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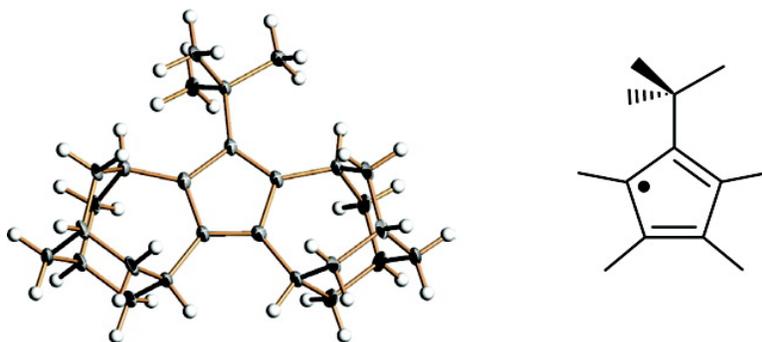
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Spin-Localized Cyclopentadienyl Radical Annelated with Homoadamantene Frameworks: Isolation, X-ray Crystal Structure, and ESR Characterization

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The cyclopentadienyl (Cp) radical is one of the simplest members of cyclic conjugated carbon radicals, but investigations of its detailed properties have been hampered by its elusive nature. Some of the isolated Cp radicals include those stabilized through delocalization of spin over π-conjugated substituents such as aryl[1] and ethynyl groups.[2] The isolation of $(i\text{-Pr})_5C_5$ radical, which led to the first X-ray crystal structure of a Cp radical, showed an effective hyperconjugative stabilization by isopropyl substituents.[3] The annelation of two homoadamantene units is expected to confer significant electronic and steric effects to the Cp ring, as has been demonstrated by annelation with rigid bicyclic σ-frameworks to various cyclic π-conjugated systems.[4] We now report the synthesis, isolation, and full characterization of a new, stable Cp radical **1**, annelated with two homoadamantene frameworks, which is entirely different from the above-mentioned Cp radicals in its unusual spin-localized structure with distinct bond alternation.
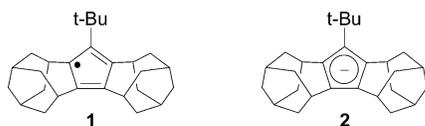
Lithiation of 4-bromo-4-homoadamantene (**3**)[5] followed by reaction with 0.5 equiv of pivaloyl chloride gave the tertiary alcohol **4**. Ionization of **4** by treatment with *p*-toluenesulfonic acid resulted in electrocyclization[6] of a carbocationic intermediate and subsequent deprotonation to form the unsymmetrically substituted cyclopentadiene **5**.[7] X-ray crystallography confirmed the position of the hydrogen in the five-membered ring.
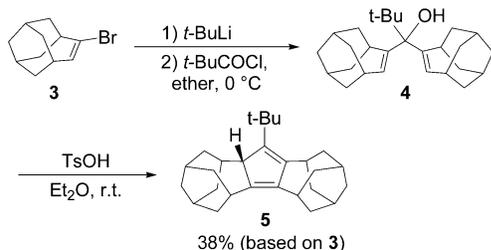
Cyclopentadiene **5** could be deprotonated to form anion **2** by using either KC_8 or KH in THF. Both methods led to the quantitative formation of **2**, as shown by ^1H NMR spectra of the reaction mixture.[8] Single crystals of $2K^+\cdot3THF$ were obtained on cooling the reaction mixture. X-ray analysis showed a monomeric ion pair between **2** and K^+, with oxygen atoms of three THF molecules coordinated to K^+.[7] This structure is similar to that of $(PhCH_2)_5C_5^-K^+\cdot3THF$,[9] the only known monomeric K^+Cp^- complex,[10] but the η^5-type coordination is somewhat stronger in $2K^+\cdot3THF$, as indicated by the $K-Cp$ ring center distance (2.739 Å), which is shorter by 0.049 Å. This suggests a higher negative charge density on the Cp ring of **2** due to the greater electron-donating
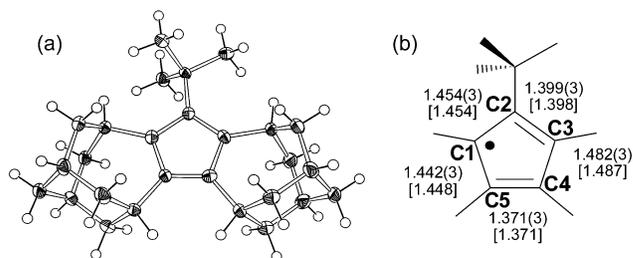
Figure 1. (a) ORTEP drawing of **1** as determined by single-crystal X-ray diffraction analysis at 100 K. Ellipsoids are drawn at the 50% probability level for non-hydrogen atoms. (b) Selected interatomic distances (Å). Values from fully optimized UB3LYP/6-31G* geometry are given in square brackets.

