We have checked that Cp*H ($Cp^* = C_5Me_5$) reacts with triphenylmethyl tetrafluoroborate and tetrakis(pentafluorophenyl)borate salts to afford derivative **2** (<50% yield; Scheme 1). This reaction is quite unexpected. Performing the previous experiments in deuterated solvents, or using Cp*D as a precursor, also leads to **2**, without deuterium atoms on C4 and C5. Therefore, we have to admit that the mechanism of this reaction is still obscure and requires further investigation.

In conclusion, there is no doubt that the reported pentamethylcyclopentadienyl cation **1**[7] is actually the pentamethylcyclopentenyl cation **2**. However, these recent developments will stimulate further research in this challenging area.

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Comment on the X-Ray Structure of Pentamethylcyclopentadienyl Cation

Thomas Müller*

In a recent communication Lambert and co-workers reported the unusual X-ray structure of singlet pentamethylcyclopentadienyl cation **1**.[1] Its molecular structure (**1a**, Figure 1) is highly localized with C1–C2 and C2–C3 distances expected for allyl cations (139.3 and 140.5 pm, respectively) and relatively long C1–C5 and C3–C4 bonds (148.2 and 150.0 pm, respectively). The most unusual and striking structural feature of this cation is, however, a very long formal C=C bond (151.0 pm) with strongly *trans* pyramidalized carbon atoms (dihedral angle $\Theta(H_3C\text{-}C4\text{-}C5\text{-}CH_3) = 107^\circ$). It is noteworthy that the sum of the bond angles around the pyramidalized carbon atoms, C4 and C5, are 327.8° and 327.7°, very close to that expected for tetravalent carbon atoms.[2] Although the authors noted that this unusual geometry of the claimed cation **1** is not supported by theory,[1, 3] they attribute this distortion to crystal packing forces "permitted by the weak π bonding" between C4 and C5.[1]

Solid-state ^{13}C NMR spectroscopy of the crystalline material gives ^{13}C NMR chemical shifts for C1–C3 characteristic for allyl cations ($\delta = 250$, 243 (C1 and C3), 153 ppm (C2)).[1, 4] A resonance at $\delta\ ^{13}C = 60$ ppm was attributed to C4 and C5 (Table 1, entry 9),[1] a very unusual upfield shifted ^{13}C NMR signal for a formally sp^2-hybridized carbon atom.

The close structural and magnetic similarity of **1a** to allyl cations prompted us to reinvestigate the structure and NMR spectroscopy parameters of **1** and related allyl cations by

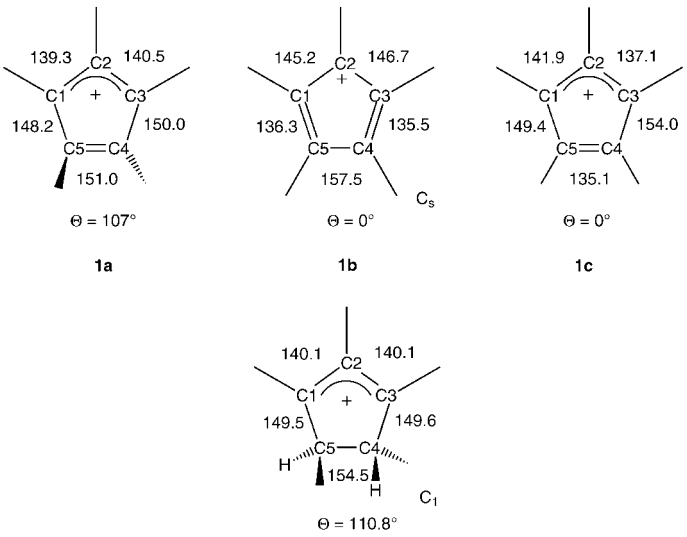

Figure 1. Experimental molecular structure of the cation **1a**[1] and calculated structures of singlet **1b** (B3LYP/6–31G(d)) and singlet **1c** (CASSCF(4/5)/6–31G(d)) and **2** (B3LYP/6–31G(d)); bond lengths [pm], dihedral angle Θ (Me-C4-C5-Me) [°].

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Table 1. Relative energies of compounds **3** and calculated ^{13}C NMR chemical shifts for compounds **1**–**3** (GIAO/B3LYP/6–311G(d,p)//B3LYP/6–31G(d)).

