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Dimerization and Ring-opening in Bis(diisopropylamino)cyclopropenylidene (BAC) Mediated by [U(NR2)3(CCPh)] (R = SiMe3)

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Complete List of Authors:	Nguyen, Thien; UCSB, Department of Chemistry and Biochemistry Pauly, Christophe; Universität Münster Kent, Greggory; UCSB, Department of Chemistry and Biochemistry Wu, Guang; UCSB, Chemistry & Biochemistry Hayton, Trevor; UCSB, Department of Chemistry and Biochemistry

COMMUNICATION

Dimerization and Ring-opening in Bis(diisopropylamino)cyclopropenylidene (BAC) Mediated by $[U(NR_2)_3(CCPh)]$ (R = $SiMe_3$)

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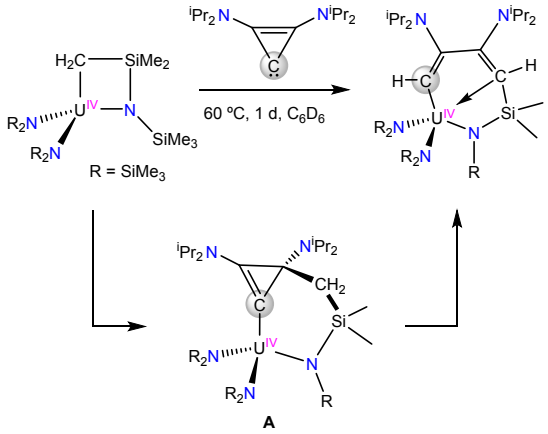
Thien H. Nguyen, Christophe Pauly, Greggory T. Kent, Guang Wu, Trevor W. Hayton*

Addition of 2 equiv of bis(diisopropylamino)cyclopropenylidene (BAC) to $[U(NR_2)_3(CCPh)]$ (1, R = $SiMe_3$), in Et_2O, results in formation of [*cyclo*-N(^{i}Pr)C(Me)$_2$CH(N^{i}Pr$_2$)C{=CHC$_3$(N^{i}Pr$_2$)$_2$}][U(NR$_2$)$_2$(*N*(SiMe$_3$)SiMe$_2$*C*H$_2$)(CCPh)] (2) in moderate isolated yield. Complex 2 is the result of coupling and protonation of two BAC molecules, where complex 1 contributes the required proton. It was characterized by NMR spectroscopy and X-ray crystallography and represents a new mode of reactivity of the cyclopropenylidene fragment.

Since it was first prepared by Yoshida and co-workers in 1977,[1] bis(diisopropylamino)cyclopropenylidene (BAC) has been studied in a variety of contexts.[2-7] As a rare example of an isolable cyclopropenylidene,[3] and member of a growing class of stable singlet carbenes,[8-11] it provides access to other unusual fragments, such as bicyclopropenylidene, cyclobutenylidene, and methylenecyclopropene.[1, 4, 12, 13] BAC also functions as an effective organocatalyst for a variety of transformations.[14-21] Chiral derivatives are also known.[22]

With respect to metals and main group elements, BAC can function as a ligand,[2, 13, 23-44] C-atom source,[45] or carbyne precursor.[46] It has also been used to functionalize Au surfaces.[47] We recently reported the reaction of BAC with the U(IV) metallacycle, $[U(NR_2)_2(N(SiMe_3)SiMe_2CH_2)]$ (R = $SiMe_3$), which results in ring-opening of the BAC fragment (Scheme 1).[48] We hypothesized that ring-opening occurs via cyclopropenyl intermediate **A**, which was formed by BAC insertion into the U-C bond. To probe the generality of this transformation, we endeavoured to explore the insertion chemistry of BAC with other U-C bonds. Herein, we report the synthesis of a U(IV) acetylide complex, $[U(NR_2)_3(CCPh)]$, along with its reactivity with BAC.

Scheme 1. Ring-opening reactivity of BAC.