inductive effect of the aliphatic substituents compared to benzyl groups. The Cp ring is nearly planar (sum of the internal angles 539.99°) and only slightly distorted from a regular pentagon $[\Delta R(C-C) < 0.034$ Å$]$.

Yellow-colored radical **1** was generated by the oxidation of anion **2** with AgCl or, more preferably, with $AgSbF_6$ in THF. The latter salt is soluble in THF, allowing instantaneous oxidation, while oxidation with AgCl took several hours due to the heterogeneous nature of the reaction mixture.

Solutions of **1**[11] are highly air-sensitive, and **1** slowly abstracts hydrogen from solvents such as THF. In the solid state, **1** stays unchanged for months under vacuum but is stable in the presence of air only for a few hours. Upon slow cooling of a pentane solution to −20 °C, X-ray-quality crystals, mp 141 °C (dec), were obtained as bright yellow prisms. The molecule has a C_s symmetry plane passing through the exactly planar Cp ring. The C−C bonds of the Cp ring revealed substantial bond alternation, characterizing **1** as a spin-localized 2,4-cyclopentadien-1-yl radical (Figure 1). The C2−C3 and C4−C5 bonds are longer by only 0.047 and 0.037 Å, respectively, than the corresponding double bonds in **5**, while other C−C bonds have lengths typical of $C(sp^2)-C(sp^2)$ single bonds. One of the $C-CH_3$ bonds of the *tert*-butyl group is oriented antiperiplanar to the radical center, with the other two methyl carbons positioned above and below the plane of the Cp ring. These structural features are in excellent agreement with the geometry calculated by DFT (Figure 1b). A spin-localized character is demonstrated by the calculated spin densities at the Cp ring carbons: C1, 0.606; C2, −0.174; C3, 0.377; C4, 0.245; and C5, −0.093. The large spin densities at C1 and C3 suggest that this radical has the characteristics of an unsymmetrical allyl radical. The presence of a *tert*-butyl group is critical to the inequality between C1 and C3, probably due to an orbital interaction between the allylic π-system and the two $C-CH_3$ σ bonds, which are
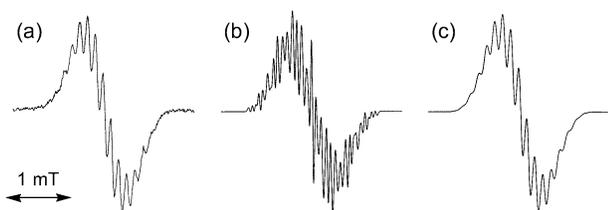
Figure 2. (a) ESR spectrum of **1**, measured in toluene at ambient temperature. (b) Simulated ESR spectrum generated using calculated (UB3LYP/6-31G*) hyperfine coupling constants and a line width 0.039 mT. (c) Simulated spectra for the time-averaged structures **1a** and **1b**.
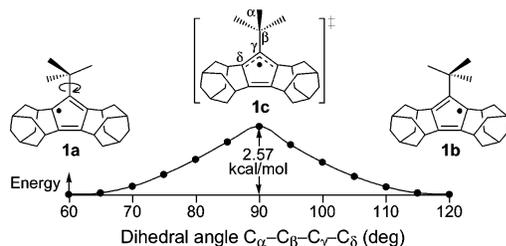
Figure 3. Energy profile for the change in spin distribution associated with rotation of the *tert*-butyl group. The energy for each conformation was calculated at the UB3LYP/6-31G* level of theory with geometry optimization at a fixed dihedral angle $C_\alpha-C_\beta-C_\gamma-C_\delta$.

