*This problem set will take longer than the last one in the sense that you may need to submit some jobs, leave, and check your results later. **Get started early**.*

Some mechanical reminders: To run a G03 job, your input file should be named `myfile.dat`. Issue the command `qg03 myfile.dat` and the script will take care of the rest. If you want to look at an output deck while a job is running, you can either `vi myfile.out` or `more myfile.out`. To examine the queue on the blade, the command is `qstat -a`; you may find that `qstat -a | egrep cm8021##` (where cm8021## is your userid) is also convenient. Links to `vi` commands and a unix primer are provided on the class webpage.

A nomenclature reminder: the notation x/y//w/z means level of theory x using basis set y at a geometry optimized at level of theory w with basis set z. E.g., MP4/6-311G(d,p)//HF/6-31G(d) means the geometry was optimized at the HF/6-31G(d) level but the energy (and/or other properties) are being calculated at the MP4/6-311G(d,p) level. The notation x/y in the absence of a trailing //w/z implies optimization and energy evaluation were performed with the same level of theory.

Some quick notes/reminders with respect to Gaussian03:

1) Template files have been provided in the directory ~cm8021pr/templates — feel free to study them carefully to ensure you have proper file formats, memory requests (`%mem=7gb`), parallel processor requests (`%nproc=4`), and checkpoint naming conventions (`%chk=myfile.chk`).

2) If you are entering geometric data in a G03 input deck (as opposed to reading it from the checkpoint file) you *must* end the input file with a blank line.

3) To find transition states *in the absence of a symmetry constraint*, use `fopt=(ts,calcfc)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS *breaks* the symmetry (in which case, don't use `ts` as a keyword) or preserves it (in which case continue to use it). If you are looking for a TS, you may often find it helpful to do `fopt=(ts,calcfc,noeigentest)`. The other keywords request calculation of analytic force constants on the first step, and that the job not die if you have other than exactly one imaginary frequency.

4) You can save a *lot* of time by using useful information from previous calculations stored in the checkpoint file. *Plan* your calculations to try to save time.

a) Keywords `guess=read` and `geom=checkpoint` get the wave function and the geometry, respectively, from the last completed calculation. So, if you have just done an optimization, and want to follow-up with a frequency calculation, for instance, you will certainly want to use these keywords. **Note: Frequencies *must* be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!** (Note that if you know ahead of time you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `fopt`).

b) If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include `readfc` in the `fopt=()` keyword, e.g., `fopt=(ts,readfc)` for a second pass at a transition-state optimization. This causes the program to start with the force constants from the previous calculation, which is efficient. **It's usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.**

2. For the organic molecules associated with norbornadiene below, fill in the table on the next page with predicted heats of formation.
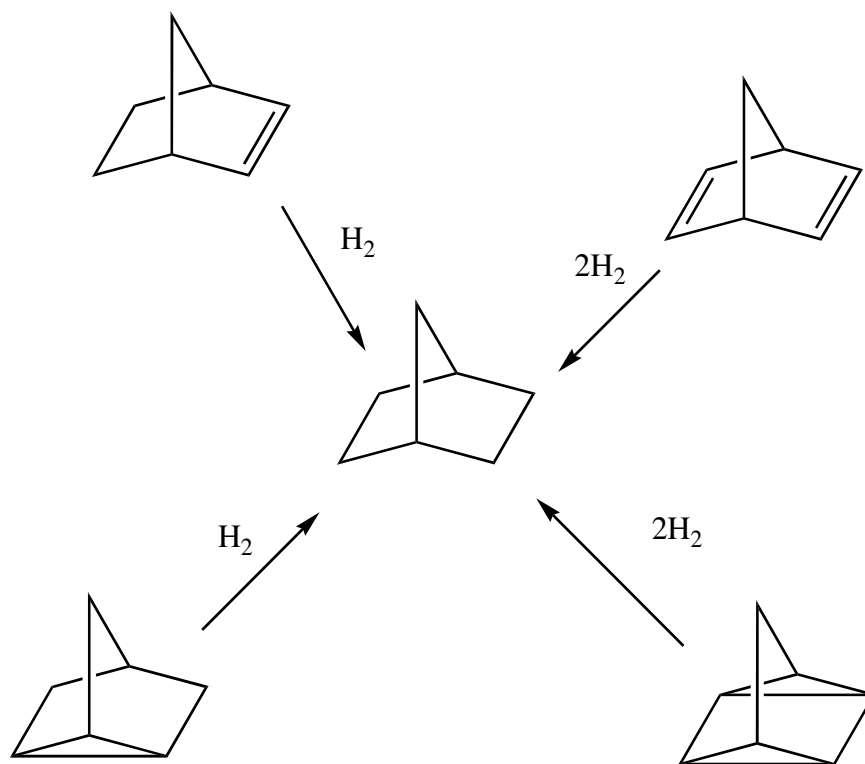
Enthalpies of Formation (kcal/mol) of the Norbornadiene Cycle