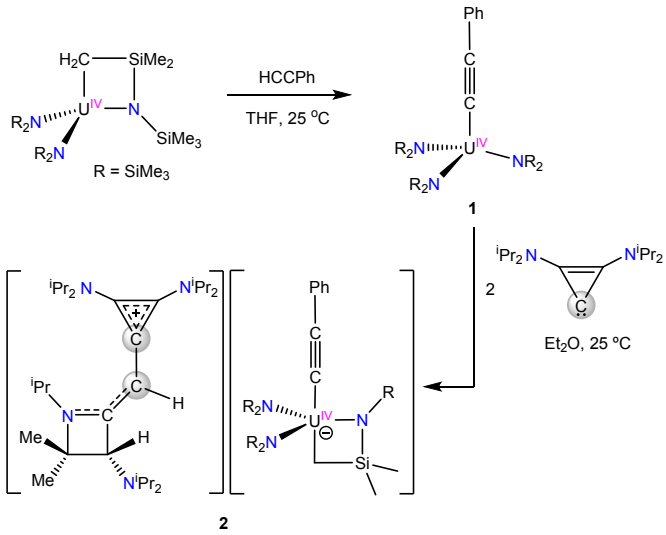
Addition of 1 equiv of HCCPh to $[U(NR_2)_2(N(SiMe_3)SiMe_2CH_2)]$ in THF results in formation of $[U(NR_2)_3(CCPh)]$ (**1**), which can be isolated as a brown solid in 17% yield after crystallization from O{$SiMe_3$}$_2$ (Scheme 2). Complex **1** was previously reported by Dormond and co-workers,[49] but was only partially characterized. The low yield of **1** is ascribed to its extremely high solubility in non-polar solvents, as ^{1}H NMR spectra of the crude reaction mixtures are quite clean. A similar synthetic procedure was used to synthesize the related actinide acetylides, $[U(NN'_3)(CCAr)]$ (NN'$_3$ = N(CH$_2$CH$_2$NSiMe$_2$^{t}Bu)$_3$) and $[U(NR_2)_3(\mu,\eta^1{:}\eta^1\text{-}C_2)Th(NR_2)_3]$.[50-52]

The ^{1}H NMR spectrum of **1** in C_6D_6 features a broad singlet at -2.24 ppm, which is assignable to the $SiMe_3$ proton environment. Also present in this spectrum are resonances at 3.47, -2.92 and -12.56 ppm, which are assignable to the *para*, *meta,* and *ortho* CH environments of the phenyl group, respectively. The ^{29}Si NMR spectrum of **1** was featureless,[53] presumably due to the complex's paramgnetism. Its IR spectrum exhibits a C≡C stretch at 2072 cm^{-1}, which is comparable to that observed for $[U(NN'_3)(CCPh)]$ (2054 cm^{-1}).[52]

Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106.

Electronic Supplementary Information (ESI) available: Experimental procedures, crystallographic data, and spectral data for complexes **1** and **2**. See DOI: 10.1039/x0xx00000x

Complex **1** crystallizes in the orthorhombic space group *P*na2$_1$ (Figure 1). Its U1-C1 and C1-C2 distances are 2.38(1) and 1.23(2) Å, respectively. These values compare well with those reported for other U(IV) acetylide complexes.[52, 54-56] For example, the U-C distances in [(C$_5$Me$_4$SiMe$_3$)$_2$U(CCPh)$_2$] are 2.390(2) and 2.369(3) Å.[57] Finally, the average U-N distance (2.24 Å) compares well with other pseudotetrahedral U(IV) silylamide complexes.[50, 58]



Scheme 2. Synthesis of complexes **1** and **2**

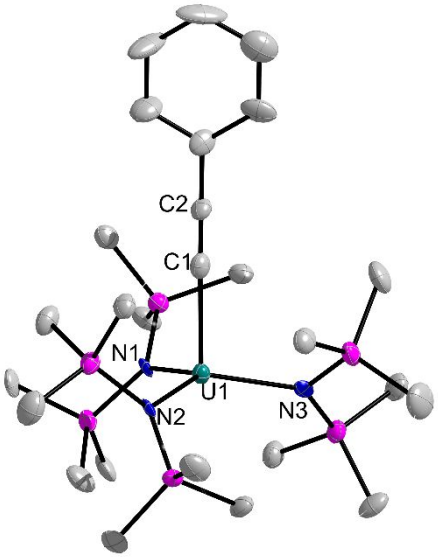


Figure 1. Solid-state molecular structure of **1**, shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

With complex **1** in hand, we explored is reactivity with BAC. In particular, we hypothesized that BAC could insert into the U-C bond of **1**, in analogy with the chemistry observed between [U(NR$_2$)$_2$(*N*(SiMe$_3$)SiMe$_2$*C*H$_2$)] and BAC (Scheme 1).[48] Surprisingly, however, addition of 2 equiv of BAC to **1** in Et$_2$O results in formation of [*cyclo*-N(^{i}Pr)C(Me)$_2$CH(N^{i}Pr$_2$)C{=CHC$_3$(N^{i}Pr$_2$)$_2$}][U(NR$_2$)$_2$(*N*(SiMe$_3$)SiMe$_2$*C*H$_2$)(CCPh)] (**2**), which can be isolated in 38% yield after work-up (Scheme 2).

