

Chemistry A European Journal



European Chemical Societies Publishing

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202003611

Link to VoR: https://doi.org/10.1002/chem.202003611

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Incorporation of Boron into Uranium Metallacycles: Synthesis, Structure and Reactivity of Boron-containing Uranacycles Derived from Bis(alkynyl)boranes

Wangyang Ma, Iskander Douair, Laurent Maron* and Qing Ye*

Abstract: The reaction of uranacyclopropene complex $(C_5Me_5)_2U[\eta^2-1,2-C_2(SiMe_3)_2]$ with B-aryl bis(alkynyl)borane PhB(C=CPh)_2 led to the first six-membered uranium metallaboracycle, while the reaction with B-amino bis(alkynyl)borane $(Me_3Si)_2NB(C=CPh)_2$ afforded an unexpected uranaborabicyclo[2.2.0] complex via [2+2] cycloaddition. The reaction with CuCl revealed the non-innocent property of the rearranged bis(alkynyl)boron species towards oxidant. The reactions with isocyanide DippNC: (Dipp = 2,6-iPr_2-C_6H_3) and isocyanate tBuNCO afforded the novel uranaborabicyclo[3.2.0] complexes. All new complexes have been structurally characterized. DFT calculations were performed to provide more insights into the electronic structures and the reaction mechanism.

The incorporation of one or more d- or f-block metal centers into the organic ring systems constitutes an important class of organometallic molecules, namely metallacycles. In general, giving deep insights into the electronic structure to help understanding the bonding mode, and developing new stoichiometric and catalytic reactions based on the metallacycles have been the focus of research.^[1] Nonetheless, although the actinide metallacyclopentadienes were reported in 1970s by Marks and co-workers^[2,3], the actinide metallacycle chemistry has been neglected for a long time. In recent years, the intense interest has been re-sparked thanks in large part to the rapid development of transition metal, in particular the group IV element metallacycle chemistry.^[4] Moreover, the resurgence is also driven by curiosity about the influence of the 5f orbitals on the bonding, as well as their potential use in catalysis, small molecule activation and C-H bond activation.^[5] In fact, the recent development of actinide metallacycle chemistry has benefited from mimicking the group IV analogues. In this context, various metallacyclopropenes,^[6] metallacyclopentadienes,[7] actinide metallacyclocumulenes^[8] and metallacyclopentyne^[9] were synthesized and have readily shown rich reaction chemistry. It should be noted, nonetheless, that the unsaturated actinide metallaheterocycles have been scarce.^[10] Most surprisingly, although three coordinate electron-deficient boron plays a pivotal role in construction of unsaturated heterocycles as functional molecular and polymeric materials, which have found wide applications including OLEDs, anion sensing, solar cells and electronic circuits,^[11] there is no single reported example of

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incorporation of three-coordinate boron into actinide metallacycles. It is believed that one important reason is the lack of applicable synthetic approach.

From a chemical composition point of view, it is well known that adding another $TiCp_2$ moiety to the titanacyclocumulene (I in Fig. 1) leads to the dinuclear zigzag-butadiene structure (II)^[12], while adding a borylene unit "BR" leads to the six-membered boat-like zirconaboracyclic structure (III)^[13]. Therefore, three essential questions need to be addressed: i) whether or not the II_{u,B} and III_{u,B} structures as depicted in Figure 1 could be realized upon adding a "BR" unit to I_{An}; ii) their structural features; iii) influence of 5f orbitals of uranium and empty p-orbital of boron on the bonding mode and the reactivity. As we recently demonstrated that the coordination of bis(alkynyl)boranes can serve as a facile synthetic approach to metallaboracycles,^[13] we decided to apply this strategy to construct the first actinide metallaboracycles.

Previous work



Figure 1. Selected d-block and f-block element metallacycles and metallaboracycles. I: group IV metallacyclocumulenes. II: group IV dinuclear zigzag-butadiene complexes. III: zirconium bis(alkynyl)borane complex featuring the boat-like zirconaboracyclic structure. I_{AN} : actinide metallacyclocumulenes. III._B and III_{U,B}: uranaboracycles in this work.

Herein, we report the first examples of reaction of uranium with bis(alkynyl)boranes, which lead to the unique fused uranium borabicyclic complexes ($II_{U,B}$) and the first uranabora-monocyclic complex ($III_{U,B}$). Moreover, we presented three different reactivity patterns of the 2-urana-5-borabicyclo[2.2.0]hexa-3,6-diene scaffold.

Scheme 1. Synthesis of 3a and 3b.



