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Borirene Ligands

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Trihapto Ligation of a Borirene to a Single Metal Atom: A Heterocyclic Analogue of the η^3-Cyclopropenyl Ligand**

Holger Braunschweig, Rian D. Dewhurst, Krzysztof Radacki, Christopher W. Tate, and Alfredo Vargas*

Abstract: *The first example of a complex containing an η^3-coordinated borirene ligand bound to a single metal atom was prepared by photolytic transfer of an arylborylene ligand to diphenylacetylene and loss of three CO ligands from the precursor. The η^3-borirene complex possesses a chromium(0) atom which is also bound to one phenyl group in an η^6 fashion. The complex was isolated in 15 % yield along with the corresponding metal-free borirene, which was isolated in 62 % yield. The bonding between the chromium center and the borirene ring was studied computationally by DFT methods.*

The cyclopropenylium cation, containing two π electrons delocalized over three p_π orbitals, is well-known for being the smallest aromatic hydrocarbon defined by Hückel's rule. Since their discovery by R. Breslow in 1957,[1] cyclopropenylium cations have been the subject of numerous investigations.[2] In contrast, the isoelectronic and isolobal neutral borirenes (Figure 1) have not received nearly as much attention, as their synthesis typically requires the tedious preparation of alkynylboranes and their subsequent rearrangement.[3]

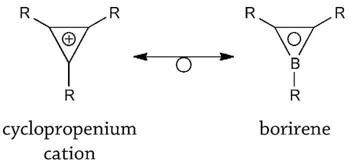

Figure 1. The isoelectronic relationship between a cyclopropenylium cation and a borirene.

Borirenes are of interest to our research group because their use as π-conjugated boron-containing structural components of materials is largely unexplored. We hope to use these heterocycles to advance the field of boron-containing functional materials for sensors, light-emitting devices, and electronic circuits.[4–6] In a recent advance in this area, the boron atoms of a number of borirenes were quaternized by addition of Lewis bases, such that the aromaticity could be switched on or off at will.[7] In addition, a facile and high-yielding route to borirenes involving photolytic transfer of borylene fragments from transition-metal borylene complexes to alkynes has emerged over the past decade, although the substituents at the boron center have thus far been limited to electron-rich amino and organometallic iron groups.[8]

While the cyclopropenylium cation can react with a host of low-valent metal centers to give (η^3-cyclopropenyl), (η^1-cyclopropenyl), and (η^3-oxocyclobutenyl) complexes,[2] the coordination chemistry of the borirenes is somewhat underdeveloped, and in our hands the *B*-aminoborirenes have so far shown no propensity towards coordination with metal centers. The two existing reports of borirene coordination complexes involve a compound in which a 2-methylborirene unit is bound to the three Fe centers of an $\{\mathrm{Fe_3(CO)_9}\}$ cluster core in an η^3:μ_3 fashion,[9] and our recent communication of a platinum complex in which a triarylborirene ligand is bound in a σ-bond manner through a boron–carbon single bond.[10] We report herein the first example of an η^3-borirene ligand bound to a single metal atom, and also show for the first time that it is possible to transfer an aryl-substituted borylene ligand (B-Ar′, $\mathrm{Ar'} = 2,6\text{-}(2,4,6\text{-}i\mathrm{Pr_3C_6H_2})_2\mathrm{C_6H_3}$) to an unsaturated organic substrate.

To this end, the bulky arylborylene complex **1**[11] was reacted with diphenylacetylene under photolytic conditions, consistently leading to an approximately 1:4 mixture of products **2** and **3**, as indicated by ^{1}H NMR spectroscopy (Figure 2). The crude product was washed with hexane then filtered, and product **2** was isolated as a red solid. Recrystallization at −30 °C gave single crystals suitable for X-ray diffraction and the molecular structure of **2** is shown in Figure 3. The complex features an η^3-$\mathrm{C_2B}$ borirene core bound to a $\{\mathrm{Cr(CO)_2}\}$ fragment, which itself is supported by an η^6-bound $2,4,6\text{-}i\mathrm{Pr_3C_6H_2}$ arm of the terphenyl ligand. The structure can be viewed as a classical arene piano-stool-type complex, in which one of the three CO "legs" has been replaced by a formally two-electron borirene ligand. The free borirene **3**, identified by a characteristic ^{11}B NMR shift of 33.0 ppm, was isolated as colorless crystals in high yield from the hexane filtrate of the mixture and a single-crystal X-ray

