Bond Theory

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Covalent Hypercoordination: Can Carbon Bind Five Methyl Ligands?

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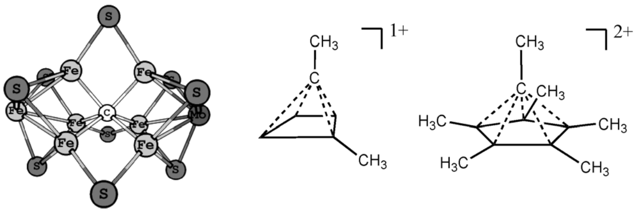
Abstract: *$C(CH_3)_5^+$ is the first reported example of a five-coordinate carbon atom bound only to separate (that is, monodentate) carbon ligands. This species illustrate the limits of carbon bonding, exhibiting Lewis-violating "electron-deficient bonds" between the hypercoordinate carbon and its methyl groups. Though not kinetically persistent under standard laboratory conditions, its dissociation activation barriers may permit $C(CH3)_5^+$ fleeting existence near 0 K.*

Literature reports of hypercoordinate-carbon-containing compounds (hcC) have increased steadily since the detection of CH_5^+ in 1952.[1] Along with numerous carboranes, carbidometal carbonyl clusters, and non-classical carbocations,[2,3] prominent early examples include the theoretical predictions of CLi_5 and CLi_6,[4] (which led to the experimental detection of the latter)[5] as well as Schmidbaur's seminal preparation of protonated tetraauriomethane $HC[Au(PPh_3)]_4^{2+}$.[6] More recently, Nagase and co-workers[7] have employed an anthracene scaffold in preparation of a purely organic hcC. HcCs are present even in biological systems; the iron-molybdenum nitrogenase cofactor present in diazotrophs (see Figure 1) is currently believed to house a six-coordinate carbon![8]



Nitrogenase cofactor **Masamune's cation** **Hogeveen's dication**

Figure 1. Site of the hypercoordinate carbon in the iron-molybenum nitrogenase cofactor,[8] and depictions of Masamune's cation and Hogeveen's dication.[10,11]

However, cases of carbon hypercoordination involving more than four contacts only to other carbon atoms remain extremely rare. In contrast to typical hcC species, where the electronegativities of the coordinating ligands differ appreciably from carbon,[9] a single carbon forming distinct bonds to more than four neighboring carbon atoms can be considered to exhibit covalent hypercoordination. Experimentally known examples are Masamune's cation[10] and Hogeveen's dication[11] (see Figure 1),[12] in both of which a C–R "cap" coordinates to an annulene, serving as an electron-donor ligand, which satisfies the $4n+2$ interstitial electron rule for 3D aromaticity.[13] A few additional covalently hypercoordinated carbon-containing species have been proposed computationally by Minkin et al.[14] and Wang et al.[15] These employ the strategy of encasing an appropriately charged central hypercoordinate carbon atom into a cage structure.

But can carbon form bonds to five separate (that is, monodentate) carbon ligands in a scaffold-free environment? The substantial challenge afforded in providing even a simple proof-of-principle of such an hcC species is evident. Bickelhaupt et al.[9g] recently reported evidence against the existence of D_{3h} $C(CN)_5^-$ as a stable intermediate. Additionally, Frenking et al.[16] found that only elements (E) more electropositive than carbon in $H_nE{-}CH_3{-}EH_n^+$ structures result in minima. Inspired by these efforts, and by the apparent lack of any reports of a $C(CX_n)_5$ species in the literature, we examine herein the limits of conventional chemical bonding theory in its application to the hypothetical $C(CH_3)_5^+$ cation, a simple analogue of CH_5^+.

Indeed, our computations now predict that $C(CH_3)_5^+$ is a minimum on the $C_6H_{15}^+$ potential energy surface. Figure 2 details its C_{3h} structure, which exhibits five C–C bonds between the central carbon and its CH_3 ligands.