As depicted in Scheme 1, as an initial attempt, we chose the uranacyclopropene complex, $(C_5Me_5)_2U[\eta^2-1,2-C_2(SiMe_3)_2]$ 1 as the " $(C_5Me_5)_2U(II)$ " synthon. The reaction of 1 with *B*-aryl bis(alkynyl)borane PhB(C=CPh)_2 2a was performed in C_6D_6 at ambient temperature and monitored by ¹H- and ¹¹B-NMR spectroscopy. The ¹¹B-NMR spectra indicated the complete conversion of 2a (δ_B 46.5) into a new boron-containing species that displays a significantly downfield-shifted resonance at δ_B 76.4. The complex 3a could be isolated in excellent yield (95%) after easy work-up. The ¹H-NMR spectrum of 3a in C_6D_6 displayed two well-separated singlets for the C_5Me_5 rings (δ_H = 8.22 and 12.01) with an integration ratio of 15:15, thus suggesting that 3b should possess two nonequivalent C_5Me_5 groups in the solution phase.



Figure 2. Molecular structures of complex **3a** (top) and **3b** (bottom) in the solid state (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **3a**: U1-C1 2.60(2), U1-C2 2.67(2), U1-C3 2.64(2), U1-C4 2.55(2), C1-C2 1.25(3), C2-B1 1.51(3), B1-C3 1.58(4), C3-C4 1.22(3), C1-C2-B1 155(2), B1-C3-C4 156(2), C2-B1-C3 114(2). for **3b**: U1-C2 2.270(7), U1-C4 2.340(7), C1-C2 1.374(10), C2-C3 1.606(10), C3-C4 1.337(10), C3-B1 1.610(11), C1-B1 1.556(11), N1-B1 1.434(10), C2-U1-C4 69.7(3).

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The atom connectivity of **3a** was further confirmed by singlecrystal X-ray diffraction analysis (Figure 2, top). The geometry revealed an overall six-membered uranaboracyclic structure with the bis(alkynyl)borane ligand η^5 -coordinated to the uranium center, which resembles that of the our previously reported zirconium analogue **VII**.^[13] The complex **3a** crystallizes in the monoclinic space group P2₁/c. The asymmetric unit cell contains two nearly identical molecules of **3a**. Taking one molecule for example, the U1–C1 and U1–C4 bond lengths of 2.60(2) Å and 2.55(2) Å lie in the expected range of M_(An)–C(_{sp2}) σ –bond distances (2.3~2.6 Å) in actinide metallacycles.^[6-8] The C1–C2, C2–B1, B1–C3 and C3–C4 bond lengths (1.25(3) Å, 1.51(3) Å, 1.58(4) Å and 1.22(3) Å) are comparable with that of the zirconium analogue **VII**.

To provide further insight into the bonding situation in complexes 3a, density functional theory (DFT, B3PW91) calculations were carried out and the bonding was analyzed using Natural Bonding Orbitals (NBO), First of all, the unpaired spin density (see Supporting Information) is clearly located at the uranium center and its value of 2.17 is in line with a presence of a U(IV) system, indicating that the borane is formally doubly reduced. The latter is also corroborated by the NBO analysis. Indeed, two U-C bonds are found which are strongly polarized toward C (70%). This bonding interaction implies overlap between a sp hybrid orbital on C and a sdf on U (65% d, 25% f and 10% s). This is due to the double reduction of the conjugated divne. that implies the relocalization of two lone pairs on the two external carbon. The associated U-C Wiberg Bond Indexes (WBI) are 0.57/0.59 for two external carbon and 0.37/0.37 for the two internal one as expected for a delocalized structure. On the other hand, no direct U-B interaction observed but rather an indirect one that comes from the U-C bond as found in the HOMO (Figure 3). This explains that the Wiberg Bond Index (WBI) for U-B is 0.24, which however remains smaller than the U-C one.



Figure 3. 3D representation of the HOMO of 3a (this orbital is doubly occupied) that displays the U-C bonds.

In order to further study the electronic effect of the *B*-substituent on the U-B interaction, we performed the same reaction with the *B*-amino group $-N(SiMe_3)_2$ substituted bis(alkynyl)borane **2b** (Scheme 1). Surprisingly, the reaction resulted in the nearly quantitative formation of the unexpected uranaborabicyclo[2.2.0] complex **3b** (isolated yield 98%) at an elevated temperature (75 °C). In sharp contrast to complex **3a** with a six-membered monocyclic structure, complex **3b** features

a unique fused bicyclic structure with a bora-cyclobutene fourmembered ring fused to a urana-cyclobutene ring. The bis(alkynyl)borane **2b** is isomerized upon 2e-reduction by U(II), with the original $C(\alpha)$ atoms of the alkynyl groups being coupled.