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[*] Prof. Dr. H. Braunschweig, Dr. R. D. Dewhurst, Dr. K. Radacki, Dr. C. W. Tate, Dr. A. Vargas
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: h.braunschweig@uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/Braunschweig/
Dr. A. Vargas
Department of Chemistry, School of Life Sciences
University of Sussex, Brighton BN1 9QJ, Sussex (UK)

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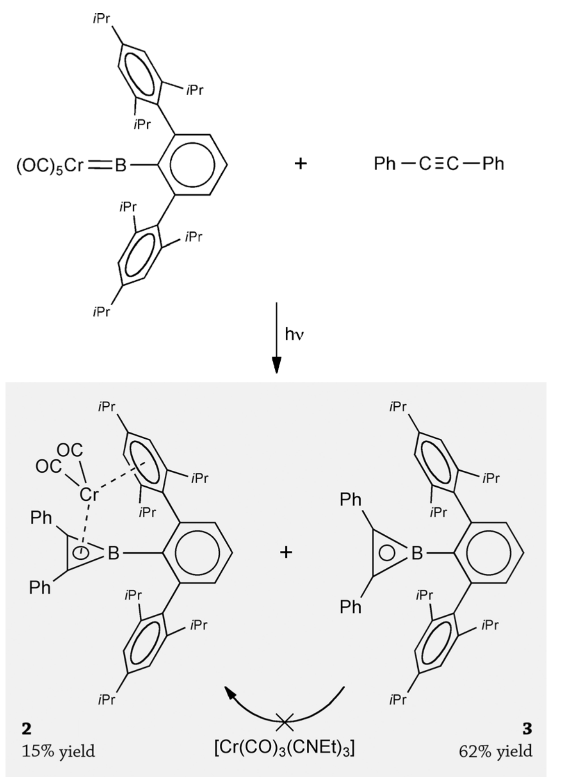

Figure 2. Photolytic reaction of **1** with diphenylacetylene to give the η^3-bound borirene **2** and free borirene **3**.

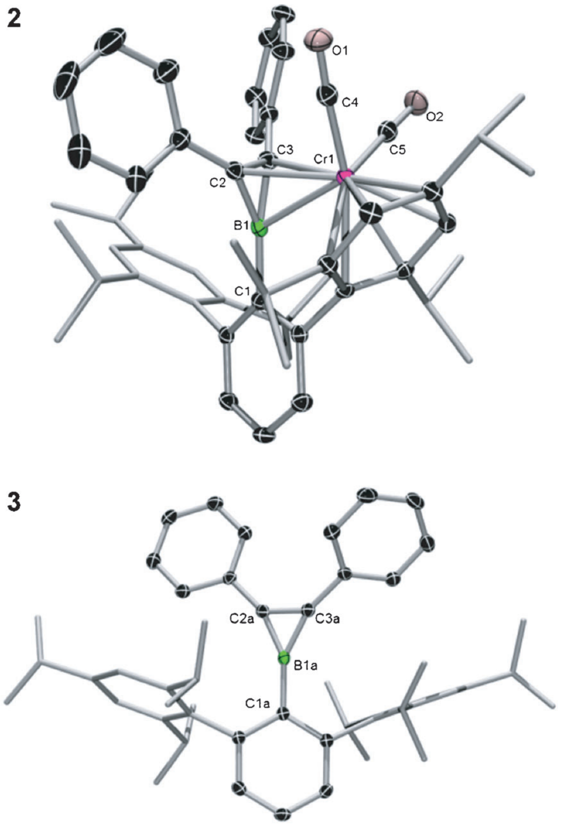

Figure 3. Molecular structures of **2** and **3**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted and some groups have been simplified for clarity. The atom labels of **2** differ from those reported in the CIF file and only one of two independent units is shown here. Selected distances [pm] and angles [°] for **2**: B1–C1 155.2(3), B1–C2 148.6(3), B1–C3 149.9(3), C2–C3 141.8(3), B1–Cr1 246.0(3), C2–Cr1 235.5(2), C3–Cr1 226.1(2), Cr1–C4 182.2(2), C4–O1 116.1(3), Cr1–C5 182.7(2), C5–O2 116.0(3); Cr2-B1-C3 56.7(2), B1-C2-C3 62.1(2), B1-C3-C2 61.2(2), C4-Cr1-C5 83.1(1). For **3**: B1a–C1a 155.3(2), B1a–C2a 147.6(2), B1a–C3a 147.8(2), C2a–C3a 136.1(2); C2a-B1a-C3a 54.9(1), B1a-C2a-C3a 62.7(1), B1a-C3a-C2a 62.5(1).

determination allows a direct comparison of the "free" and η^3-bound C_2B rings (Figure 3).