Complex **2** crystallizes as a discrete cation/anion pair in the triclinic space group *P*-1, as the pentane solvate, **2**·0.5C$_5$H$_{12}$ (Figures 2 and S1). The cation is derived from the coupling and protonation of two BAC molecules and features a new azetidin-2-ylidenemethyl ring, formed by ring-opening of the BAC fragment. Similar ring-openings were observed by the groups Chauvin,[59] Stephan,[60] Bertrand,[61] and Iwamoto.[12] For example, an identical azetidin-2-ylidenemethyl ring was formed upon reaction of PPh(pip)$_2$ with [HBAC][BF$_4$] at 60 °C.[59] The anion in **2** consists of a 5-coordinate U(IV) centre ligated by a phenylacetylide ligand, two silylamide ligands, and a bidentate [*C*H$_2$SiMe$_2$*N*(SiMe$_3$)]$^{2-}$ ligand. The latter ligand is evidently the source of the extra proton found in the cation. Within the cation, the C34-C41 (1.355(7) Å) and C41-C42 (1.436(7) Å) distances, along with the C34-C41-C42 angle (127.6(5)°), support the protonation and sp^2 hybridization of C41. Moreover, the C-C distances within the 3-membered ring are equivalent (C42-C43 = 1.380(7), C43-C44 = 1.389(7), C44-C42 = 1.376(7) Å) and consistent with its cyclopropenium character. For comparison, the average intra-ring C-C distance in [HBAC][BPh$_4$] is 1.37 Å.[3] The metrical parameters of the azetidin-2-ylidenemethyl ring are similar to those observed previously.[59] For instance, the N5-C34 distance (1.360(7) Å) is shorter than a typical N-C single bond,[62] suggesting delocalization of the π system across N5, C34, and C41. In addition, the sum of angles around N5 (Σ(C-N-C) = 355°) is consistent with sp^2 hybridization at this atom. Finally, within the anion, the U-C$_{acetylide}$ distance (2.493(5) Å) is longer than that observed in **1**, consistent with its higher coordination number and anionic charge.

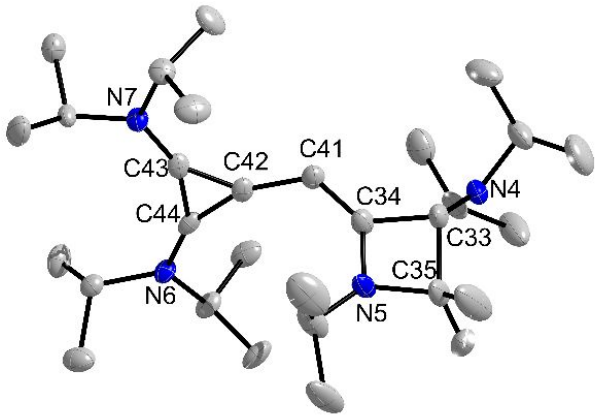
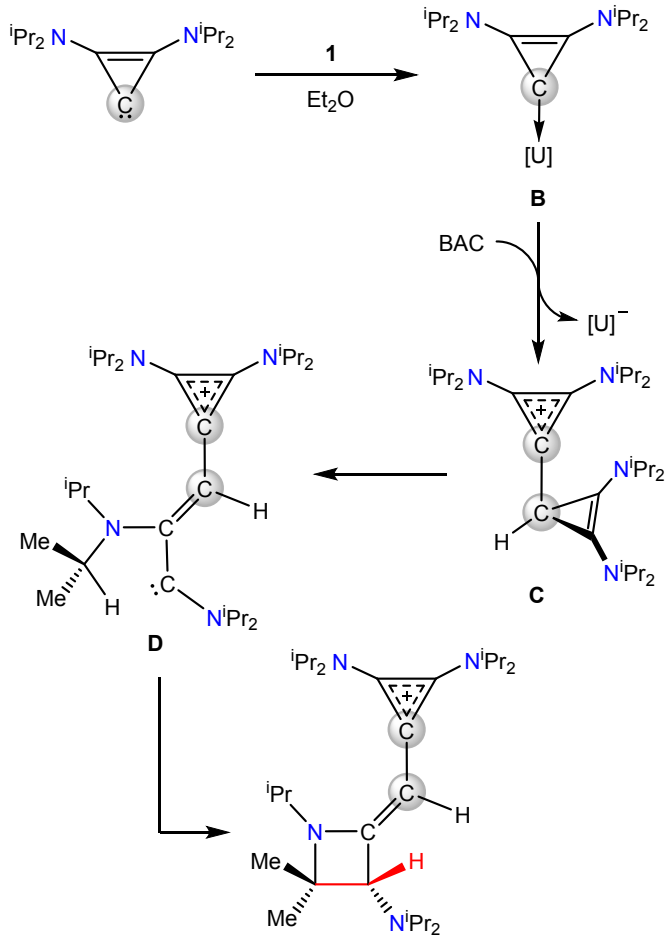