Complex **3b** is stable under N₂ atmosphere, and can be stored as solids in a N₂ glove box for months without any sign of decomposition, yet **3b** is fairly air- and moisture-sensitive. Complex **3b** is easily soluble in most ordinary solvents such as pentane, diethyl ether and toluene. The singlet signal of SiMe₃ group at $\delta_{\rm H}$ 2.06 and the singlet peak of C₅Me₅ at $\delta_{\rm H}$ –1.53 with an intensity ratio of 18:30 suggested a symmetric structure of **3b** in the solution phase. The ¹¹B-NMR signal of **3b** displayed a slightly upfield-shifted resonance at 28.2 ppm with respect to that ($\delta_{\rm B}$ 31.3) of the free ligand **2b**.

Single crystals suitable for X-ray diffraction analysis were grown from saturated pentane solution of **3b**. The molecular structure of **3b** is shown in Figure 2 (bottom). Complex **3b** crystallizes in the monoclinic space group P2₁/c. The fused boracyclic ring is nearly planar (C1-C2-C3-C4 torsion angle: 177.5°). The U1-C2 and U1-C4 bond lengths (2.270(7) Å, 2.340(7) Å) are remarkably shorter than that of reported the $M_{(An)}-C_{(sp2)}$ distances (~2.5 Å).^[6-8] The C1-C2 and C3-C4 bond lengths (1.374(10) Å, 1.337(10) Å) are within the normal range of C=C bonds while the C2-C3 bond lengths (1.606(10) Å) are notably longer than the average value of a C-C single bond (~1.5 Å). The tricoordinated boron center adopts a trigonal planar geometry. The B-C bond lengths (1.556(11) Å, 1.610(11) Å) are as expected for a B-C single bond.

more stable by 8.6 kcal/mol than **3b#**. This is in line with the fact that complex **3b** is obtained rather than complex **3b#**.

With the novel and unique fused ring structure of uranaborabicyclo[2.2.0] complex **3b** in hand, we further tested its reactivity towards different types of inorganic/organic substrates, including CuCl, isocyanates and isocyanides.

The reaction of 3b with 2 equiv. of CuCl was conducted in C₆D₆ at 80 °C for 2 h, during which period the reaction was situ ¹H-NMR spectroscopy monitored by in with hexamethylbenzene as an internal standard. (Scheme 2a, See Supporting Information for more in situ NMR monitoring details). It clearly revealed the nearly complete consumption (>92%) of 3b $(d(C_5Me_5) - 1.53)$ and the formation of $(C_5Me_5)_2UCI_2$ $(d(C_5Me_5))_2UCI_2$ 13.49) and the free bis(alkynyl)borane ligand 2b (d(SiMe₃) 0.51). The uranium center remains its +IV oxidation state, while the Cu(I) in CuCl is reduced to copper black and the Cl⁻ anions are transferred to uranium. Apparently, the electrons transferred to Cu(I) derive from the dianionic variant of bis(alkvnvl)borane. The loss of two electrons leads to the cleavage of the bridged C2-C3 σ -bond^[14] and the regeneration of the original bis(alkynyl)borane 2b. Therefore, the rearranged bis(alkynyl)boron ligand in complex 3b is chemically non-innocent and acts as electron shuttle for multielectron transfer process. Similarly, the reaction of 3a with 2 equiv. of CuCl leads to the formation of (C5Me5)2UCl2 and regeneration of the free bis(alkynyl)borane ligand 2a.

Scheme 2. The reactivity of uranaborabicyclo[2.2.0] complex **3b** with CuCl, isocyanate **BuNCO**, and isocyanide DippNC:.

(a) + 2 CuC

CoDo 80 °C 2 H

(b) + *t*Bu-N=C=O Hexane, r.t., 2 h

(c) + Dipp-NC

Hexane, r.t., 12 h

SiMe:

siMe₂

5

3b



Figure 4. Calculated reaction barrier on the formation pathway of complex 3b.

Alike complex 3a, DFT calculations were also carried out to provide further insight into the bonding situation in complexes 3b. The unpaired spin density (2.13) is consistent with a U(IV) system (See Supporting Information). The NBO clearly shows that two U-C polarized covalent bond are present (75% C-25% U) involving overlap between a sp hybrid on C and a sdf on U (11% s, 53% d and 36% f). The U-C WBI are 0.85/0.90 indicating a slightly more covalent interaction than in complex 3a. Based on the isolation and structure determination of complex 3a and 3b, a possible reaction mechanism pathway to yield complex 3b was computed at the DFT level (B3PW91). It is clearly showed that the coordination of the bis(alkynyl)borane with low-valent (C₅Me₅)₂U(II) firstly give rise to the equivalent of complex 3a, (labeled 3b#) which further undergoes an intramolecular [2+2] cycloaddition to yield complex 3b. (Figure 4) The reaction is kinetically facile (barrier 16.1 kcal/mol) and the complex 3b is



SiMe₃

SiMe

5-DMAP, 95%

The reaction of complex **3b** with 1 equiv. of isocyanate *t*BuNCO yielded complex **4** featuring a 2-oxa-3-urana-7-aza-6-

ea.)