The central phenyl ring of the terphenyl group of **2** is tilted by 68.6° relative to the borirene ring, while that of **3** is tilted only slightly (32.0°). Whereas in **3** the phenyl groups of the borirene are found in the BC_2 ring plane, in **2** these are folded back to accommodate a bonding interaction with {Cr(CO)$_2$}. The borirene C–C bond of **3** (136.1(2) pm) is much shorter than that of **2** (141.8(3) pm). The former bond length is in general shorter than values recorded for transition-metal η^3-cyclopropenyl complexes,[12] and both the values of **2** and **3** are shorter than that of the trinuclear η^3:μ_3 borirene complex described by Fehlner (150(1) pm).[9] Similarly, the endocyclic B–C distances in **2** (148.6(3), 149.9(3) pm) are marginally longer than those of the free borirene **3** (147.6(2), 147.8(2) pm), but are still markedly shorter than those of Fehlner's complex (159.6(15), 159.7(15) pm). The fact that the borirene ring of **2** is significantly smaller than that in the η^3:μ_3 borirene complex of Fehlner is presumably due to the lower number of coordinated metals as well as the lower electron density of Cr^0 compared to Fe^0. At 246.0(3) pm, the Cr1–B1 distance of **2** is notably longer than reported metal–borirene bonds.[9,10] This is consistent with the very different bonding situations represented in these compounds. The Cr–C distances are not unusual when compared with cyclopropenyl–metal interactions.

Additional characteristic data for **2** include a new set of borirene peaks in the ^{1}H NMR spectrum and a ^{13}C NMR signal for the carbonyl ligands found at 244.8 ppm. Three strong metal–carbonyl IR bands were also identified at 1901, 1863, 1844 cm^{-1}, appearing at lower frequencies than those described for complexes of the type [M(η^3-cyclopropenyl)(η^5-C_5H_5)(CO)$_2$] (where M = Mo, W).[12a] No signal was observed in the ^{11}B NMR spectrum of **2**.

Interestingly, complex **2** can also be thought of as a snapshot of the borylene-transfer process, providing a picture of the situation between the presumed complexation of the diphenylacetylene to the borylene precursor and liberation of the free borirene. It appears, from our attempts, that it is not possible to synthesize **2** by reaction of **3** with [Cr(CO)$_3$(EtCN)$_3$] under thermal or photolytic conditions; thus the route reported here remains the only one to mononuclear η^3-borirene metal complexes at present.

As complex **2** is an unprecedented species in which an η^3-borirene ligand is bound to a single metal atom, its bonding was studied and the corresponding physicochemical basis was elucidated with the aid of the Kohn–Sham density functional theory (DFT). Geometry optimization and bonding analysis were conducted at the OLYP/TZP and B3LYP/6-311G* levels of theory. A first useful comparison is that of the bonding energetics of $[(\eta^6\text{-}C_6H_3i\text{Pr}_3)\text{Cr(CO)}_3]$ (**2a**) and of η^3-borirene complex **2** in the framework of the so-called EDA formalism, in which the $\{\text{Cr(CO)}_3\}$ fragment is made to interact with the $\{C_6H_3i\text{Pr}_3\}$ fragment in **2a**, and the $\{\text{Cr(CO)}_2\}$ fragment with **3** in complex **2**. Calculated structures of **2** and **2a** are shown in Figure 4.

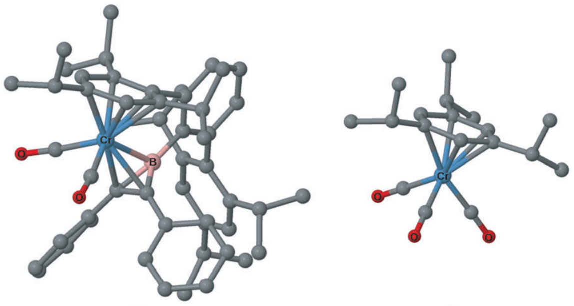

Figure 4. Calculated structures of **2** and **2a**.

