Barium Triphenylmethanide: An Examination of Anion Basicity**

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Interest in the organometallic compounds of calcium, strontium, and barium has focused mainly on those complexes with π-type ligands such as cyclopentadienyl, fluorenyl, and indenyl.[1a] In contrast, organometallic compounds of these metals with metal–C σ bonds have been relatively unexplored owing largely to their high reactivity.[2] The recently discovered utility of these compounds as polymerization initiators,[3] in the synthesis of functionalized polymers,[4] and in organic synthesis outlines the need for intensified investigation.[5] Examples of structurally characterized organometallic compounds with metal–C σ bonds are mainly focused on calcium, whereas strontium and barium compounds of this type are less well known.[1b] Structurally authenticated examples include the acetylides $[\mathrm{M(CCSiPh_3)_2([18]crown\text{-}6)}]$ ($\mathrm{M = Ca, Sr, Ba}$) published by our group.[6] Other examples include a barium derivative exhibiting a barium–alkenyl bond, and a barium compound bearing phosphonium dibenzylide anions.[7, 8]

Recent research in our laboratory has focused on the use of triphenylmethane as a hydrocarbon source. Previous work using the triphenylmethanide anion concentrated on alkali metals, and resulted in an array of monomeric species displaying contact ion pairs, in which the geometry around the anion is slightly removed from planarity.[9–13] Structurally authenticated examples of alkaline earth metal triphenylmethanides are limited to $[\mathrm{Mg(CPh_3)Br(OEt_2)_2}]$.[14]

Our initial reaction scheme involved transamination in the presence of a crown ether, a synthetic method well proven for the above-mentioned acetylides [Eq. (1)].[6]

$$[\mathrm{Ba\{N(SiMe_3)_2\}_2(thf)_2}] + 2\,\mathrm{HCPh_3} \xrightarrow{\text{[18]crown-6, THF}} [\mathrm{Ba(CPh_3)_2([18]crown\text{-}6)}] + 2\,\mathrm{HN(SiMe_3)_2} \tag{1}$$

However, this reaction did not afford the target compound. Rather, the product of an ether-cleavage reaction was obtained, the novel heteroleptic vinyl ether amide **1** [Eq. (2)].

$$2\,[\mathrm{Ba\{N(SiMe_3)_2\}_2(thf)_2}] + 4\,\mathrm{HCPh_3} \xrightarrow{\text{[18]crown-6, THF}} \underset{\mathbf{1}}{[\{\mathrm{Ba(C_{12}H_{23}O_6)N(SiMe_3)_2}\}_2]} + 2\,\mathrm{HN(SiMe_3)_2} + 4\,\mathrm{HCPh_3} \tag{2}$$

Ring opening of the crown ether by a strongly basic anion is an undesirable but common side reaction. Compound **1** is a rare example of structural verification of the event and allows rationalization of the mechanism of its formation (see Figure 1).

Considering the species involved in this reaction, it was proposed that after the deprotonation of the triphenylmethane by the bis(bis-silylamide) a transient metal–carbon bond is formed with the barium center, thus preventing the planarization of the ligand at the central carbon atom. From this favorable position, the very reactive quasi-pyramidal anion readily deprotonates the crown ether, which leads to the regeneration of the triphenylmethane and to the formation of the observed product.

The pK_a values of the amide $^{-}\mathrm{N(SiMe_3)_2}$ and of the $\mathrm{Ph_3C^-}$ ions are very similar and indicate that either anion could be responsible for the deprotonation of the crown ether, but the reproducible isolation of $\mathrm{HCPh_3}$ indicates the involvement of $\mathrm{Ph_3C^-}$ in this deprotonation reaction. This argument is further supported by the vivid red color of the solution, which indicates the intermittent formation of the $\mathrm{Ph_3C^-}$ ion. This result supports previous work by Bradley et al. who, on the basis of ^{1}H NMR spectroscopic results, propose cleavage of the crown ether in its reaction with the barium amide $[\mathrm{Ba\{N(SiMe_3)_2\}_2(thf)_2}]$ in THF under release of the amine $\mathrm{HN(SiMe_3)_2}$.[23]

