Formation of a Stable Cyclopropenylium Betaine[†]

Gerhard Erker,* Wolfgang Ahlers, and Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40 D-48149 Münster, Germany

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Cyclopropenylium ions (1) are very important organic compounds since they represent the smallest carbocyclic aromatic ring systems.¹ Dealing with these substances is often



hampered by their ionic nature, which often makes cyclopropenylium salts kinetically unstable in the absence of sufficiently stabilizing substituents. In principle, it would be highly desirable to have neutral compounds with cyclopropenylium character available, i.e., cyclopropenylium compounds that have their counterion covalently bonded to them. We have now prepared for the first time to our knowledge an example of such a cyclopropenylium betaine (2), a substance that is very stable and can readily be characterized by conventional techniques.

Our synthesis of the metal-free title compound makes use of a novel organometallic template reaction that we recently discovered and described.² This allows for the preparation of a suitably substituted three-membered ring system by very simple means in the coordination sphere of a group 4 bent metallocene unit. The synthesis utilizes the combined action of a group 4 transition metal and a very Lewis-acidic boron center to circumvent the kinetic and thermodynamic restraints of methylenecyclopropene formation by means of dimerization of two acetylenic units.³ Typically, a bis(propynyl)metallocene (3, M = Zr or Hf) is treated with 1 molar equiv of tris-(pentafluorophenyl)borane to give the organometallic coupling product 4 by means of a σ -ligand transfer⁴/insertion route (Scheme 1). Complexes 4 apparently are in an endothermic equilibrium situation with their (triafulvenyl)metallocene isomers 5 by means of a reversible subsequent intramolecular alkynyl insertion reaction. The less favored isomer 5 is effectively trapped from the equilibrium by the addition of isonitrile or nitrile reagent to give the stable organometallic product 6 or 7, respectively.2

Scheme 1



These systems could serve as easily available starting materials for the preparation of novel cyclopropenylium betaine examples (2) by cleaving the transition metal to carbon or nitrogen linkage. While the complexes 6 appear to be resistant to a clean hydrolytic cleavage at ambient conditions so far, the reaction of the ketimido complexes 7 has provided a successful entry into this novel class of organic compounds.

Complex 7b (M = Hf) was treated with methanol (3 molar equiv) in toluene at room temperature. In a rapid and clean reaction, the hafnocene unit was cleaved off and the transition metal-free organic product 8 isolated (84% yield).⁵ The product still contains the borate group (¹¹B NMR in [D₆]benzene, δ -18.7). Slow diffussion of pentane into a toluene solution of 8 gave single crystals for the X-ray crystal structure analysis.

The $C(sp^2) - C(sp^2)$ bond in the three-membered ring of 1,2,3triphenylcyclopropenylium tetrafluoroborate is 1.373(5) Å.⁷ In the neutral system 8 (Figure 1), the C2-C3 bond is identical in length at 1.372(3) Å, and the adjacent C-C distances inside the three-membered ring are closely around this typical cyclopropenylium value [1.341(3) Å, C1-C2; 1.399(3) Å, C1-C3]. The bonding angles inside the three-membered ring of 8 are $60.1(2)^{\circ}$ (C1-C2-C3), $62.1(2)^{\circ}$ (C2-C1-C3), and $57.9(2)^{\circ}$ (C1-C3-C2). These structural features are much more characteristic of cyclopropenylium than those of the organo-