Compound	MMX	AM1	PM3	Expt.
Norbornadiene				
Norbornene				
Norbornane				
Nortricyclane				
Quadricyclane				

Comment on the data—are the models useful? Were they fast?

Ensuring that you take advantage of symmetry (ask if you're in doubt about how to accomplish this—also, see Z-matrix handout on class website), compute the $\Delta H_{f,298}$ for quadricyclane (using its atomization energy and Table 10.2 in the text) at the HF/6-311G(2df,p), MP2/6-311G(2df,p)//HF/6-311G(2df,p), and TPSS/6-311G(2df,p)/auto levels (note that the keyword in Gaussian for TPSS is `tpsstpss`). Also compute $\Delta H_{f,298}$ using the G3 method (there is a G3 keyword in Gaussian 03). For the HF/6-311G(2df,p) level, demonstrate in detail how you did one of the calculations of the heat of formation.

Now, (symmetry again!) compute the 298 K enthalpy of norbornadiene *relative* to quadricyclane at the HF/6-311G(2df,p), MP2/6-311G(2df,p)//HF/6-311G(2df,p), TPSS/6-311G(2df,p)/auto, and G3 levels.

Compare and contrast the various models with respect to speed and accuracy. What have you learned? If your research assignment were to learn how things would change if the methylene bridge in these systems were to be replaced with an oxygen atom, what level of theory would you use to do the calculations?

2.   In the attached communication from *Angewandte Chemie, International Edition in English*, Lambert et al. report the isolation and X-ray crystal structure of the pentamethylcyclopentadienyl (Cp*) cation. Note that Cp*+ is formally antiaromatic, so its been an attractive synthetic target for many years.

Lambert et al. report structural data and ^{13}C NMR data. Optimize the structure of the Cp* cation at the HF/3-21G level (don't worry about trying to impose symmetry). How do your structural data compare to the reported data? Now compute the isotropic ^{13}C NMR chemical shifts for all carbons at the B3LYP/6-31G(d)//HF/3-21G level (simply include the keyword `nmr` in a single-point calculation). Since NMR calculations provide *absolute* shieldings, you will also need to know the computed shieldings for tetramethylsilane (TMS, which is the standard for $\delta = 0$ on the ^{13}C chemical shift scale). I have done this calculation for you, and it may be found in the file ~cm8021pr/templates/tmsnmr.out (note the lovely T_d symmetry!). A *de*shielding ^{13}C shift δ is then determined as shielding for TMS minus shielding for carbon of interest. How do your data compare to those reported by Lambert et al.? (Use a picture to report your structural and NMR data).

Now consider the pentamethylcyclopent*enyl* cation (i.e., not *di*enyl, but just *mono*enyl; add the two H atoms trans to one another on adjacent carbon atoms). Compute structural and ^{13}C chemical shifts for this structure at the same levels of theory as already done for Cp*+. How do your data compare to those reported by Lambert et al.?

Which of these two molecules do you think was actually made?

3. Here begins a problem that will carry over to the third problem set and ultimately the final exam. Take a look at

    pollux.chem.umn.edu/8021/C5H8N2/

    While there, select `View Surface`. You will see my contributions to mapping the $C_5H_8N_2$ surface (click on either `00.html` or `900.html` to see them in 3D — you'll need a browser with Java capabilities — you'll also see text cartesian coordinates, which you can always visualize in ChemBio-3D after pasting them into a text file, adding a new first line with the total number of atoms (13), and opening it as cartesian coordinates from ChemBio-3D, or by using the coordinates in a Gaussian 03 input file and using GaussView). My points on the surface are an N-heterocyclic carbene and the TS structure for a 1,2-methyl shift in this carbene.