Previous work by Power et al. has shown that coordinatively saturating the cation to form a charge-separated species would induce the formation of a resonance-stabilized planar triphenylmethanide ion.[15] It can be assumed that such stabilization reduces the basic character of the anion, thus preventing ether scission. These grounds prompted the use of hexamethylphosphoramide (HMPA) in addition to the crown ether to afford such a complex. Utilization of this route, however, also gave the cleaved ether product **1**. It was not until the recently available dibenzylbarium was used as a starting material that the reaction afforded the desired product, the monomeric barium triphenylmethanide compound **2** [Eq. (3)].[18]

$$\mathrm{Ba(C_7H_7)_2} + 2\,\mathrm{HCPh_3} \xrightarrow[\text{HMPA}]{\text{[18]crown-6, THF}} \underset{\mathbf{2}}{[\mathrm{Ba(CPh_3)_2([18]crown\text{-}6)(HMPA)_2}]} + 2\,\mathrm{C_7H_8} \tag{3}$$

It is probable that the larger difference in the pK_a value of the benzyl anion and the amide allows a larger thermodynamic drive toward an irreversible reaction with triphenylmethane, while the small difference in the pK_a values between the amide and triphenylmethane allows possible frequent proton exchanges and consequently leads to the cleavage of the crown ether.[22]

The barium centers in **1** are seven-coordinate (Figure 1); the coordination sphere of each Ba atom is filled by two μ_2-oxo bridges, four oxygen atoms from the ether, and the amide ligand. The bridging oxygen atoms are slightly asymmetric with metal–oxo distances of 2.611 Å and 2.573 Å, a Ba1-O1-Ba1A bridging angle of 105.32°, and a O1-Ba1-O1A angle of 74.68°. The distances between the metal center and the ether oxygen atoms increase slightly moving along the chain (2.860–2.954 Å). These slightly elongated distances are reasonable when compared with those of known compounds with less ring strain. The Ba–N distance of 2.714 Å, and the

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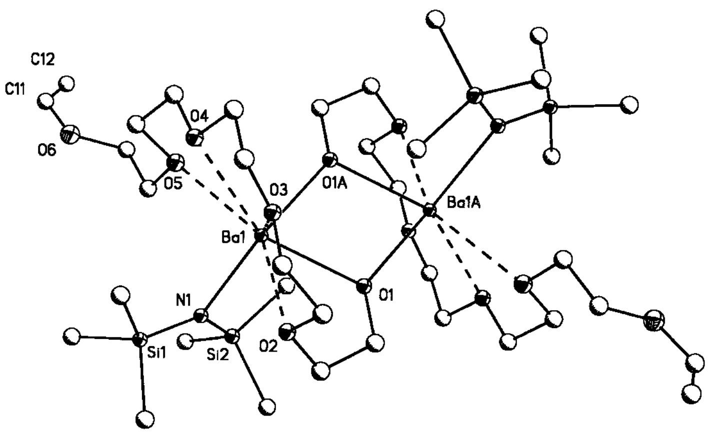

Figure 1. Structure of **1** (anisotropic displacement parameters of non-carbon atoms depict 30% probability; hydrogen atoms are omitted for clarity).

C11–C12 double-bond length of 1.294 Å are unexceptional. The Ba–Ba distance of 4.122 Å belies any metal–metal interaction.

The structure analysis of **2** reveals a charge-separated barium triphenylmethanide (Figure 2). The dication is surrounded by [18]crown-6 and two HMPA molecules. The barium atom resides on a crystallographic center of symmetry, and lies in the center of the ether ring with an average Ba–O distance of 2.785 Å. The O donors of the HMPA molecules are 2.587 Å from the metal. Of particular interest is the environment around the anionic center. The planar conformation of the anion resembles that of the anion in separated structure of [Li([12]crown-4)$_2$][CPh$_3$], while the central atoms of the contact ion pairs exhibit slight (0.05–0.1 Å) deviations from planarity, lending credence to resonance stability in **2**.[15] The phenyl rings in **2** adopt the familiar propeller geometry with angles of 35.6°, 32.7°, and 24.9°, as well as an average torsion angle of 31.1°. These values agree well with those reported earlier as well as that predicted by calculations (35 ± 2°).[16] The bond lengths from the central carbon are noteworthy; the C1–C2 distance of 1.445 is slightly shorter than the C1–C8 and C1–C14 distances of 1.464, but is not unexpected considering this phenyl group is oriented closest to planarity to give maximum orbital overlap. The sp^2 character of the anionic center is clearly indicated with little deviation from 120°.

