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Synthesis and Structure of a Carbene-Stabilized Boraallene Coordinated to Rhodium

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Ⓢ *Supporting Information*

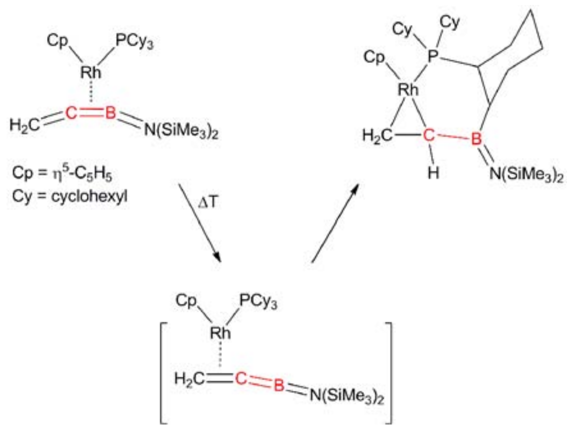
ABSTRACT: Reaction of the (B,C-η^2)-1-aza-2-borabutatriene rhodium complex **1** with 1,3-dimethylimidazol-2-ylidene) (*I*Me, **2**) afforded the N-heterocyclic carbene-stabilized (C,C-η^2)-1-boraallene rhodium complex **3**, which has been characterized in solution and by X-ray crystallography. Density functional theory calculations were carried out to elucidate the observed base-induced B−C to C−C coordination mode shift, which suggested that the latter is 25 kJ/mol lower in energy.

Boracumulenes have attracted interest not only because of their highly unsaturated structure but also because of their potential application in the synthesis of boron-based compounds, which have in recent years turned out to be of great importance in materials science.[1] However, this class of compounds is strongly limited to a few examples of amino-(methylene)boranes that adopt an allene-like structure with a linear C═B═N skeleton.[2] Here, the highly reactive B═C double bond is electronically (π-electron donation from the amino group) and kinetically stabilized by the bulky substituents. Moreover, 1-boraallenes $R_2C{=}C{=}BR'$ were only mentioned as transient intermediates at −120 °C.[3] In 2011, the group of Aldridge published the first iminoborylene complexes, $[L_xFe{=}B{=}N{=}CR_2]$, that feature the cumulenylidene ligands, prepared by halide abstraction from the corresponding neutral iron boryl complexes.[4a]

More recently, the first [3]boracumulene $H_2C{=}C{=}B{=}N(SiMe_3)_2$ was prepared by coupling of the isoelectronic vinylidene $:C{=}CH_2$ and aminoborylene $:BN(SiMe_3)_2$ moieties in the coordination sphere of rhodium.[4b] This highly unsaturated molecule is effectively stabilized by coordination of the central B−C bond to the transition metal, which is thermodynamically favored over C−C coordination according to density functional theory (DFT) calculations. However, a B−C to C−C coordination mode shift was observed under thermally forcing conditions, but the released B═C double bond underwent instantly an intramolecular C−H activation, leading to borylation of the PCy_3 ligand (Scheme 1).

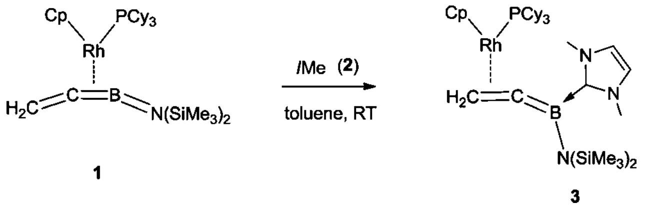
Because recent studies proved N-heterocyclic carbenes (NHCs) and related carbenes to be versatile stabilizing ligands for low-valent boron species such as free borylenes,[5] diborenes,[6] and diborynes,[6c] we were prompted to synthesize a NHC-stabilized neutral boraallene on the basis of our previous work. Herein we describe the synthesis of a carbene-stabilized 1-boraallene coordinated to a rhodium fragment.

Scheme 1. Thermally Induced Coordination Mode Change from B−C to C−C



When the NHC 1,3-dimethylimidazol-2-ylidene (*I*Me, **2**) was added to an equimolar amount of $[CpRh(PCy_3)\{(\eta^2\text{-B,C})\text{-}(SiMe_3)_2N{=}B{=}C{=}CH_2)\}]$ (**1**) in toluene at room temperature (Scheme 2), the color of the reaction mixture turned from light yellow to deep red immediately. The formation of a new boron- and phosphorus-containing species was indicated by the presence of a new resonance at δ_B 18 in the ^{11}B NMR spectrum and a new signal at δ_P 55.1 ($^1J_{Rh-P} = 208.7$ Hz) in the ^{31}P NMR spectrum. The remarkable high-field shift of the ^{11}B resonance by ca. 50 ppm in comparison to the starting material is most likely due to an increased coordination number of the boron center, which strongly suggests the formation of a carbene−boron adduct. After workup, single crystals were obtained upon storage of a saturated toluene/hexane solution at −30 °C for 2 weeks. The product **3** crystallizes in the triclinic space group $P\bar{1}$, and the