    Your task is to find two points of your own on the potential energy surface (PES)—both a minimum and a transition-state structure—*that are not already in the table* (easy if you're the first to finish, harder and harder the longer you wait...) To complete each entry, you will need a frequency calculation at the HF/6-31G(d) level (and thus, of course, you will first have to have optimized the structure at this level of theory). When you have the data, click on `Submission Form` and paste in the number of imaginary

frequencies (0 or 1), the HF energy, enthalpy, and free energy, and finally the optimized cartesian coordinates (you can cut and paste right from the output file of the frequency calculation). If you make any mistakes and fail to realize until after submission, contact me with the details and I will fix the website.

Each new submission will be visible to all students, so you can see if the structure you're working on has already been taken. Full credit for this problem simply consists of entering sensible data. In future exercises, we will make comparisons of different levels of theory and different isomers to learn more about the chemistry of the surface.

[9] J. Manna, K. D. John, M. D. Hopkins, *Adv. Organomet. Chem.* **1995**, *38*, 79.

[10] X-ray structure analysis of **6**: Crystal grown from CH₂Cl₂/hexane; crystal dimensions $0.33 \times 0.33 \times 0.10$ mm³; $C_{18}H_{24}O_2P_2W$ ($M_r = 518.16$); monoclinic, space group $P2_1/c$, $a = 9.256(2)$, $b = 12.571(2)$, $c = 17.942(6)$ Å, $\beta = 103.15(4)°$, $V = 2032.9(9)$ Å³, $Z = 4$, $\rho = 1.693$ Mg m⁻³, $\mu(Mo_{K\alpha}) = 5.845$ mm⁻¹, $\lambda = 0.71073$ Å (Mo$_{K\alpha}$ radiation, Nonius CAD4 single crystal diffractometer). Data collection at 293(2) K, ω-2θ scans, $2.0 < \theta < 25.97$. A total of 3984 unique reflections were collected, of which 2645 were observed with $I > 2\sigma(I)$. Crystal structure was solved by direct methods (SHELXS-97).[11a] An anisotropic least-squares refinement was carried out with SHELXL-97.[11b] The final cycle of full-matrix least-squares refinement based on 3984 reflections and 213 parameters converged to a final value of $R1$ ($F^2 > 2\sigma(F^2)$) = 0.0405, w$R2$ ($F^2 > 2\sigma(F^2)$) = 0.1071. Residual electron density 0.76/ − 1.30 e Å⁻³. CCDC-1777731 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] a) G. M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, SHELXL-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**.

[12] M. C. Lukehart, *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole, Belmont CA, **1985**, p. 77.

[13] G. Consiglio, R. M. Waymouth, *Chem. Rev.* **1989**, *89*, 257.

[14] For proposed migrations of this kind, see: D. Cui, N. Hashimoto, S. Ikeda, Y. Sato, *J. Org. Chem.* **1995**, *60*, 5752.

[15] H. tom Dieck, H. Friedel, *J. Organomet. Chem.* **1968**, *14*, 375.

[16] N. S. Nudelman, C. Carro, *Synlett* **1999**, *12*, 1942.

[17] M. Ishikura, M. Kamada, I. Oda, T. Ohta, M. Terashima, *J. Heterocyclic. Chem.* **1987**, *24*, 377.

[18] M. Almeida, M. Beller, G. Wang, J. Bäckvall, *Chem. Eur. J.* **1996**, *2*, 1533.

[19] N. B. Lorrette, W. L. Howard, *J. Org. Chem.* **1961**, *26*, 4857.

The Stable Pentamethylcyclopentadienyl Cation**

Joseph B. Lambert,* Lijun Lin, and Vitaly Rassolov

The cyclopentadienyl anion, $C_5H_5^-$ (**1**, Cp⁻), was first prepared one hundred years ago.[1] In due course it became a classic example of aromaticity, exemplifying the Hückel $4n+2$ rule for π electrons, along with benzene (**2**) and the tropylium cation (**3**).[2–4] In contrast, the cyclopentadienyl cation, $C_5H_5^+$ (**4**, Cp⁺) has languished experimentally as an elusive charge
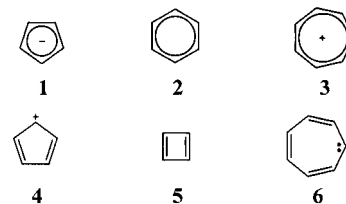
variant. It shares with cyclobutadiene[5–7] (**5**) and the cycloheptatrienyl anion[8] (**6**), among others, the characteristics of possessing $4n$ π electrons and thus potentially being antiaromatic.