Three of the useful interactions that are quantified by the EDA method include the attractive electrostatic and orbital interactions and the repulsive Pauli interaction. Interestingly, for both systems, the repulsive portion is equal to 77 % of the total attractive interaction in absolute value; furthermore, in **2** all of the bonding energy components are systematically larger than those in **2a** (electrostatic: 50; orbital: 76; Pauli: 96; total bonding: 30 kcal mol^{-1} higher). More interestingly, the value of each of the components is systematically higher in **2** than in **2a** by the same factor of 1.6; in other words, considering that the electrostatic metal–aryl interaction does not significantly vary (the Cr atom does not change the oxidation number and furthermore such observation is in contrast to the characteristics of the known cation–quadrupole interactions),[13–15] the increase of the bonding energy can be almost entirely ascribed to the interaction of Cr with the borirene. This demonstrates that the borirene core does not merely replace one CO unit, but is also a much stronger ligand for Cr. This is in line with the fact that the average Cr–C$^{\text{Ar}}$ distance is nearly identical for both **2a** and **2** (2.25 Å vs. 2.27 Å, respectively). Meanwhile, the Hirshfeld charge at the Cr center upon interaction of fragments is less negative in **2**; that is, there is less charge transfer to Cr even though there are only two CO ligands bound to the metal. This suggests that the borirene core efficiently stabilizes the Cr^0 center not necessarily through extensive charge donation and electrostatic interaction such as with a CO ligand but through the combination of several types of interactions.

In the gas phase, the exocyclic B–C bond length in **3** does not vary upon coordination of the $\{\text{Cr(CO)}_2\}$ fragment, while all of the borirene ring bonds are elongated, in particular the C=C bond. The Mayer bond orders (MBOs) for these bonds are along the same line, albeit they are more sensitive to the above-mentioned structural variation (MBOs: C_{exo}–B: 0.98→0.93; B–C_{endo}: 1.03→0.89 and 1.04→0.95; C_{endo}=C_{endo}: 1.37→0.91). The mapping of molecular electrostatic potential (MEP) based on natural charge in NBO basis (Figure 5) clearly shows that the C=C segment in the borirene moiety is most affected in terms of charge variation when the metal is inserted between the aryl arm and the borirene.

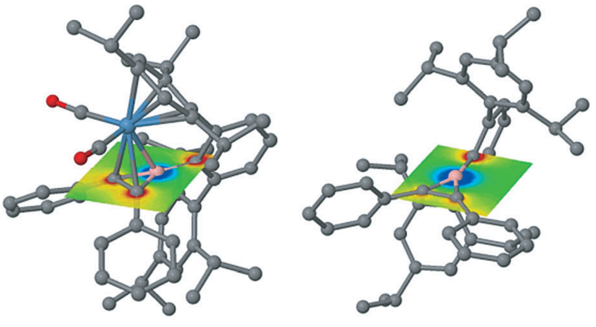

Figure 5. Mapping of the molecular electrostatic potential on the borirene plane for **3** and **2**. Red: negative, blue: positive.

The Hirshfeld charge on each of the borirene atoms shows greater sensitivity between the free and the *ansa* forms. While the carbon atoms lose charge density upon metalation, the boron atom becomes less positively charged, that is, it acquires charge density. These results converge to suggest a charge dynamics mechanism consisting of simultaneous charge donation and orbital interactions between the unsaturated carbon atoms (donors) and the chromium atom (acceptor), which is synergistically augmented by back-donation to the boron center. Modeling of chemically related compounds further confirms this bonding mechanism and is discussed in detail in the Supporting Information.

In conclusion, the first example of a π-bound mononuclear borirene complex (**2**) has been prepared by borylene transfer with an arylborylene complex, along with the free arylborirene (**3**) as the major product. The formation of **2** and **3** is also significant in that it shows for the first time that, like its more electron-rich and π-stabilized amino/organometallic counterparts, an aryl-substituted borylene ligand can be transferred from a transition-metal borylene.

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