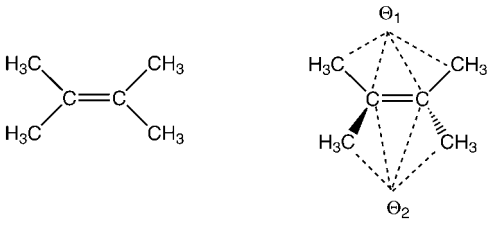
Entry	Compound	E_{rel} [kcal mol^{-1}]	δ ^{13}C(C1)[a]	δ ^{13}C(C2)[a]	δ ^{13}C(C3)[a]	δ ^{13}C(C4)[a]	δ ^{13}C(C5)[a]
1	**3a**	0.0				133.0	133.0
2	**3b**	54.3				181.1	181.1
3	**3c**	12.6				163.4	163.4
4	**3d**	58.9				207.7	207.7
5	**1b**		144.3	282.0	144.2	191.0	204.4
6	**1c**[b]		258.2	154.9	282.6	164.9	176.8
7	**2**		256.7	158.6	256.7	67.8	69.3
8	**2** (X-ray)[c]		253.3	156.1	251.1	63.6	62.7
9	**1a** (exp)[d]		243/250	153	243/250	60	60

[a] Calculated relative to tetramethylsilane (TMS):$\sigma(^{13}C) = 183.8$. [b] A CASSCF(4/5)/6–31G(d) optimized geometry was used. [c] Heavy-atom geometry taken from ref. [1], all 15 methyl hydrogen positions and the C(4)- and C(5)-methin hydrogen positions optimized at B3LYP/6–31G(d). [d] Experimental data for **1a** reported in ref. [1].

quantum-mechanical calculations.[5] The results suggest that the X-ray structure reported by Lambert and co-workers[1] is not that of **1** but that of the pentamethylcyclopentenyl cation, **2**.

Pyramidalization of a C=C bond is energetically a very unfavorable process. For example, tetramethylethene (**3**) in its equilibrium geometry (**3a**) is lower in energy by 54.4 kcal mol^{-1} than in the pyramidalized structure **3b** (Figure 2, Table 1). The C=C bond in **3b** is slightly elongated upon pyramidalization (134.9 pm (**3a**); 139.9 pm (**3b**) at B3LYP/6-31G(d)[6]). It is, however, still markedly shorter (by 11.1 pm) than the C4–C5 bond in the crystal structure **1a**. In addition, NMR calculations at the GIAO/B3LYP/6-311G(d,p) level of theory[7] reveal that this distortion of the C=C bond is connected with a significant *downfield* shift of the ^{13}C NMR chemical shift of the unsaturated carbon atoms ($\Delta\delta =$ 48.1 ppm, see Table 1, entries 1 and 2). This is in contrast to the finding by Lambert et al. who report a significant *upfield* shift for the resonance signals of C4 and C5 compared to the expected range for tricoordinate carbon atoms.[1] Even in the case of a weak π bond, modeled by **3** with a fixed C=C bond of 151 pm (**3c**), the pyramidalization is a quite unfavorable process, (energy difference **3c**/**3d**: 46.4 kcal mol^{-1}) and it results in a *downfield* shift of the ^{13}C NMR resonance of the tricoordinate carbon atoms ($\Delta\delta = 44.3$ ppm).

In Figure 1 the theoretical structures of singlet pentamethylcyclopentadienyl cation (**1b**,**c**) obtained at different levels of theory are compared with the molecular geometry derived from Lambert and co-worker's X-ray structure (**1a**). In agreement with previous ab initio calculations,[3c] the DFT optimization of singlet **1** results in a Jahn–Teller-distorted bisallylic structure, **1b**,[3e] while multi configuration self-consistent-field (MCSCF) calculations[8] predict the allyl–ene isomer, **1c**, to be more stable.[1] It is important to notice that



3a: $\Theta_1 = \Theta_2 = 0°$
3c: $\Theta_1 = \Theta_2 = 0°$; (C=C) = 151 pm
3b: $\Theta_1 = 0°$; $\Theta_2 = 107°$
3d: $\Theta_1 = 0°$; $\Theta_2 = 107°$; (C=C) = 151 pm

Figure 2. Pyramidalization of **3**.

both theoretical singlet structures differ significantly from the experimental geometry **1a**. In particular, the distortions apparent in **1a** destabilize it considerably compared to both isomers **1b** and **1c**. That is, **1a** is higher in energy by 61.3 kcal mol^{-1} and 47.8 kcal mol^{-1} compared to **1b** and **1c**, respectively (at B3LYP/6-311G(d,p)//B3LYP/6-31G(d)(**1a**/**1b**) and at CASSCF(4,5)/6-31G(d)(**1a**/**1c**)).[9] This situation suggests that π bonding in both isomers is no less important than in the regular alkene **3**. Also the calculated ^{13}C NMR chemical shifts for singlet **1b** and **1c** deviate noticeably from the experimental data (Table 1), which indicates that neither **1b** nor **1c** have been obtained.

In sharp contrast, not only the theoretical structure for the permethylated allyl cation **2** closely matches the experimental structure (Figure 1), also the calculated ^{13}C NMR chemical shifts compare favorably with the ^{13}C NMR data provided by Lambert and co-workers (Table 1). The agreement between the calculated NMR chemical shifts for **2** and those determined experimentally is further improved when the NMR calculations employ not the theoretical gas-phase structure, but the experimental structure with hydrogen atoms attached to the carbon atoms C4 and C5,[10] thus transforming the alleged cation **1** into the cyclopentenyl cation **2** (Table 1).