No simple cyclopentadienyl cation has been structurally characterized. Several studies have reported electron spin resonance (ESR) spectra,[9] and some studies have implied the species as an intermediate.[10] These investigations variously looked at the pentachloro, pentaphenyl, and pentamethyl derivatives as well as the unsubstituted molecule. In general, the observed cations were relatively unstable, possessed triplet multiplicity, and needed protective environment.

We now report the preparation of the pentamethylcyclopentadienyl cation $C_5Me_5^+$ (Cp*⁺) as the tetrakis(pentafluorophenyl)borate (TPFPB⁻) salt. The crystalline material obtained is stable for weeks at room temperature and can be left exposed to the open atmosphere without serious decomposition. We have solved the X-ray structure and obtained NMR spectra in the solid state and in solution. This material may be obtained in one step at room temperature by hydride abstraction from commercially available pentamethylcyclopentadiene [Eq. (1)].[11, 12] The trityl cation (Ph₃C⁺, with the

$$\text{(cyclopentadiene-H)} + Ph_3C^+TPFPB^- \longrightarrow Ph_3CH + Cp^{*+}TPFPB^- \qquad (1)$$
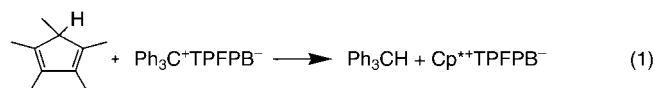
anion TPFPB⁻) is converted into triphenylmethane, whereas pentamethylcyclopentadiene is converted into the corresponding cation. Crystals of the product began forming immediately and spontaneously. The overall yield is nearly quantitative, and yields of crystals have reached 40%. The reaction has been carried out in several solvents (benzene, toluene, dichloromethane) and with alternative (silyl) leaving groups.

The remarkable stability of this material may be attributed to a number of factors. First, the methyl groups clearly are critical, as analogous experiments with the unsubstituted system were unsuccessful. The methyl group serves as an electron donor and also may play a steric role, as described subsequently. The second key factor is the choice of the counteranion. Many anions of low nucleophilicity now are available.[13] We previously utilized TPFPB⁻ in the preparation of the first silylium cation[14] and employ this same anion in the present study. Finally, choice of solvent also is critical, as

[*] Prof. J. B. Lambert, L. Lin
Department of Chemistry
Northwestern University
Evanston, IL 60208-3113 (USA)
Fax: (+1) 847-491-7713
E-mail: jlambert@northwestern.edu

Prof. V. Rassolov
Department of Chemistry
University of South Carolina
Columbia, SC 29208 (USA)

solvents with higher nucleophilicity than those of arenes or halocarbons react with the cation.

The crystal structure[15] of the cation with its anion is depicted in Figure 1. As the edge view (Figure 2a) shows, the molecule is modestly nonplanar (the five internal ring dihedral angles are 4.1(6), 6.6(6), 4.6(5), 6.9(6), and 0.5(5)°). Three carbon atoms (C1, C2, C3) and their attached methyl groups form a nearly planar substructure closely resembling a 1,2,3-trimethylallyl group. Atoms C4 and C5, respectively, are below and above this plane, and their attached methyl groups protrude appreciably from the plane, the CH₃-C4-C5-CH₃ dihedral angle being 106.9(6)°.
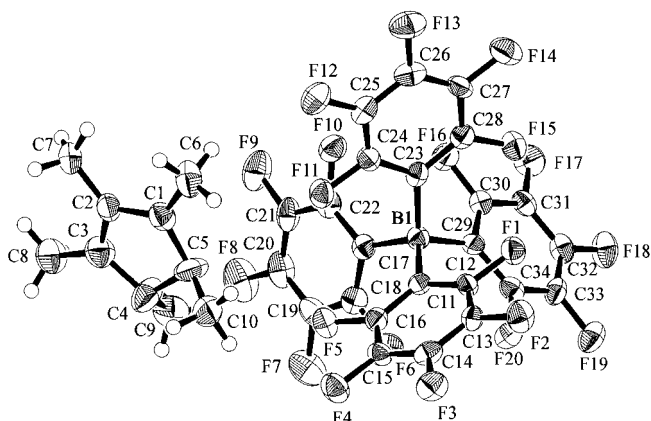