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^{(5) (}a) Preparation of the hafnium complex 7b: 2.0 g (5.1 mmol) of bis-(propynyl)hafnocene (3a)⁶ was treated with 2.6 g (5.1 mmol) of B(C₆F₅)₃ in 15 mL of toluene (-78 °C to ambient temperature) to yield 3.9 g (77%) In 15 mL of tolucie (-78 °C to anticent temperature) to yield 3.5 g (17.6°) of 4a.² A sample of 4a (1.5 g, 1.51 mmol) was suspended in 15 mL of tolucene and reacted with 0.75 g (7.2 mmol) of benzonitrile (3 days at 25 °C) to yield 1.37 g (83%) of 7b, mp 215 °C (DSC); ¹H NMR ([D₈]thf) δ 7.70–7.45 and 7.4–7.05 (m, 10H, Ph), 6.19 (br s, 10H, Cp), 1.67 (s, 3H, CH₃), 1.11 (s, 3H, CH₃); ¹³C NMR ([D₈]thf) δ 181.1 (PhC=NHf), 151.5, 145.6 (CC) CO2 (124.4) 28.2 md 14.4 (CE) 123.2 md 132.6 (132.6) 146.5 (C2, C3), 147.4, 138.3 and 136.4 (C6F5), 133.3, 133.0, 132.1, 131.5, 128.7 127.6, 127.1, 126.2 (Ph), 112.7 (PhCN), 109.9 (Cp), 87.3 (C4), 14.6 (CH₃), 7.6 (CH₃) (ipso-C of C₆F₅ and C1 not observed); IR (KBr) $\tilde{\nu}$ 2254 (C=N), 1823, 1513 cm⁻¹ (methylenecyclopropene). (b) Preparation of 8: 650 mg (0.59 mmol) of 7b was treated with 0.11 g (3.52 mmol) of methanol in 10 mL of toluene to yield 350 mg (84%) of 8 after washing with pentane. Treatment of the corresponding zirconium complex 7a with methanol or water also led to the formation of **8**. X-ray crystals were obtained by diffusion of pentane into a toluene solution of **8**, mp 216 °C (DSC); ¹H NMR ([D₈]toluene, 220 K) δ 6.8–6.1 (m, 5H, Ph), 3.76, 3.29 (s, each 1H, NH₂), 1.43 (s, 3H, CH₃), 0.99 (s, 3H, CH₃); ¹³C NMR ([D₈]toluene) δ 178.4 (C1), 168.1 (PhC=NH₂), 167.3 (C3), 159.2 (C2), 136.2 (ipso), 131.5 (p), 129.8 and 129.3 (Ph), 120.3 (ipso), 139.7 (p), 148.5, 137.5 (C₆F₅), 90.2 (C4), 14.1 (CH₃), 10.1 (CH₃); IR (KBr) $\tilde{\tau}$ 3522, 3418 (NH₂), 1817, 1548 (tertative, methylenecyclopropene), 1645 (tentative, C=N); MS (EI) m/z
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Figure 1. View of the molecular structure of 8.

metallic precursor 7, which exhibits a typical methylenecyclopropene framework with a distorted three-membered ring having two long and one short bond [7a, 1.423(3), 1.394(3), and 1.335-(4) Å, ref 2]. In 8, the C3-C4 bond [1.396(3) Å] is slightly longer than the adjacent C4-C5 bond [1.383(3) Å], opposite of what is observed for 7a [1.366(3) Å, C3-C4; 1.426(3) Å, C4-C5].

The H₂N moiety of **8** gives rise to two IR bands at 3523 and 3418 cm⁻¹, and there is a C=N stretching band at 1645 cm⁻¹. The combination of C=C IR bands typical of methylenecyclopropene-type compounds⁸ is observed at 1817 and 1549 cm⁻¹.

Compound 8 exhibits ¹³C NMR resonances of the threemembered ring at δ 178.4 (C1), 167.3 (C3), and 159.2 (C2). These signals are at markedly higher δ values as compared to the corresponding resonances of the N-metalated methylenecyclopropene precursor 7b (M = Hf) (δ 146.2, 151.2, C1/C3). The C4 ¹³C NMR resonances of 8 (δ 90.2) and 7a (δ 87.3) are very similar.

In [D₈]toluene at 230 K, compound **8** exhibits ¹H NMR methyl singlets at δ 1.43 and 0.99 and two well-separated NH resonances at δ 3.76 and 3.29. With increasing temperature,

the latter two signals rapidly broaden and eventually show coalescence at 306 K (200 MHz). From this characteristic spectroscopic behavior, a H_2N-C rotational barrier of $\Delta G^{\pm}_{rot} = 14.5 \pm 0.5$ kcal mol⁻¹ was derived.⁹ This is a smaller rotational barrier than expected for a typical ketiminium salt and is within the range of $R_2N-C(sp^2)$ rotational barriers often observed for tertiary enamines.¹⁰ To our knowledge, the C-N rotational barriers of primary enamines are still unknown, but they are expected to be smaller than those of the tertiary enamines.

Thus we conclude, on the basis of the observed structural and spectroscopic data and the dynamic behavior of 8, that this compound exhibits characteristic features that place it between the extreme formulations of a methylenecyclopropene bearing a ketiminium and a borate functional group (A) and an enaminosubstituted cyclopropenylium triarylborate betaine structure (B). The particular example 8 of this novel class of organic threemembered ring compounds clearly exhibits some cyclopropenylium betaine character and is probably best described as a resonance hybrid with equal contributions by structures A and **B**. It is likely that our novel synthetic approach to this new type of compound will make examples available where the cyclopropenylium betaine character will be even more pronounced than in 8. This should allow for the development of a chemistry of *neutral* cyclopropenylium-type systems that have not been available by conventional synthetic routes so far. Such investigations are currently being actively pursued in our laboratory.

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Supplementary Material Available: Details of the X-ray crystal structure analysis of **8**, including complete listings of bond lengths and angles and atomic coordinates (8 pages); observed and calculated structure factors (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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