While its equatorial and apical C–C bond lengths (1.612 and 1.736 Å, respectively) are longer than the normal 1.54 Å value associated with alkane C–C single bonds, they are substantially shorter than twice the vdW radius of carbon (3.4 Å). Such elongated C–C distances are consistent with electron-deficient bonding, as the formal octet of valence electrons about the central carbon precludes the possibility of five 2-electron C–C bonds. The crowding of five methyl

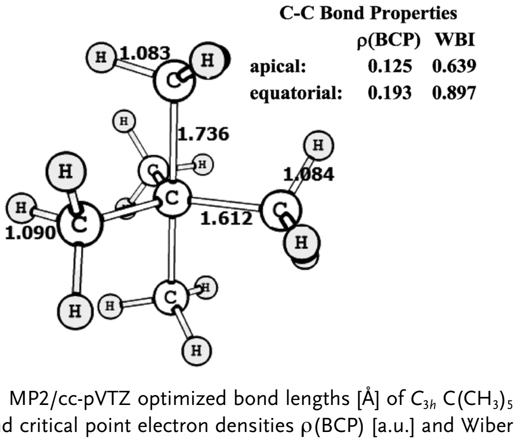


Figure 2. MP2/cc-pVTZ optimized bond lengths [Å] of C_{3h} $C(CH_3)_5^+$. C–C bond critical point electron densities ρ(BCP) [a.u.] and Wiberg bond indices (WBI) were obtained at the B3LYP/6-311+G** level.

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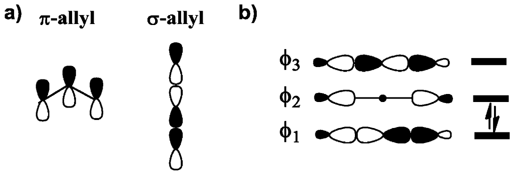
groups about a single carbon may also contribute to C–C lengthening; circa 1.7 Å C–C single bonds have been observed in sterically congested alkanes.[17]

The electron density topology of $C(CH_3)_5^+$, with its five bond paths and associated C–C bond critical points (BCPs), also supports the assignment of five covalent C–C bonds connecting the central carbon to its neighboring carbon ligands. The electron density values at the apical and equatorial C–C BCPs (0.125 and 0.193 a.u., respectively) are 53 % and 81 % of the ethane C–C BCP value of 0.238 at the B3LYP/6-311+G** level. Interestingly, the network of five distinct bond paths originating at the hypercoordinate carbon in $C(CH_3)_5^+$ contrasts with that observed for CH_5^+, which exhibits three bond paths to three hydrogen atoms, and a fourth terminating at the H–H BCP of its H_2 ligand.[18] Thus, unlike the hydrogen atoms in CH_5^+, the methyl groups of $C(CH_3)_5^+$ serve as five distinct ligands according to the BCP criterion.[12]

The MO description of the C–C bonding in $C(CH_3)_5^+$ does not employ d orbitals as valence functions;[19] these serve only as polarization functions. The central carbon in $C(CH_3)_5^+$ is unconventionally sp^3-hybridized; its sp^2 moiety helps describe the equatorial C–CH_3 bonds. The remaining p orbital contributes to the apical C–CH_3 bonding of the "σ-allyl" type, which has been invoked to describe the linear 3-center 2-electron bonds present in trihalide anions,[20] the triquinane cation (and its silicon-substituted derivatives),[21] as well as other exotic carbonium ions,[22] where collinear arrangements of three p orbitals overlap in a σ rather than in a π fashion. The most favorable of the three MOs (Scheme 1), delocalizes two electrons over three atomic centers.



Scheme 1. a) π-Allyl versus σ-allyl p-p-p overlap. b) Qualitative MO description of linear 3-center 2-electron bonding in $C(CH_3)_5^+$.