Figure 1. The crystal structure of pentamethylcyclopentadienyl tetrakis-(pentafluorophenyl)borate. There is no covalent bonding between the cation on the left and the anion on the right.
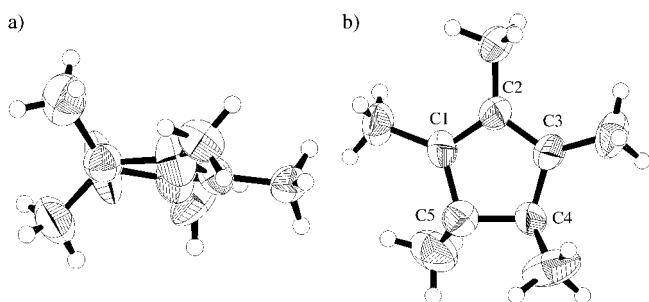

Figure 2. a) Edge view of the pentamethylcyclopentadienyl cation, sighting down the C4-C5 bond on the left. The nearly planar allyl portion is on the right. b) Top view.

The view from the top (Figure 2b) shows an irregular pentagon. The irregularity is quantified in structure **7** (the methyl groups are omitted from the following structures for clarity). The bond lengths in the allyl-like portion across the
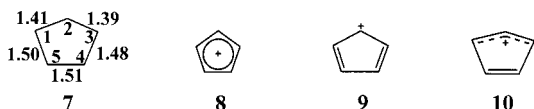
top of the drawing are relatively short, that is, approximately 1.40 Å (benzene-like), as expected for charge delocalization. The other bond lengths are somewhat shorter than a single bond between sp³ carbon atoms (typically ca. 1.54 Å) and

longer than a single bond between unconjugated sp² carbon atoms (typically ca. 1.48 Å).

Several valence bond structures may be considered.[3] The fully delocalized form **8**, which would suffer from antiaromaticity, is eliminated because of the observed irregularity of the pentagon. Structure **9** requires a localized cation at C1 and localized double bonds, whereas the observed C3−C4 and C1−C5 lengths are closer to single bonds. Structure **10** best describes the C1-C2-C3 (allyl-like) portion. The observed C4−C5 bond is closer to a single bond and is poorly depicted by all the structures.

The best reported calculations on the pentamethyl derivative[16] indicate strong bond alternation resembling **9**, with a nearly single C4−C5 bond (1.56 Å) but no pyramidalization at these carbon atoms. Our own calculations on the pentamethyl derivative[17,18] at higher level, however, favor structure **10**, with lengths of 1.38 and 1.39 Å (observed 1.406(6) and 1.394(6) Å) for the bonds (C1−C2, C2−C3) in the allyl portion, 1.52 and 1.53 Å (observed 1.500(6) and 1.481(6) Å) for the next adjacent bonds (C1−C5 and C3−C4), and 1.36 Å (observed 1.510(6) Å) for the bond (C4−C5) opposite the allyl portion. All calculations[16,17] have indicated a planar structure. Thus the major differences between our calculations and observations are an observed lengthening of C4−C5 by 0.15 Å and pyramidalization of C4 and C5.[19]

The solid-state ¹³C NMR spectrum reflects the nonequivalence of the five ring carbon atoms in the crystal. As a result, all ten carbon atoms in the molecule give distinct or nearly distinct peaks. There are five methyl resonances in the region $\delta = 7-22$. The cationic region contains two equal peaks at $\delta = 243$ and 250, corresponding to C1 and C3. The central carbon atom (C2) in the allyl-like fragment gives a sharp signal at $\delta = 153$, indicative of the absence of charge at the nodal position of the allyl group. The resonances for C1-C2-C3 closely resemble those for the 1,3-dimethylallyl cation ($\delta = 236$ and 147).[20] Finally, a peak at $\delta = 60$ is intermediate between the normal alkane and alkene regions and fits well for the pyramidalized carbon atoms, C4 and C5. Higher symmetry is indicated in solution, as the C1/C3 resonances appear at the approximate average positions of those in the solid.

