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## Synthesis and Structure of a Hexacoordinate Carbon Compound

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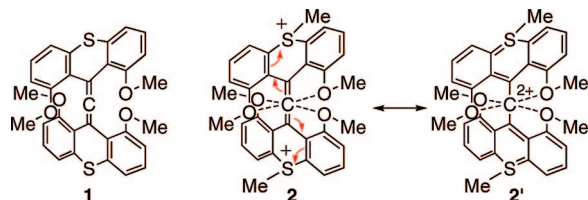
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Carbon is a central element of chemistry. It enjoys a limitless molecular diversity in millions of molecules and yet, for new students of chemistry and experienced researchers alike, the structures of carbon compounds are typically understood in terms of the very simplest of bonding concepts. Whether di-, tri-, or tetracoordinate, carbon obeys the octet rule with great predictability and has four 2-electron (2e) covalent bonds. Atoms with more than four bonds are known as hypervalent,<sup>1</sup> while those with fewer are said to be electron-deficient. Hypervalence is common in heavier main group compounds (e.g., PF<sub>5</sub> and SF<sub>6</sub>) but very rare in carbon compounds. It is widely accepted in the transition state of an S<sub>N</sub>2 reaction, but the high improbability of actually isolating examples of hypervalent carbon was dogma for a long time.

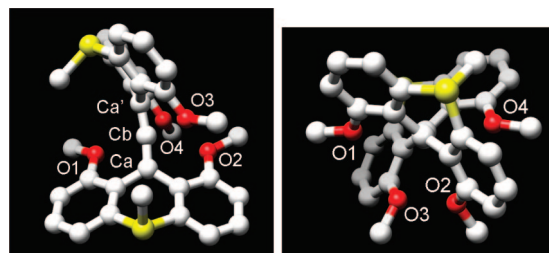
Although this problem has been confronted, especially by Breslow<sup>2</sup> and by Martin,<sup>3,4</sup> the definitive characterization of hypervalent carbon was not established until 1999 with the X-ray structure of a pentacoordinate carbon cation exploiting a sterically rigid anthracene skeleton.<sup>5</sup> A second example with a flexible pincer-type ligand followed in 2005.<sup>6</sup> We now report an example of hexacoordinate carbon with arguable hypervalence. Hexacoordinate carbon compounds such as (Ph<sub>3</sub>PAu)<sub>6</sub>C<sup>2+</sup> have been characterized,<sup>7</sup> but orbital analysis does not support hypervalence. Indeed, most high-coordinate carbon compounds are obviously electron-deficient, having three-center two-electron (3c–2e) bonds.

Our strategy to obtain hexacoordinate, potentially hypervalent carbon was to twice exploit the anthracene motif used to prepare pentacoordinate carbon.<sup>5</sup> Thus, the synthetic targets were allene **1** and the (*S,S'*)-dimethylated dication **2**.

Allene **1** was prepared as shown in the scheme. The reduction

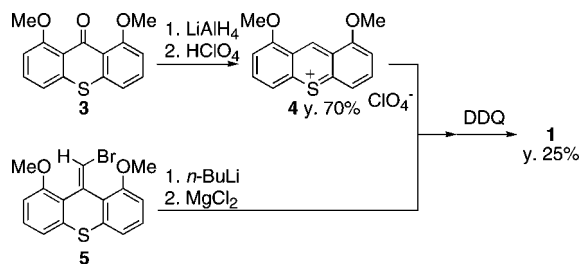


of thioxanthone **3**<sup>8</sup> and treatment by HClO<sub>4</sub> afforded **4**. Vinyl bromide **5**<sup>8</sup> was converted to the Grignard reagent by lithiation followed by treatment with MgCl<sub>2</sub>, and reaction of the Grignard



**Figure 1.** Two perspective views of the dication **2** in the X-ray structure of the CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub><sup>−</sup> salt.