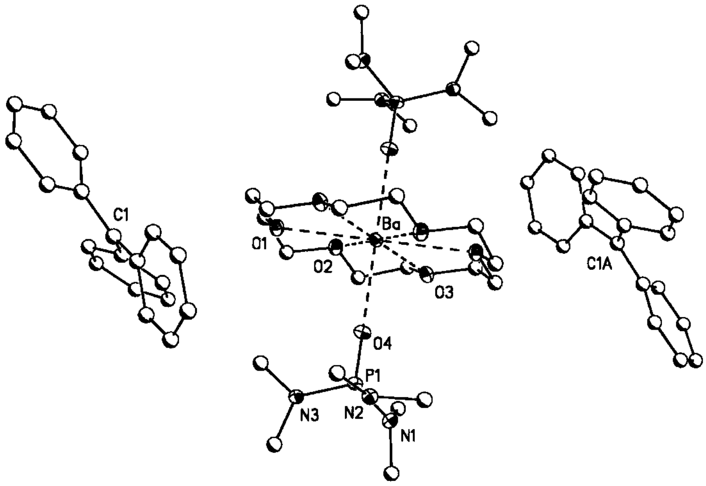

Figure 2. Structure of **2** (anisotropic displacement parameters of non-carbon atoms depict 30% probability; hydrogen atoms are omitted for clarity).

In summary, we present two novel barium organometallic compounds with distinct structural characteristics. While the exact mechanistic rationale for the formation of these interesting compounds is still under intense scrutiny, we are certain that a combination of anion basicity as well as the choice of appropriate starting material is critical. Recent results for the calcium and strontium congeners have confirmed this to be the case.[24]

Experimental Section

All reactions were performed under vigorous exclusion of water and oxygen. The compounds [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] and Ba(C$_7$H$_7$)$_2$ were prepared by literature methods.[17, 18] All reagents and solvents were purified by standard procedures.

1: Solutions were prepared of [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.8 g, 1.4 mmol), Ph$_3$CH (0.72 g, 3.0 mmol), and [18]crown-6 (0.4 g, 1.54 mmol) each in THF (25 mL). The amide solution was subsequently cooled to −80°C and triphenylmethane added dropwise. After the mixture had been cooled, the crown ether was added dropwise and the solution was stirred at −80°C for two hours. The pale yellow solution was allowed to warm slowly to room temperature, turning ruby red at about 0°C. The red solution, resulting from some contamination by the vibrant trityl anion, was filtered, concentrated, and layered with hexane. This solution was stored at −20°C and colorless crystals formed overnight. M.p. 88–89°C; yield: 0.32 g, (57.0%); ^{1}H NMR (300 MHz, 25°C, [D$_6$]benzene): $\delta = 0.45$ (s, 36H; SiMe$_3$), 3.00, 3.10, 3.19, 3.34, 3.52, 3.59, 3.82, 3.93, 4.19 (t, cleaved crown), 3.97 (d; OCH*CH*$_2$), 6.41 (dd; O*CH*CH$_2$); ^{13}C NMR (300 MHz, 25°C, [D$_6$]benzene): $\delta = 6.97$ (SiMe$_3$), 63.30, 67.05, 68.10, 69.58, 70.01, 70.17, 70.61, 70.90, 77.22, 87.04 (cleaved [18]crown-6), 87.40 (OCH*CH*$_2$), 152.24 (O*CH*CH$_2$).

2: Three 100 mL Schlenk flasks were charged with dibenzylbarium (0.43 g, 1.0 mmol), PH$_3$CH (0.48 g, 2.0 mmol), and [18]crown-6 (0.27 g, 1.0 mmol) and cooled to −80°C. Subsequently, THF (15 mL) was added to each flask. The triphenylmethane solution was added slowly to the dibenzylbarium solution followed by HMPA (0.4 mL, 2.1 mmol), affording a bright red solution. The crown ether was added and the solution was stirred at −80°C for three hours, the volume was reduced, and the solution stored at −20°C. Dark red crystals formed within 12 h. M.p. 158–160°C; yield: 0.54 g, (35.9%); ^{1}H NMR (300 MHz, 25°C, [D$_8$]THF): $\delta = 3.42$ (m, 32H; [18]crown-6, THF), 1.58 (8H; THF), 2.42 (d, 36H; HMPA), 7.06–7.11 (m, 30H; Ph$_3$C); ^{13}C NMR (300 MHz, 25°C, [D$_8$]THF): $\delta = 37.27$ (HMPA), 71.82 ([18]crown-6), 127.12 (*p*-C), 129.14 (*m*-C), 130.42 (*o*-C), 132.0 (*C*C$_6$H$_5$), 145.24 (*C*C$_6$H$_5$).