Quantum-mechanical calculations show that the distortions which are apparent in the unusual structure **1a** strongly destabilize **1**. Therefore, it is unlikely that relatively weak crystal-lattice forces are responsible for the elongated, *trans* pyramidalized formal C=C bond in **1a**. On the other hand, calculations of geometry and ^{13}C NMR chemical-shift parameters for the pentamethylcyclopentene cation **2** are in good agreement with the experimental data reported by Lambert et al. In conclusion, our computational results provide strong evidence that the species obtained by Lambert and co-workers is indeed the pentamethylcyclopentene cation **2**.

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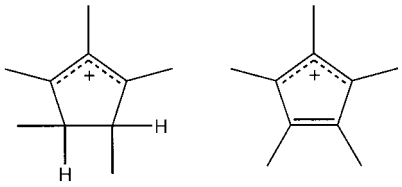
[9] Calculated from single-point energies using the heavy-atom geometry of **1a** with all 15 hydrogen positions of **1** optimized at B3LYP/6 – 31G(d).

[10] Calculated by using the heavy-atom geometry of **1a** with all 17 hydrogen positions of **2** optimized at B3LYP/6 – 31G(d).

Statement

Joseph B. Lambert*

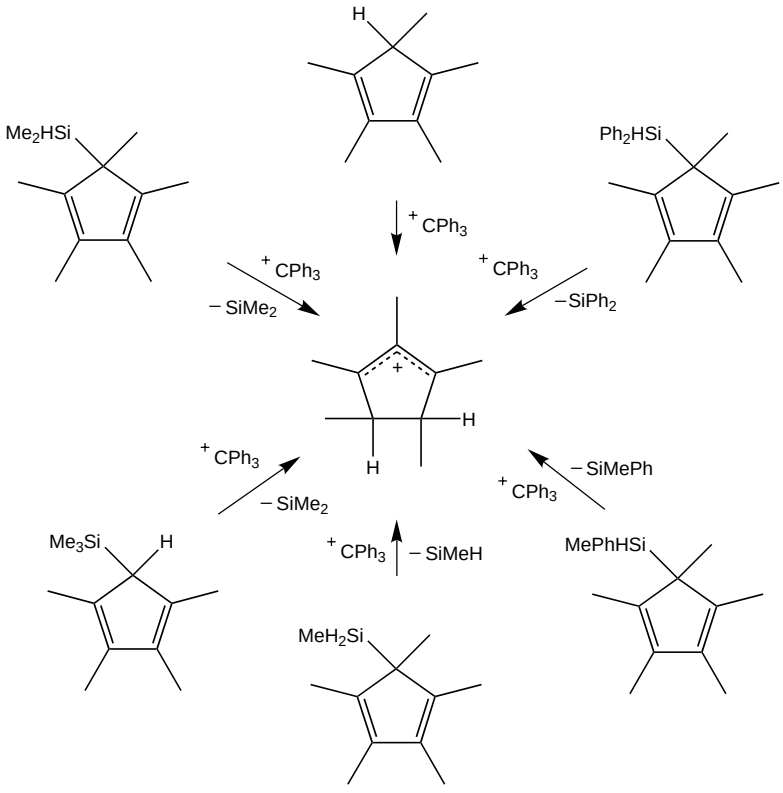
As we conclude in the accompanying Correspondence,[1] the X-ray structure described recently[2] is of the pentamethylcyclopentenyl cation (**A**) rather than the pentamethylcyclopentadienyl cation (**B**). The



A **B**

key resonance of the CH protons in the NMR spectrum of **A** is broad and featureless, inexplicably lacking the expected quartet splitting. In the ^{1}H/^{13}C 2D spectrum, the CH group exhibits a weak to negligible cross peak, in contrast to the strong cross peaks for all the methyl groups. Consequently, the methine carbon appears to show no hydrogen connectivity.

In addition to the method of formation described in ref. [2], we previously prepared the same cation by five other methods (Scheme 1), all of which admit of logical pathways to **B** rather than to **A**. Triphenylcarbinol is not a product, only triphenylmethane in each case. We are currently exploring mechanistic pathways that can explain these unusual observations.



Scheme 1.

Because of the evidence presented in ref. [1], I am retracting the conclusions of ref. [2], which were entirely my own and imply no reflection on the part of my co-workers (whose experimental and theoretical work is valid).

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[2] J. B. Lambert, L. Lin, V. Rassolov, *Angew. Chem.* **2002**, *114*, 1487; *Angew. Chem. Int. Ed.* **2002**, *41*, 1429.

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