reagent with **4** followed by oxidation with DDQ afforded **1** in 25% overall yield. Its allenic character is shown in the <sup>13</sup>C NMR spectrum (94.2 and 216.1 ppm) and IR spectrum (1909 cm<sup>−1</sup>). X-ray analysis reveals a bent allene framework with C–C–C = 168.5(3)°, which must result from steric crowding of the two thioxanthone substituents. Two types of nonequivalent oxygen atoms are present in the X-ray structure, consistent with two singlets for the OMe groups observed in the <sup>1</sup>H NMR at −85 °C. Only one singlet (12H) was observed at room temperature, indicating that relatively fast interconversion between bent structures occurs in solution.



The target dication **2** was prepared by the reaction of **1** with MeI and Ag<sup>+</sup>CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub><sup>−</sup>, and single crystals of the carborane salt were obtained from CD<sub>2</sub>Cl<sub>2</sub>.

The structure of **2** is shown in Figure 1, and selected interatomic distances and angles are shown in Table 1. Overall, **2** is quite similar to **1**, having a comparably bent allene and four O atoms approaching the central carbon atom with similar O–C–O angles. The C–O distances of 2.641(5)–2.750(5) Å in **2** are generally shorter than those of **1** (2.663(4)–2.815(4) Å), consistent with the dipositive charge on **2**. A significant difference between the two structures is that, in the allene **1**, the C–O distances separate into two shorter and two longer C–O lengths whereas all four are more nearly

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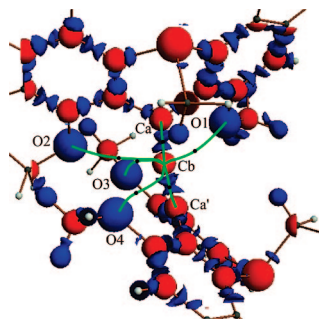
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**Figure 2.** Isosurface Laplacian ( $\nabla^2\rho(r)$ ) distribution plot of **2** with six bond paths to Cb (green lines). The isosurfaces are drawn at 10,  $-0.7 e/a_0^5$  levels for red and blue, respectively. Dots on bond paths indicate bond critical points.

**Table 1.** Selected Interatomic Distances and Angles in **1** and **2**

	distances (Å)					
	Cb–Ca	Cb–Ca'	Cb–O1	Cb–O2	Cb–O3	Cb–O4
<b>1</b> (X-ray)	1.319(5)	1.314(5)	2.663(1)	2.770(4)	2.815(4)	2.689(4)
<b>1</b> (calcd) <sup>a</sup>	1.321	1.321	2.742	2.834	2.834	2.742
<b>2</b> (X-ray)	1.319(6)	1.310(6)	2.641(5)	2.706(5)	2.750(5)	2.673(5)
<b>2</b> (calcd) <sup>a</sup>	1.325	1.325	2.705	2.735	2.735	2.709
	angles (Å)					
	Ca–Cb–Ca'	O1–Cb–O3	O2–Cb–O4	O2–Cb–O3	O1–Cb–O4	
<b>1</b> (X-ray)	168.5(3)	76.7(1)	78.2(1)	58.9(1)	164.3(2)	
<b>1</b> (calcd) <sup>a</sup>	169.9	76.9	76.9	58.3	168.9	
<b>2</b> (X-ray)	166.8(4)	76.5(1)	76.2(1)	60.7(1)	162.7(2)	
<b>2</b> (calcd) <sup>a</sup>	172.7	74.3	74.1	61.7	158.8	

<sup>a</sup> Optimized at B3PW91/6-31G(d) level.

equivalent in **2**. In both structures, all four C–O distances are considerably longer than that of a typical covalent C–O bond (1.43 Å) but significantly shorter than the sum of the van der Waals radius (3.25 Å). The result implies that the resonance structure **2'** does not play an important role. The key question is whether these short distances correspond to attractive bonding interactions or whether they are nonbonding and simply the result of steric crowding.<sup>9</sup>