The unsaturated region of the ¹³C NMR spectrum is best attributed to the allyl fragment of **10** (two carbon atoms bearing positive charge, plus one on the node). Structure **9** has only one carbon atom bearing positive charge. Thus NMR spectroscopic analysis confirms the conclusions from the crystal structure that **10** best describes the pentamethylcyclopentadienyl cation.

To probe the spin multiplicity of this cation, we examined pure crystals and diluted powder by ESR spectroscopy. No significant signals were obtained at either 77 or 298 K. A triplet state thus is unlikely. The sharpness of the NMR signals both in the solid and in solution strongly supports the absence of unpaired electron spins, which should have broadened the signals. The pentamethylcyclopentadienyl cation therefore appears to be a stable singlet molecule. Our calculations[17] found the planar singlet state of the pentamethyl derivative to be lower by 1.5 kcal mol⁻¹ than the symmetrical (D_{5h}) triplet state.

Crystallography, NMR spectroscopy, and theory support a structure most closely resembling **10**. The pyramidality of C4 and C5 and the Me-C4-C5-Me dihedral angle in the crystal (107°), however, indicate significant deviations from a double bond. The estimated barrier to torsion around the C4−C5 bond is quite small, perhaps under 100 cal mol^{-1}. Thus in both calculation and observation, this formally double bond is very unusual. The pyramidality seems to imply a fourth coordination, yet there is no fourth atom within the sum of the ionic radii. The closest atom to C4 is F6 (3.092 Å) from the counteranion (Figure 1), and the closest atom to C5 is F14 (3.394 Å) from the second anion in the asymmetric unit. Fluorine atoms at 3.1 – 3.4 Å distance can provide only a very small perturbation to pyramidalize C4 and C5 and lengthen C4−C5. In the solid state, there is a fluorine atom on the anion close to a hydrogen atom on each of the methyl groups on C4 and C5 (H12····F20 2.70 Å, H14····F18 2.50 Å). These distances would be about 1 Å shorter if the ring substituents moved into the plane of the ring. Crystal packing between the anion and the cation pyramidalizes C4 and C5, a distortion permitted by the weak π bonding. These are noncovalent, nonbonded interactions. The resulting deformations are a tradeoff between coulombic attractions and nonbonded repulsions.

11
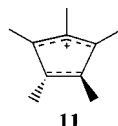
In summary, we have observed that the pentamethylcyclopentadienyl cation is a stable singlet with a largely localized electronic structure best described by **11**.

[1] J. Thiele, *Chem. Ber.* **1901**, *34*, 68 – 71.

[2] No single localized ("Kekulé") structure is correct for $4n + 2$ molecules, so the circle within the ring is used to depict electron delocalization. The $4n$ molecules are drawn as localized, Kekulé structures.

[3] P. J. Garratt, *Aromaticity*, Wiley, New York, **1986**; V. I. Minkin, M. N. Glukhovtsev, B. Y. Simkin, *Aromaticity and Antiaromaticity*, Wiley, New York, **1994**.

[4] R. Breslow, *Acc. Chem. Res.* **1973**, *12*, 393 – 398; K. B. Wiberg, *Chem. Rev.* **2001**, *101*, 1317 – 1331; A. D. Allen, T. T. Tidwell, *Chem. Rev.* **2001**, *101*, 1333 – 1348.

[5] L. Watts, J. D. Fitzpatrick, R. Pettit, *J. Am. Chem. Soc.* **1965**, *87*, 3253 – 3254.

[6] G. Maier, H.-O. Kalinowski, K. Euler, *Angew. Chem.* **1982**, *94*, 706; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 693 – 694; H. Irngartinger, M. Nixdorf, *Angew. Chem.* **1983**, *95*, 415; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 403 – 404.

[7] M. Orendt, B. R. Arnold, J. G. Radziszewski, J. C. Facelli, K. D. Malsch, H. Strub, D. M. Grant, J. Michl, *J. Am. Chem. Soc.* **1988**, *110*, 2648 – 2650; D. J. Cram, M. E. Tanner, R. Thomas, *Angew. Chem.* **1991**, *103*, 1048; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1024 – 1027.