Thus, the apical C–C bonding in $C(CH_3)_5^+$ can be described as a collinear sp^3-p-sp^3 (rather than p-p-p) orbital arrangement, which gives rise to a "linear" 3-center 2-electron bonding MO. As the formal electron count around the central carbon is eight, the higher-energy apical CH_3-C-CH_3 nonbonding and antibonding MOs are unoccupied. The qualitative picture of three nearly normal equatorial C–CH_3 bonds and one linear 3-center 2-electron apical CH_3-C-CH_3 bond is supported well by the C–C Wiberg bond indices (0.90 and 0.64) for the equatorial and apical C–C bonds of $C(CH_3)_5^+$, respectively. The covalent character of all C–C bonds is evidenced by natural population analysis,[23] which indicates that the natural charge differences between $C_{central}$ versus C_{apical} and $C_{central}$ versus $C_{equatorial}$ carbons are less than 0.2 electrons.

The exotic nature of $C(CH_3)_5^+$ naturally raises the question of its viability.[24] We considered possible dissociation pathways resulting in classical structures, in particular the ejection of a methyl cation to give CH_3^+ and neopentane, as well as dissociation into ethane and the *tert*-butyl cation. Our results are based on MP2/cc-pVTZ geometries and ZPEs (derived from harmonic frequency computations), and CCSD(T) electronic energies extrapolated to the complete basis set (CBS) limit by the focal point procedure (see the Computational Methods section in the Supporting Information and Refs. [25–27]).

As is evident from the results in Table 1, the computed energy changes associated with $C(CH_3)_5^+$ dissociation are strongly affected by the inclusion of electron correlation, which tends to stabilize the hypercoordinate structure. This is consistent with the observation that electron correlation energies of hydrocarbons are related to their relative molecular compactness.[28] Intriguingly, the +5.26 kcal mol^{-1} CCSD(T)/CBS electronic energy change of the $C(CH_3)_5^+$ dissociation into CH_3^+ and neopentane is endothermic. However, the ZPE corrections favor this dissociation, as might be expected due to the smaller number of vibrational modes in the dissociated products than in $C(CH_3)_5^+$. Thus, the energy change at 0 K corresponding to the ejection of a methyl cation is predicted to be close to zero (see Table 1, last column).

However, direct CH_3^+ ejection seems not to be a minimum energy dissociation pathway for $C(CH_3)_5^+$. Following the IRC of the transition state (TS1 in Figure 3) results only in partial methyl dissociation; a barrierless hydride abstraction by CH_3^+ from neopentane then ensues. This process gives methane and the neopentyl cation initially, but the latter then undergoes the well-known 1,2-methyl shift to give the tertiary 2-methyl-2-butyl (*tert*-amyl) cation. Thus, rather than giving CH_3^+ and neopentane, TS1 connects $C(CH_3)_5^+$ to methane and the 2-methyl-2-butyl cation. According to our best estimate, the latter process is exothermic by −79.55 kcal mol^{-1}, with an activation barrier of only +1.65 kcal mol^{-1}.

Table 1: Energy changes and activation barriers [kcal mol^{-1}] for selected $C(CH_3)_5^+$ dissociation pathways.

Equation[a]	HF/cc-pVTZ	HF/CBS[b]	CCSD(T)/cc-pVTZ	CCSD(T)/CBS[b]	CCSD(T)/CBS+ZPE[c]
$C(CH_3)_5^+ \rightarrow CH_3^+ +$ neopentane	−33.79	−33.86	+4.79	+5.26	−0.13
$C(CH_3)_5^+ \rightarrow$ 2-methyl-2-butyl cation + CH_4	−104.13	−104.45	−70.73	−70.90	−75.99
$C(CH_3)_5^+ \rightarrow$ **TS1**	−13.48	−13.58	+4.48	+4.35	+1.65
$C(CH_3)_5^+ \rightarrow$ *tert*-butyl cation + ethane	−102.44	−102.79	−65.85	−66.09	−70.98
$C(CH_3)_5^+ \rightarrow$ **TS2**	−1.26	−1.28	+2.42	+2.32	+1.37

[a] Transition states 1 and 2 (**TS1**, **TS2**) dissociate into methane + 2-methyl-2-butyl cation and into ethane + *tert*-butyl cation, respectively.
[b] Extrapolation to the complete basis set limit based on focal point analysis (see Methods). [c] Zero-point energy-corrected data based on MP2/cc-pVTZ harmonic frequencies.

