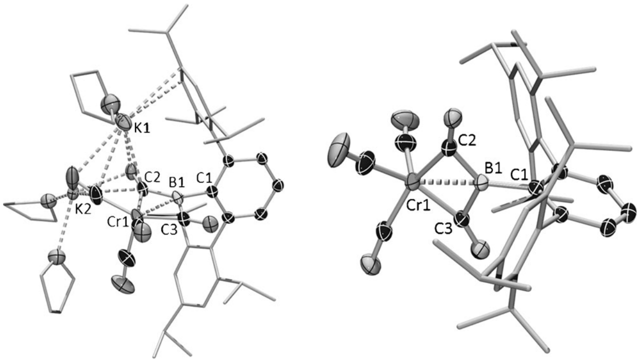

Figure 2. Molecular structure of the dianion of **2**. One of the three aggregate subunits is shown. The atom labels differ from those reported in the CIF file. Left: representation showing potassium cations and THF molecules. Right: view of the dianionic fragment with cations not shown. Ellipsoids are set at 50% probability. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°] for this fragment: Cr1–B1 206.7(4), B1–C1 157.4(5), B1–C2 155.5(5), B1–C3 163.8(5), Cr1–C2 193.9(4), Cr1–C3 188.4(4); C1-B1-C2 130.1(4), C1-B1-C3 107.2(3), C2-B1-C3 122.6(3).

a clean conversion with a new set of ligand peaks. Analysis by IR spectroscopy showed the presence of several CO vibrations at values different from the typical metal pentacarbonyl fragment ($\tilde{\nu} = 1907, 1766, 1645, 1514\ \text{cm}^{-1}$) and the identity of the product was determined to be $[K(thf)_2]_2[(OC)_3Cr\{\eta^3\text{-}C(O)B(Ar')C(O)\}]$ (**2**) by a single-crystal X-ray diffraction study.[23]

Remarkably, and in contrast to the result of reduction of well-known Group 6 hexacarbonyl $[Cr(CO)_6]$[16] or the analogous amine derivative $[(CO)_5Cr(NMe_3)]$,[17] the molecular structure of **2** revealed no loss of metal-bound ligands. The unit cell contains three subunits, each of which feature a common $[(OC)_3Cr\{\eta^3\text{-}C(O)B(Ar')C(O)\}]^{2-}$ dianion core motif (Figure 2). All five CO moieties are retained with three residing in a terminal fashion, while the other two bridge to the arylborylene fragment. The average Cr1–B1 distance (206.7 pm) is longer than that found in **1** (190.4(5) pm). The observed heterocoupling between a borylene and carbonyl ligands is one of only a few characterized examples,[10a] and indeed is unprecedented for chromium. The B–CO bonds (150.4–170.4 pm) in **2** are significantly shorter than similar interactions reported for several manganese-based compounds,[10a,18] while the average B–C bond between boron and the aromatic ring of the terphenyl ligand in **2** (157.5 pm) is slightly longer than the equivalent bond in **1** (153.7(6) pm). The dianion is closely associated with the two potassium cations through the carbon and oxygen atoms of both bridging and non-bridging carbonyl ligands, as well as the central phenyl ring of the Ar′ substituent. Overall these anion–cation interactions lead to a 1D network in the crystal.

By applying the common formalisms and considering the boron-bound COs as two anionic ligands (that is, a "bis(acyl)" ligand), we would come to a valence electron count of 16 and a formal oxidation state of Cr of zero. However, the real electronic structure of the species is certainly more complex, particularly in terms of the details of the Cr–B interaction, and therefore we attempted to elucidate the electronic structure by DFT methods. However, owing to the known deficiencies of DFT methods when calculating highly negatively charged species, this was not successful. Taking into account the rather small Cr–B separation of 206.7 pm, which is only slightly longer than typical 3d metal–boron single bonds,[7] we assume a non-negligible Cr–B interaction. This is further supported by our DFT calculations on complex **1** in its excited triplet state, which shows a structure very similar to that of **2** (see the Supporting Information for further details).