Toluene, r.t., 12 h

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borabicyclo[3.2.0]hepta-1(7),4-diene scaffold as a brown crystalline solid in high yield (86%, Scheme 2b). The X-ray single crystal diffraction analysis of complex **4** showed a fused bicyclic structure including a N→B dative bond (Figure 5, top). The **2b** skeleton is presumably regenerated in the first step, followed by the [2+2+1] cycloaddition between the alkynyl, C=O of isocyanate and the U(II) center. The U1-C1 bond length (2.373(3)Å) and the U1-O1 bond length (2.297(2) Å) are both within the expected range of U-C(_{sp2}) bond and U-O s-bond. The short C1-C2 distance of 1.363(4) Å illustrated its C=C bond character, while C2-C3 (1.507(4) Å), C3-N1 (1.311(3) Å), N1-B1 (1.667(4) Å) and B1-C2 (1.707(4) Å) bond lengths are also in accordance with its bora-azetine four-membered ring structure.



Figure 5. Molecular structures of complex 4 (top) and 5-DMAP (bottom) in the solid state (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for 4: U1–C1 2.373(3), U1–O1 2.297(2), C1–C2 1.363(4), C2–C3 1.507(4), C2–B1 1.707(4), C3–N1 1.311(3), N1–B1 1.667(4), B1–N2 1.517(4), C1–U1–O1 86.34(8). For 5-DMAP: U1–C2 2.450(3), U1–C5 2.429(3), U1–N3 2.617(2), C1–C2 1.390(4), C2–C3 1.490(3), C3–C4 1.516(3), C4–B1 1.627(4), B1–C1 1.545(4), C3–C5 1.365(3), C4–N2 1.284(3), B1–N1 1.454(4), C2–U1–C5 61.05(8).

The reaction of complex **3b** with 1 equiv. of isocyanide DippNC: (Dipp = $2,6-iPr_2-C_6H_3$) resulted in the ring-expansion of the C₃B bora-cyclobutene ring by selective insertion of the terminal carbon of isocyanide into the B1–C3 bond in **3b**, thus leading to complex **5** (Scheme 2c). The attempt for obtaining publishable single crystal structure for complex **5** is unsuccessful due to the severe twin nature of the obtained crystals. Instead, we prepared the DMAP-adduct of **5** in almost quantitative yield (Scheme 2, bottom) by treatment of **5** with an equimolar amount of DMAP. The X-ray diffraction analysis of complex **5-DMAP** confirmed the atom connectivity in **5**, which features an intriguing bora-cyclopentene structure (Figure 5, bottom). The U1–C2 and U1-C5 bond lengths (2.450(3) Å, 2.429(3) Å) are within the expected range of the U-C_(sp2) distances. The C1-C2 and C3-C5 bond lengths (1.390(4) Å, 1.365(3) Å) are in line with the C=C distances, while the C2-C3 and C3-C4 separations (1.490(3) Å, 1.516(3) Å) clearly indicate their single bond character. The short C4-N2 bond length of 1.284(3) Å is corresponding to the exocyclic imine group.^[15]

In summary, we have reported the synthesis of the first uranium metallaboracycles upon complexation of bis(alkynyl)boranes with the "(C5Me5)2U" fragment. The boroncontaining ligand is doubly reduced by the low-valent U(II) center, leading to the dianionic species that is isoelectronic to the bis(isonitrile) borylene.^[16] Depending on the type (amino or phenyl) of the exocyclic boron-substituent, a boat-like six-membered uranaboracycle and a U/B-dinuclear zigzag-butadiene complex could be prepared in excellent yields. In both cases, the calculated unpaired spin density of ca. 2.1 is consistent with a U(IV) system. Moreover, three reactivity patterns (i.e. noninnocent behavior, ring-expansion, [2+2+1] cycloaddition) have been established, suggesting that 3b can be applied as precursor for the construction of uranaboracyclic systems of next generation.

Acknowledgements

QY gratefully acknowledge the start-up fund of SUSTech. LM is a senior member of the Institut Universitaire de France.Humboldt foundation and the Chinese Academy of Science are acknowledged for support as well as CalMip for a generous grant of computing time.

Conflict of interest

The authors declare no conflict of interest.

Keywords: bis(alkynyl)borane • uranium • boron-centered ligand • uranacylce • boracycle

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bis(alkynyl)borane-supported actinide complexes are reported. Depending on the *B*-substituent, the bis(alkynyl)borane ligand can either coordinate in a η^5 -manner or undergo a U(IV)-assisted intramolecular [2+2] cycloaddition to give a highly unusual fused bicyclic structure.



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