Crystal structure analyses: **1**: BaC$_{18}$H$_{41}$NO$_6$Si$_2$, $M_r = 561.04$, triclinic, space group $P\bar{1}$, $a = 10.2359(9)$, $b = 11.1793(10)$, $c = 12.5402(11)$ Å, $\alpha = 83.299(2)$, $\beta = 69.827(2)$, $\gamma = 87.176(1)°$, $V = 1337.7(2)$ Å^3, $T = 94(2)$ K, $Z = 2$, $\mu = 1.602$ mm^{-1} (Mo$_{K\alpha}$ radiation); colorless blocks $0.40 \times 0.30 \times 0.20$ mm^3; 6047 independent reflections ($3.5 \leq 2\theta \leq 56.58°$); $R_1 = 0.0338$ ($I > 2\sigma(I)$), w$R_2 = 0.0909$ (all data). **2**: BaC$_{70}$H$_{106}$N$_6$O$_{10}$P$_2$, $M_r = 1390.89$, monoclinic, space group $P2_1/n$, $a = 12.8699(9)$, $b = 21.1572(14)$, $c = 13.3671(9)$ Å, $\beta = 100.855(1)°$, $V = 3574.6(4)$ Å^3, $T = 94(2)$ K, $Z = 2$, $\mu = 0.659$ mm^{-1}(Mo$_{K\alpha}$ radiation); red blocks $0.40 \times 0.20 \times 0.10$ mm^3; 6288 independent reflections ($3.6 \leq 2\theta \leq 50.00°$); $R_1 = 0.0447$ ($I > 2\sigma(I)$), w$R_2 = 0.1208$ (all data). The crystals were mounted on the diffractometer as described previously,[19] and the data were collected using a Bruker SMART system (CCD detector).[20] Both crystal structures were solved by using direct methods and were refined by full-matrix least-squares refinement on F^2.[21] All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157686 and CCDC-157687. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Dicyclopenta[*a*,*d*]cyclooctene: A [14]Annulene Containing Two Zero-Atom Cross-Links[**]

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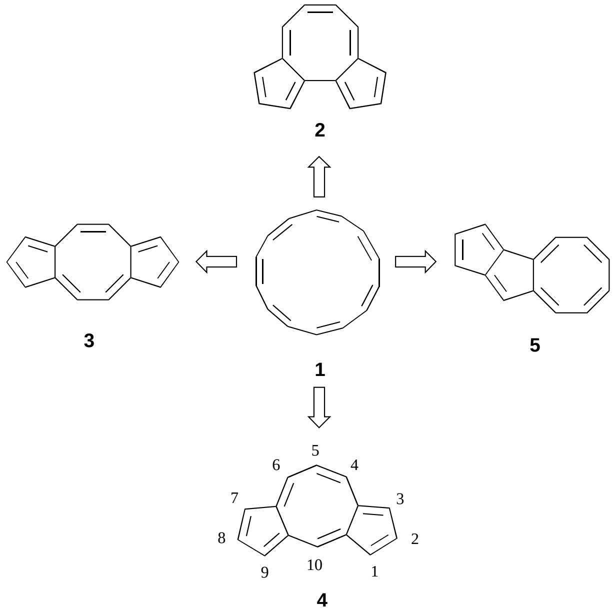
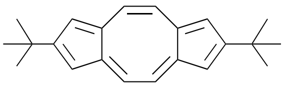
The insertion of two zero-atom cross-links between the carbon atoms of the hypothetical all-*cis*-[14]annulene (**1**) provides many types of (benzenoid and non-benzenoid) tricyclic hydrocarbons of the formula $C_{14}H_{10}$, depending on the site of the linkages. With constitutional restriction limited to the production of five- and eight-membered rings, four nonalternant hydrocarbons are formed: dicyclopentacyclooctenes **2**–**4** and cyclooctapentalene (**5**).[1] Compared to alternant benzenoid isomers, such as anthracene and phenanthrene, very little is known about these relatively small parent nonalternant hydrocarbons. Prinzbach and co-workers reported on attempts to synthesize the [*a*,*c*]isomer **2**,[2] and Hafner et al. published the synthesis of the 2,7-di(*tert*-butyl) derivative (**6**) of the [*a*,*e*]isomer **3**.[3] Hydrocarbon **6** has a planar structure and diamagnetic character and, most notably, exhibits the

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