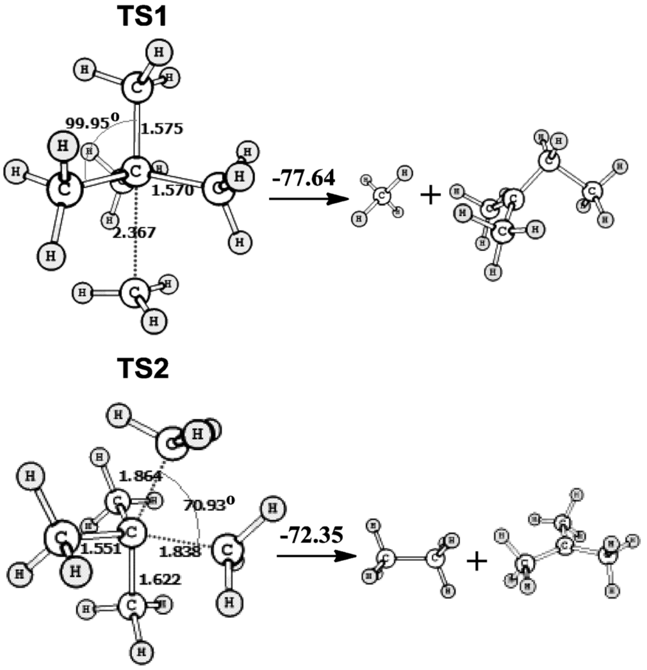


Figure 3. CCSD(T)/CBS//MP2/cc-pVTZ ZPE corrected dissociation energies [kcal mol^{-1}], and selected bond lengths [Å] and angles for transition states 1 and 2 (**TS1**, **TS2**).

A second low-energy $C(CH_3)_5^+$ dissociation pathway proceeds through TS2, and involves the loss of one apical and one equatorial methyl group to give ethane and the *tert*-butyl cation. (Attempts to locate a transition state corresponding to the loss of two equatorial methyl groups to give the same products were unsuccessful.) Our computations predict TS2 to be 1.37 kcal mol^{-1} higher in energy than the C_{3h} $C(CH_3)_5^+$ minimum, and the dissociated products to be 70.98 kcal mol^{-1} lower in energy. Thus dissociation of $C(CH_3)_5^+$ into ethane and the *tert*-butyl cation appears to be kinetically favored, albeit slightly, over dissociation into methane and the 2-methyl-2-butyl cation, while the latter process is favored thermodynamically. We note that these products (Figure 3) might subsequently form neutral-cation complexes with the composition $C_6H_{15}^+$.

The low activation barriers and highly exothermic reaction energies of these dissociation pathways preclude any kinetic persistence of $C(CH_3)_5^+$ under standard laboratory conditions. Moreover, thermal and free-energy corrections further favor dissociation; at 298 K and 1 atm, our computations suggest spontaneous dissociation of $C(CH_3)_5^+$ via both pathways considered above. Therefore it is not surprising that searches for corresponding $m/z = 87$ peaks in alkane mass spectra catalogues and literature were not fruitful, except for protonated *n*-hexane.[29] Limited kinetic persistence of $C(CH_3)_5^+$ seems possible only in inert environments at temperatures near 0 K, such as in helium nanodroplets.

It is remarkable that new C–C bonding motifs of carbon are still possible. Although its viability is only borderline, $C(CH_3)_5^+$ emphasizes a shift in reasoning about "non-Lewis" hypercoordinate bonding. More than the usual four covalent bonds to a carbon are possible within octet-rule restrictions, when the bonds, on average, involve fewer than two electrons. Importantly, our results provide a proof-of-principle. Carbon is indeed capable of covalently binding five independent carbon ligands; we hope that additional examples of such species with improved kinetic persistence will be identified in the future.

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