Figure 2. Solid-state molecular structures of **2**·0.5C$_5$H$_{12}$, shown with 50% probability ellipsoids. Hydrogen atoms and [U(NR$_2$)$_2$(*N*(SiMe$_3$)SiMe$_2$*C*H$_2$)(CCPh)]$^-$ anion omitted for clarity. The complete structure of **2** is presented in Figure S1.

The ^{1}H NMR spectrum of **2**, recorded in THF-*d*$_8$, features paramagnetically-shifted resonances at -229.81 and 38.71 ppm, in a 2:9 ratio, which are assignable to the CH$_2$ and SiMe$_3$ environments of the bidentate [*C*H$_2$SiMe$_2$*N*(SiMe$_3$)]$^{2-}$ ligand. Also present is a broad resonance at -9.25 ppm, integrating to 36H, which is assignable to the two [N(SiMe$_3$)$_2$]$^-$ ligands. In

addition, the unique methine proton of the azetidin-2-ylidenemethyl ring is found at 3.71 ppm, whereas the vinyl CH environment is found at 3.94 ppm. Our formulation is further supported by the observation of singlets at 1.15 and 1.11 ppm, each integrating for 3, which correspond to the diastereotopic methyl groups attached to the azetidin-2-ylidenemethyl ring.

Scheme 3. Proposed mechanism of formation of the cation in **2**.



To explain the formation of **2**, we hypothesize that BAC reacts with **1** to form an adduct **B**, which activates the bound BAC moiety (Scheme 3). Intermediate **B** then reacts with another equivalent of BAC to form intermediate **C** and the anion $[U(NR_2)_2(N(SiMe_3)SiMe_2CH_2)(CCPh)]^-$. This intermediate subsequently undergoes ring-opening to form carbene **D**, which inserts into an isopropyl methine CH bond to form the final product. A similar carbene intermediate was proposed by Iwamoto in their silylene-promoted ring-opening of BAC.[12]

For comparison, Chauvin and co-workers argued that BAC ring-opening occurring upon attack of $[HBAC][BF_4]$ by strongly nucleophilic phosphines.[59] In our hands, however, reaction of BAC with $[HBAC][BF_4]$ in pyridine-d_5 resulted in no reaction, consistent with the need for a Lewis acid to mediate the dimerization. That said, the low solubility of $[HBAC]^+$ in non-polar solvents necessitated the use of pyridine, whose basicity and/or polarity could affect the outcome of the experiment. It is also interesting to note that we do not observe formation of any $[HBAC]^+$ in the *in situ* reaction mixture, which would be formed by direct protonation of BAC by **1**. This observation also suggests that formation of the cation in **2** requires the presence of a Lewis acid.

Conclusions

In summary, we have discovered a new mode of reactivity of the cyclopropenylidene fragment, which involves dimerization, protonation, ring-opening, and finally methine C-H activation to generate an azetidin-2-ylidenemethyl ring. While nucleophilic attack of BAC has been observed for a variety of Lewis bases, including phosphines,[59] metallaphosphirines,[60] and CAACs,[61] the current work represents the first instance of nucleophilic attack of BAC by BAC itself. Overall, these finding provide new insights into the chemical reactivity of this important reagent, which has found increasing use in catalysis and materials science in recent years. Finally, we observe no evidence of BAC insertion into the U-C bond of **1**, as originally intended. This observation suggests that insertion may require a strained M-C bond to occur, which we plan to test in a future study.

Conflicts of interest

There are no conflicts to declare.

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