We have addressed the question of C–O bonding both by experiment and by computation. High intensity precision/high-resolution X-ray diffraction<sup>10</sup> data of **2** with  $\text{CHB}_{11}\text{H}_5\text{Cl}_6^-$  as counterion were performed using synchrotron radiation. Bond paths were found between the central carbon atom and all four oxygen atoms (Figure 2). The existence of these bond paths indicates that the central carbon atom should be described as hexacoordinate and that attractive C–O interactions are present. The relatively low value of the electron density ( $\rho(r)$ ) (0.0121(7) (Cb–O1), 0.0166(7) (Cb–O2), 0.0110(7) (Cb–O3), 0.0176(6) (Cb–O4)  $e/a_0^3$ ) and the positive Laplacian values ( $\nabla^2\rho(r)$ ) (0.06768(8) (Cb–O1), 0.0641(1) (Cb–O2), 0.0498(1) (Cb–O3), 0.06021(8) (Cb–O4)  $e/a_0^5$ ) at the bond critical points indicate that the interactions are not strong and have largely ionic character. The values of  $\rho(r)$  of **2** are similar to or less than that of the pentacoordinate carbon compounds (0.022  $e/a_0^3$ ,<sup>5</sup> 0.017  $e/a_0^3$ ).<sup>6</sup> The Laplacian map also indicates the character of the C–O bonds involved at Cb. The electron concentration region (blue) around each O atom is directed toward the electron-deficient region (red) around the Cb atom (Figure 2). These arrangements of electron densities clearly show ionic character of the C–O bonds. On the other hand, the Cb–Ca and Cb–Ca' bonds concentrate electrons along the bonds resulting from covalent bonds.

The structures of **1** and **2** were optimized using the hybrid density functional theory (DFT) at the B3PW91/6-31G(d) level (Table 1).

The calculated structures are similar to the experimental structures although the C–O distances are generally slightly longer and more symmetrical in **2**. The separation of the four C–O distances in **1** into a short pair and a long pair is reproduced. Interestingly, no bond paths are found between the long pair Cb–O2 and Cb–O3 (2.834 Å), indicating that the central carbon atom in **1** is tetracoordinate. Consistent with the experimental charge density analysis, calculation of **2** showed bond paths between the central carbon atom and all four oxygen atoms. The calculated values of the electron density ( $\rho(r) = 0.015 - 0.014 e/a_0^3$ ) and the Laplacian values at the bond critical points ( $\nabla^2\rho(r) = 0.055 - 0.051 e/a_0^5$ ) agree well with experimentally obtained values.

In conclusion, on the basis of experimental charge density analysis and DFT calculations, the dimethylated allenyl dication **2** contains hexacoordinate carbon. Weak interactions in modern chemistry continue to challenge traditional bond formalisms,<sup>11</sup> necessitating molecular orbital analysis. For **2**, this shows the donation of four O atom lone pairs into empty  $\pi^*$  orbitals on the central carbon atom, making it demonstrably electron-rich and arguably hypervalent. This MO description is conceptually related to a charge transfer interaction, involving donation of electron density from the HOMO of a donor into the LUMO of an acceptor, suggesting that it may exist as an intermolecular interaction in crystals.<sup>12</sup> Indeed, analysis of the Cambridge crystal database reveals ca. 2000 structures of the type  $\text{O}\cdots\text{CR}_2$  with intermolecular distances in the range of 2.6 to 2.8 Å. Many can be classified as at least pentacoordinate, so high-coordinate carbon, despite being remarkably rare in discrete molecules, is an apparently common but previously unrecognized structural motif and bonding interaction.

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**Supporting Information Available:** Synthetic methods and spectral data for **1**, **2**, **4**, details of X-ray measurements, cif data for **1** and **2**, molecular orbital analysis of **2**, and optimized geometries of **1** and **2** based on DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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