[8] H. J. Dauben, Jr., M. R. Rifi, *J. Am. Chem. Soc.* **1963**, *85*, 3041 – 3042; W. v. E. Doering, P. P. Gaspar, *J. Am. Chem. Soc.* **1963**, *85*, 3043; S. W. Staley, A. W. Orvedal, *J. Am. Chem. Soc.* **1974**, *96*, 1618 – 1620.

[9] R. Breslow, H. W. Chang, R. Hill, E. Wasserman, *J. Am. Chem. Soc.* **1967**, *89*, 1112 – 1119; M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, V. J. Kuck, *J. Am. Chem. Soc.* **1973**, *95*, 3017 – 3018.

[10] P. Jützi, A. Mix, *Chem. Ber.* **1992**, *125*, 951 – 954; G. A. Dushenko, I. E. Michailov, I. A. Kamenetskaya, R. V. Skachkov, A. Zhunke, K. Myugge, V. I. Minkin, *Russ. J. Org. Chem.* **1994**, *30*, 1559 – 1564; A. D. Allen, M. Sumonja, T. T. Tidwell, *J. Am. Chem. Soc.* **1997**, *119*, 2371 – 2375.

[11] This is an example of the Bartlett – Condon – Schneider reaction, whereby hydride is transferred intermolecularly from one carbon atom to another and charge is shifted between molecules. The equilibrium is driven to the right either because the products are more stable than the starting materials or because the cationic product is removed by precipitation.

[12] P. D. Bartlett, F. E. Condon, A. Schneider, *J. Am. Chem. Soc.* **1944**, *66*, 1531 – 1539.

[13] S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927 – 942.

[14] J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse, B. Kuhlmann, *J. Am. Chem. Soc.* **1999**, *121*, 5001 – 5008.

[15] Measurements were made on a Bruker SMART-NT CCD area detector with graphite monochromated Mo$_{K\alpha}$ radiation. Cell constants corresponded to a primitive cell with dimensions $a = 13.216(7)$, $b = 13.689(7)$, $c = 17.409(9)$ Å, $V = 3149.7(24)$ Å^3, $\beta = 89.978(9)°$. For $Z = 4$ and $M_r = 1628.54$ for $C_{34}H_{15}F_{20}B$, the calculated density is 1.72 g cm^{-3}. The systematic absences of $h0l$ ($l \pm 2n$) and $0k0$ ($k \pm 2n$) uniquely determined the space group to be $P2_1/c$. Data were collected at $-120 \pm 1°C$ to a maximum of 2θ value of 46.7°. Of the 20700 reflections collected, 4803 were unique ($R_{int} = 0.099$). Equivalent reflections were merged. A Gaussian face-indexed absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved with direct methods and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions but not refined. The final cycle of full-matrix least-squares refinement on F^2 was based on 4569 observed reflections and 496 variable parameters and converged with an unweighted agreement factor of $R1 = 0.042$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.79 and -0.78 e$^-$ Å^{-3}, respectively. CCDC-178042 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[16] H. Jiao, P. von R. Schleyer, Y. Mo, M. A. McAllister, T. T. Tidwell, *J. Am Chem. Soc.* **1997**, *119*, 7075 – 7083; B. Reindl, P. von R. Schleyer, *J. Comput. Chem.* **1998**, *19*, 1402 – 1420.

[17] Geometry optimization and energy calculations were carried out at the CASSCF(4.5)/6-31G* level of theory with the GAMES program.[18] Inclusion of nondynamic correlation effects allows mixing of electronic configurations for **9** and **10** and favors geometry **10** with a singlet ground state. The MP2 calculations used by previous authors[15] for geometry optimization are based on a single determinant reference and, therefore, do not permit such mixing. These calculations favor molecular structure **9** rather than **10** and the triplet rather than the singlet.

[18] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347 – 1363.

[19] The C4−C5 bond is clearly a double bond in calculation and must be considered formally to be a double bond in observation to account for all the π electrons. Because of pyramidalization, however, its length is closer to that of a single bond.

[20] G. A. Olah, P. R. Clifford, Y. Halpern, R. G. Johanson, *J. Am. Chem. Soc.* **1971**, *93*, 4219 – 4222.