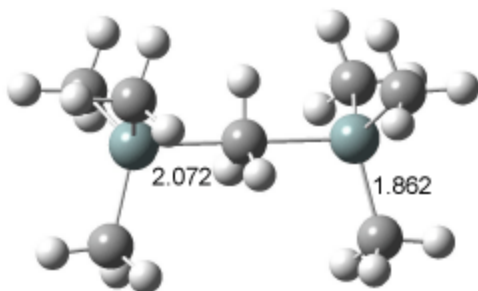


HYPERCOORDINATE CARBON

The search for a stable molecule containing a hypercoordinated carbon atom may finally be over. Abboud and Yáñez¹ report mass spectra and computations on the unusual cation $\text{Si}(\text{CH}_3)_3\text{CH}_3\text{Si}(\text{CH}_3)_3^+$ (**1**). Using low pressure FT-ICR, upon ionization of $\text{Si}(\text{CH}_3)_4$ (TMS) they observe a small signal with m/z 161.12, which corresponds to the mass of **1**⁺.

When $\text{Si}(\text{CH}_3)_4$ and $\text{Si}(\text{CD}_3)_4$ are mixed, introduced into the spectrometer and ionized, the mixed isotopomer of **1**⁺ is observed, and scrambling to the CH_3 and CD_3 groups occurs.

The geometry of **1**⁺ was optimized at B3LYP/6-311+G(3df,2pd) and QCISD/6-311+G(d,p). The latter structure is shown in Figure 1, though the geometry differs little between the two computations. The enthalpy for the dissociation of **1**⁺ into TMS and $\text{Si}(\text{CH}_3)_3^+$ is 23.2 kcal mol⁻¹ at QCISD. This compares very well with the experimental² value of 22.3 kcal mol⁻¹.



xyz file

Figure 1. QCISD/6-311+G(d,p) optimized structure of $\mathbf{1}^+$.¹

The structure has C_{3h} symmetry with the central carbon to silicon distance of 2.071 Å, a bit more than a 10% increase over the length of a typical C-Si bond.

Topological electron density analysis indicates a bond critical point does connect the central carbon atom with each silicon atom, and the value of the Laplacian of the electron density at this critical point is negative. This analysis strongly suggests that the central carbon atom is pentacoordinate!

Abboud and Yáñez argue that $\mathbf{1}^+$ can be considered as a complex of methyl cation and two $\text{Si}(\text{CH}_3)_3$ radicals. The empty p orbital of the central methyl carbon can then interact with the radical-bearing orbital on each silicon, forming a three-center two-electron bonding molecular orbital (Scheme 1).

The positive charge is delocalized, with the central methyl group having a charge of +0.26 while the charge on each $\text{Si}(\text{CH}_3)_3$ groups is +0.37.

Though not discussed in this paper, the all carbon analogue, namely



is *not* a stable structure when restricted to have C_{3h} symmetry (see Figure 2).

Rather, this geometry corresponds to the transition state for the transfer of a methyl group from one $\text{C}(\text{CH}_3)_3$ group to the other.

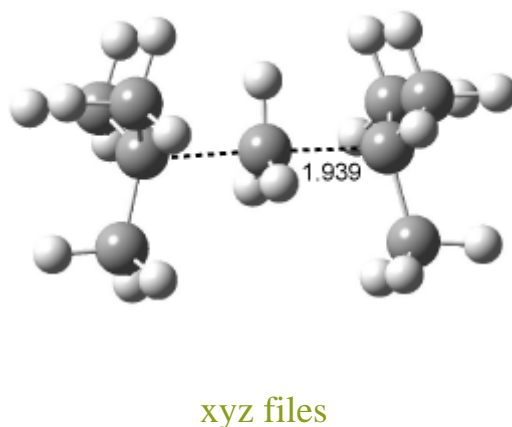


Figure 1. B3LYP/6-311+G(d,p) optimized geometry of $\text{C}(\text{CH}_3)_3\text{CH}_3\text{C}(\text{CH}_3)_3^+$.

Source: <http://comporgchem.com/blog/?p=18>