Analogously, reduction of the aminoborylene complex $[(OC)_5Cr\{BN(SiMe_3)_2\}]$ (**3**) by KC_8 was carried out in $[D_8]$THF (Scheme 1). A nearly quantitative formation of a new boron-containing species was indicated by the new resonance at $\delta_B = 48$ ppm in the ^{11}B NMR spectrum and two singlet peaks at $\delta_H = 0.06$ and -0.03 ppm in a ratio of approximately 1:1 in the ^{1}H NMR spectrum. Remarkably, these distinct NMR spectroscopic features, in particular the ^{11}B resonance, implied a different chemical response of **3** compared with **1** upon reduction. After work-up, colorless crystals of the boron-free dinuclear complex $K_2[Cr_2(CO)_{10}]\cdot(THF)_2\cdot([18]crown\text{-}6)_2$ **4** were isolated in a yield of 70%. This finding suggested a selective liberation of the borylene moiety $\mathbf{:}BN(SiMe_3)_2$, which can nevertheless only be regarded as transient species. However, previous computational studies revealed that one hydrogen atom of borylnitrene $\mathbf{:}NBH_2$ could migrate between B and N with the hydrogen atom adopting a bridging position in transition state.[19] Thus, we assume an analogous rearrangement of the borylene unit $\mathbf{:}BN(SiMe_3)_2$ with migration of one $SiMe_3$ group from N to the adjacent B, leading to a side-on coordinated iminoborane, which might subsequently undergo the established iminoborane cyclodimerization.[20] Indeed, considering the influence of boron-bound silyl groups on ^{11}B NMR chemical shifts (for example, $\delta_B = 65$ ppm for $Cl_2B(CMe_2iPr)$[21] and $\delta_B = 79$ ppm for $Cl_2B(SiMe_3)$[22]), the ^{11}B NMR resonance at $\delta_B = 48$ ppm,[20b] as well as the ^{1}H NMR spectrum (see above) are consistent with the postulated diazadiboretidine *cyclo*-$B_2N_2(SiMe_3)_4$ (**5**).

Unfortunately, owing to its oily consistency and poor stability (slow decomposition during the work-up), all attempts to isolate the boron-containing species from the mother liquor failed. Investigation by GC-MS showed the oxidized product $B_2N_2(SiMe_3)_4O$, which could be explained by the lability of the B−Si bond.

The gas-phase structures of **1** and **3** were optimized within the Kohn–Sham density functional theory (DFT) without simplification of the molecules. Selected geometrical parameters, bond orders, and also molecular electrostatic potentials (MEP) mapped on a plane containing the *trans*-CO-Cr-B-C(Ar) segment for **1** are indicated in the Supporting Information, Figure S3. The bonding and electronic structure of **1** as well as the computational details are described in the Supporting Information.

One notable difference between **1** and **3** is their respective behavior upon reduction: whereas liberation of the boron-containing moiety occurs in **3**, in the case of **1** the reactivity is limited to a structural rearrangement, namely the migration of two carbonyl groups to a bridging position between the chromium and the boron (see above). An explanation of these observations is rooted in the electronic structure of each system. Indeed, the LUMO of **1** is essentially a nonbonding orbital, one that is highly centered on the [BAr′] side of the complex (Figure 3). When this [BAr′] moiety is considered as an independent fragment, its LUMO is quasi-isoenergetic with respect to the LUMO of the molecule (Supporting Information, Figure S4), that is, it is nonbonding. Therefore, subsequent population (for example through one-/two-electron reduction or through excitation to the triplet state) of this orbital does not lead to facile liberation of the borylene unit, in contrast to the case of the related aminoborylene system (see below). Rather, population of this orbital leads to a) migration of the two transverse carbonyl groups into a bridging position ($2\,e^-$ reduction (Figure 2) or excitation to the lowest triplet ^3A state (Supporting Information, Figure S5)); or b) an intermediate structure in which the transverse carbonyl groups adopt a bowed structure ($1\,e^-$ reduction (Supporting Information, Figure S5)); further computational characterization of the bridged species can be found in the Supporting Information. In any case, the empty boron p orbital, which is coplanar with the two CO ligands, acts as an efficient electron acceptor for the two equatorial CO moieties. On the other hand, the LUMO of **3** is not a nonbonding level and is extended over the whole of the molecule (Figure 3; Supporting Information, Figure S6), in contrast to **1** in which it is almost exclusively centered on the arylborylene ligand. Thus it can be expected that any addition of electrons to the system will likely induce a Cr−B bond cleavage, as was described above. Importantly, energy minimization calculations on the $[(OC)_5Cr\{BN(SiMe_3)_2\}]^-$ anion lead to a structure corresponding to the migration of one $SiMe_3$ to the adjacent boron atom (Figure 4). It is worth noting that the experimental detection of $K_2[Cr_2(CO)_{10}]$ (**4**) and *cyclo*-$[B_2N_2(SiMe_3)_4]$ (**5**) is in line with an overall $2\,e^-$ reduction, affording for the first time the observation of intramolecular B-N-Si ring formation in the coordination sphere of Cr. Lastly, calculation of the triplet state of $[(OC)_5Cr\{BN(SiMe_3)_2\}]$ shows a migration of CO units towards a bridging position between the Cr and B, akin to the resulting structure of $[(OC)_5Cr(BAr')]$ upon similar treatment (see above), clearly demonstrating reactivity of the boron-centered p orbital as an acceptor and lending the boron atom transition-metal-like properties.