Scheme 2. Synthesis of the Carbene-Stabilized Boraallene Rhodium Complex 3



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results of X-ray diffraction analysis partially confirm our speculation (Figure 1). That is, the carbene–boron bond formation is accompanied by a B–C to C–C coordination mode change. Interestingly, while the ^{1}H NMR signals of the nitrogen-bound trimethylsilyl groups (δ_H 0.12) and of the nitrogen-bound methyl groups (δ_H 3.63) appear as broad singlets at ambient temperature, the ^{1}H NMR spectrum shows clearly two signals for $N(SiMe_3)_2$ (δ_H 0.38 and 0.00) and for NMe (δ_H 3.98 and 3.02) at −50 °C. This finding implies a certain degree of rotational barrier about the B–N1 and B–C3 bonds. Nevertheless, the significantly elongated B–N1 bond of 1.533(3) Å indicates the absence of substantial B–N π interaction. The B–C3 bond length of 1.585(3) Å is comparable with that of NHC-coordinated borabenzenes [1.596(2) Å] or 9-boraanthracenes [1.607(4) Å].[7] Hence, it can be anticipated that the rotational barrier around the B–N1 and B–C3 bonds is due to steric congestion between the bulky trimethylsilyl groups and the N-bound methyl groups of the carbene unit. The B–C1 bond length of 1.438(3) Å is comparable with those of noncoordinated amino(methylene)boranes [e.g., 1.424(3) Å],[2c] thus indicating the presence of a B═C double bond. In contrast to the previously reported thermally induced B–C to C–C coordination mode shift, the released B═C double now displays no reactivity toward the C–H bond of the coligand PCy_3, thus confirming the stabilizing effect of the carbene.

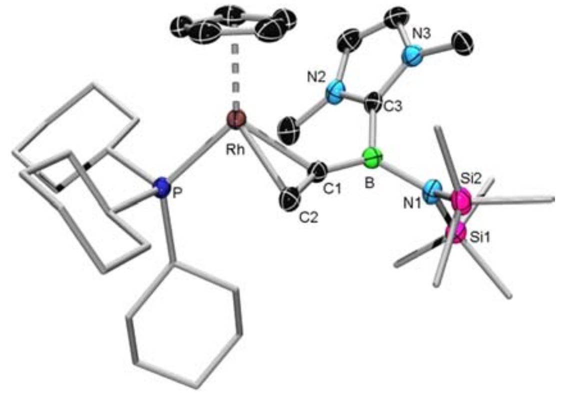

Figure 1. Molecular structure of **3**. Hydrogen atoms and ellipsoids of ligands have been omitted for clarity. Ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Rh–C2 2.126(2), Rh–C1 2.120(2), C1–C2 1.397(3), C1–B 1.438(3), B–C3 1.585(3), B–N1 1.533(3); C2–C1–B 146.0(2), Rh–C1–C2 71.0 (1), Rh–C1–B 135.1(2).

To gain further information about the observed B–C to C–C coordination mode shift, DFT calculations on the model species **CC** and **BC** were performed at the B3LYP level of theory (Figure 2). The calculated geometry of the model species **CC**, which is derived from the title compound **3** by formal exchange of the PCy_3 ligand by a PMe_3 group, is in excellent agreement with the results of the X-ray structure analysis. Not surprisingly, the calculations predict that the B–C coordination mode is 25 kJ/mol higher in energy, thus suggesting that the model species **CC** represents the thermodynamically favored product. Furthermore, the central B–C bond in the hypothetical isomer **BC** coordinates in a highly distorted η^2–π fashion, as indicated by the calculated geometry. That is, the Rh–B bond (2.381 Å) is significantly longer than the endocyclic Rh–C bond (2.053 Å). In contrast, the crystal structure of the aforementioned (carbene-free) (B,C-η^2)-1-aza-2-borabutatriene rhodium complex **1** reveals a highly symmetrical η^2-coordination of the B–C unit, as indicated by almost identical Rh–B [2.027(8) Å] and Rh–C [2.056(7) Å] bond lengths.[4]

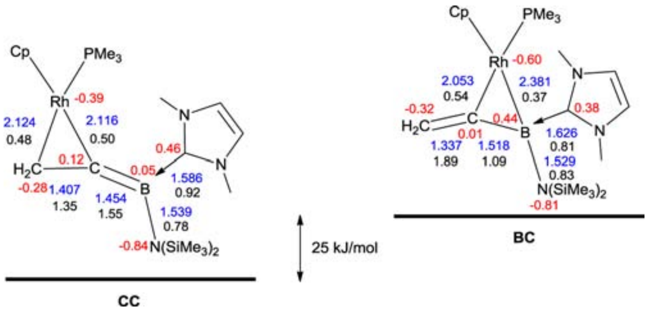

Figure 2. Results of DFT calculations on complexes **BC** and **CC**. Bond lengths are shown in blue (Å), Wiberg bond indices in black, and natural charges in red.

In this contribution, we have reported the synthesis and full characterization of a NHC-stabilized 1-boraallene coordinated to rhodium by the reaction of (B,C-η^2)-1-aza-2-borabutatriene rhodium complex **1** with **2**. The addition of the carbene to the boron center induces a shift of the coordinated allene from BC (**BC**) to a typical η^2-CC (**CC**) mode. Interestingly, the released B═C double bond is in this case effectively stabilized by the NHC and shows no subsequent intramolecular CH activation, as observed in previous studies. DFT calculations on model species **CC** and **BC** suggest that C–C coordination is thermodynamically favored over B–C coordination by 25 kJ/mol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, X-ray crystallographic details including a CIF file, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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