directed out of the symmetry plane. Indeed, optimizing the geometry of the corresponding C2-unsubstituted radical resulted in a perfectly symmetrical allylic structure.

This is in sharp contrast to the almost equal C−C bond distances reported for the Cp ring of crystalline $(i\text{-Pr})_5C_5{}^{\bullet}$ at 110 K.[3a,b] Theoretical calculations predicted that the ground state of $H_5C_5{}^{\bullet}$ would have a C_{2v} symmetry as a consequence of a Jahn−Teller distortion.[12] However, due to the low barriers for the degenerate conformational change between the equivalent C_{2v} structures (eq 1), time-averaged D_{5h} (or C_5) symmetry is normally observed for $R_5C_5{}^{\bullet}$ radicals. In the case of **1**, annelation with homoadamantene frameworks appeared to selectively stabilize a structure shown in Figure 1b with a lower symmetry.
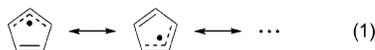
The ESR spectrum of **1** recorded in toluene at ambient temperature exhibited a multiplet signal with ca. 15 lines at $g = 2.0025$ (Figure 2a). A simulated ESR spectrum, generated on the basis of the DFT-calculated coupling constants (a_Hs), resulted in poor agreement with the observed spectrum (Figure 2b). This clearly indicates that the spin-localized structure is not static in solution and suggests a rapid exchange between the two equivalent states, **1a** and **1b** (Figure 3), which would give a time-averaged C_{2v} structure. This exchange includes not only the change in the geometry of the Cp ring but also the rotation around the *t*-Bu-Cp bond, so that one of the methyl carbons is positioned anti relative to the radical center. Simulation using coupling constants averaged over the two structures perfectly reproduced the observed spectrum (Figure 2c). The transition state, symmetrical allylic radical **1c**, is predicted to be only 2.57 kcal/mol higher in energy than **1a** or **1b** (Figure 3). Due to this small barrier, the interconversion is so fast that no line broadening was observed by ESR when the temperature

was lowered to −130 °C in pentane. However, this exchange is frozen in the solid state, presumably due to crystal packing.

Cyclic voltammetry of radical **1** showed a reversible oxidation wave at $E_{1/2} = +0.30$ V and an irreversible reduction wave at $E_p{}^{red} = -1.78$ V vs Fc/Fc$^+$ in degassed CH_2Cl_2. These values indicate that **1** is more easily oxidized and reduced than $(i\text{-Pr})_5C_5{}^{\bullet}$, the oxidation and reduction potentials ($E_{1/2}$) for which have been reported to be +0.58 and −1.91 V vs Fc/Fc$^+$, respectively.[3b] The lowering of the oxidation potential represents the effective cation-stabilizing effect of annelated homoadamantenes by $\sigma-\pi$ conjugation, suggesting the possibility of generating a stable Cp cation via the oxidation of **1**.

In conclusion, a novel Cp radical **1**, incorporating annelated homoadamantene units, was isolated as stable crystals, and its structure was determined by X-ray crystallography. A significant bond alternation demonstrated a spin-localized nature, which was shown to exist even in solution. These characteristics are fundamentally different from those previously reported for uniformly substituted Cp radicals, thus displaying the distinctive effect of annelation with rigid homoadamantene frameworks on the nature of cyclic π-conjugated systems.

Supporting Information Available: Experimental procedures, NMR spectra of new compounds, crystallographic data for **1**, **2**, and **5**, and the results of DFT calculations for **1** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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