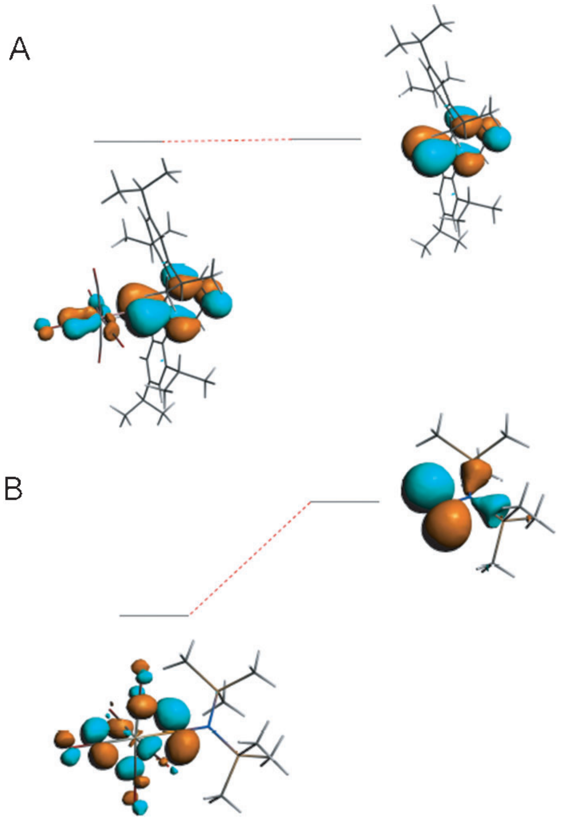

Figure 3. A: The LUMO of **1** (left) and its energetic relationship with the [BAr′] fragment (right). B: Analogously, the energetic relationship of **3** (left) with the $[BN(SiMe_3)_2]$ fragment. In the case of the former the LUMO is non-bonding whereas for the latter the LUMO is not iso-energetic with the constituent aminoborylene fragment.

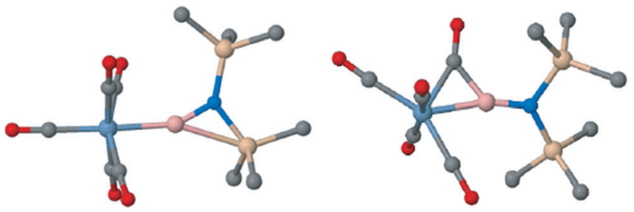

Figure 4. Calculated structure of $[(OC)_5Cr\{BN(SiMe_3)_2\}]^-$ (left) and the triplet $[(OC)_5Cr\{BN(SiMe_3)_2\}]$ (right). Pink: B; grey: C; dark blue: N; red: O; yellow: Si; light blue: Cr. Hydrogen atoms have been removed for clarity.

In conclusion, compound **2** was formed upon two-electron reduction of the bulky arylboylene complex **1**, with concomitant borylene–CO coupling. This reactivity can be partly attributed to the LUMO of **1**, which was found to be centered predominantly on the [BAr′] part of the complex. In contrast, reduction of the aminoborylene complex **3**, the LUMO of which comprises antibonding interactions spread all around its metal center, led to liberation of the boron-containing moiety from the chromium scaffold. While reduction of **3** mirrors the reactivity patterns seen for [Cr(CO)$_6$] and [(OC)$_5$Cr(NMe$_3$)], compound **2** exhibits a unique type of reactivity for this class of compound and shows that the reduction products of chromium borylenes might be selected by tuning the functionality at the boron center.

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[23] CCDC 937868 (**1**) and CCDC 937869 (**2**) 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.