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Pentaisopropylcyclopentadienyl: Singlet Anion, Doublet Radical, and Triplet Cation of a Carbocyclic π System[†]

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Abstract: Chemical or electrochemical oxidation of pentaisopropylcyclopentadienylsodium yields yellow-green crystals of the pentaisopropylcyclopentadienyl radical (**1**), which is very air sensitive under formation of tetraisopropylcyclopentadienone (**2**). **1** has been characterized by EPR/ENDOR, proton NMR spectroscopy, and mass spectrometry. X-ray structural analysis of **1** reveals stacks of eclipsing, equally spaced, planar five-membered rings. Cyclovoltammetric measurements as well as a low-energy first PES ionization band of **1** at 7.02 eV are in accordance with facile generation of the pentaisopropylcyclopentadienyl cation **5** from pentaisopropylcyclopentadienyl chloride (**4**) or bromide (**3**) and antimony pentachloride. In accordance with MNDO/CI calculations cation **5** is a ground-state triplet. Its EPR spectrum at 115 K shows a zero field splitting parameter $D = 0.1615(4)$ cm^{-1} with coincidence of the x and y lines, indicating no detectable distortions from axial symmetry and only weak electron-delocalizing properties of the isopropyl substituents.

Introduction

Cyclopentadienyl radicals, a class of carbon radicals,[1] are very unstable except for the pentaaryl derivatives.[2] C_5R_5 radicals with R = F,[3a] Cl,[3b] CH_3,[4] H, D,[1,5] and COOMe[1] have only been characterized by ESR,[2b,d,3,4] electron-nucleus double resonance (ENDOR),[2c] and UV[2b,d] and laser-induced fluorescence spectroscopy (LIF)[5] in solution,[2c,d,4] in the gas phase,[5] or in a matrix.[3]

With four π electrons in a conjugated system, cyclopentadienyl cations are potential triplet ground state molecules. Investigations of substituted cyclopentadienyl cations in solution have shown that three donor substituents such as NR_2 or OR[6] or five p-C_6H_4-OMe groups[7] are necessary to obtain thermally stable cyclopentadienyl cations. However, these and all of the known pentaarylcyclopentadienyl cations have a singlet ground state.[8] The only known cyclopentadienyl cations with a triplet ground state are the parent compound $C_5H_5^+$[9] and the pentachloro derivative $C_5Cl_5^+$.[10a] Unfortunately, these are extremely unstable, and all efforts aiming at more stable triplet ground state cyclopentadienyl cations have been rather frustrating so far.[10b] A good candidate for another triplet ground state cyclopentadienyl cation which could recently be generated in solution and trapped with a variety of nucleophiles is the pentamethyl derivative.[11a] In contrast to the planar $C_5H_5^+$ system, derivatives of the tetragonal pyramidal $C_5H_5^+$ isomer have been obtained by OH^- abstraction from alkyl-substituted tricyclopentanols.[11b]

The adventitious discovery of the stable pentaisopropylcyclopentadienyl radical as a main product upon reacting pentaisopropylcyclopentadienylsodium with iron(II) chloride[12a] has focused our attention on the redox behavior of the pentaisopropylcyclopentadienyl system. Oxidation of the $[C_5(i\text{-Pr})_5]^-$ anion in two steps is expected to result in formation of the $[C_5(i\text{-Pr}))_5]^+$ cation via the intermediate $[C_5(i\text{-Pr})_5]^\bullet$ radical. The synthesis of pentaisopropylcyclopentadienylsodium by stepwise alkylation and metalation of cyclopentadiene and its oxidation by ferrous chloride are outlined in Scheme I.[12b-d]

Results and Discussion

The original synthesis of the pentaisopropylcyclopentadienyl radical by oxidation of pentaisopropylcyclopentadienylsodium with ferrous chloride is a slow reaction which needs careful temperature control.[12a] Even then, the yield is below 40%. In contrast, oxidation of pentaisopropylcyclopentadienylsodium in pentane at -78 °C with bromine affords the radical **1** straightforwardly in 70% yield (eq 1). Radical **1** can be isolated as yellow-

$$2Na[C_5(i\text{-Pr})_5] + Br_2 \xrightarrow{\text{pentane, -78 °C}} 2C_5(i\text{-Pr})_5^\bullet + 2NaBr \quad (1)$$

[†] Dedicated to Prof. O. J. Scherer on the occasion of his 60th birthday.

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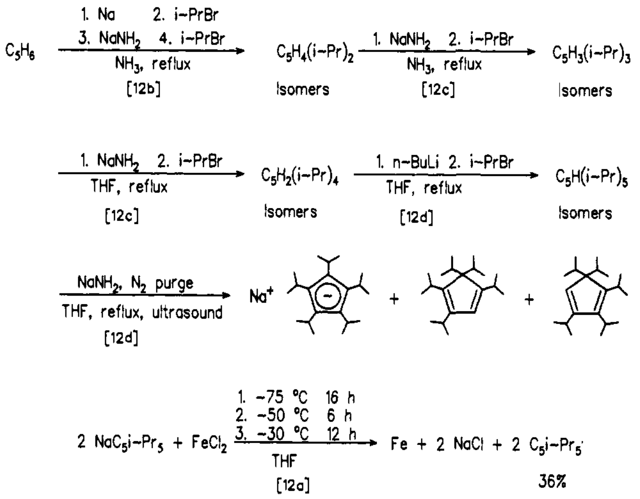
Scheme I. Synthesis of pentaisopropylcyclopentadienylsodium from cyclopentadiene and the pentaisopropylcyclopentadienyl radical by oxidation of pentaisopropylcyclopentadienylsodium with ferrous chloride



green crystals[13] by vacuum sublimation at about 75 °C. It is readily soluble in pentane, toluene, diethyl ether, and THF, for example. The ^{1}H-NMR spectrum[14] of a solution of **1** saturated at 60 °C shows two broad signals for the methyl and methine protons in an intensity ratio of 6:1. When the solution is warmed to 100 °C, the methyl signal shifts from $\delta = 22.0$ to $\delta = 19.4$, its half-width decreasing from 1700 to 1400 Hz, and the methine signal shifts from $\delta = 13.5$ to $\delta = 14.5$, its half-width increasing from 850 to over 1100 Hz. On cooling the solution to room temperature, **1** crystallizes unchanged from solution. The sealed NMR tube containing a C_6D_6 solution and crystals of **1** could be kept in daylight at room temperature for 2 years without decomposition.

EPR/ENDOR Spectra of Pentaisopropylcyclopentadienyl (1). A partially air-oxidized sample of $Na[C_5(i\text{-}Pr)_5]$ was used for EPR/ENDOR measurements. The spectra were recorded in toluene solution (Figure 1). At 293 K a resolved EPR spectrum with a *g* value of 2.0024 and coupling constants $a_H(CH_3) = 0.032$ mT, $a_H(CH) = 0.016$ mT, and $a_{^{13}C}(CH_3) = 0.49$ mT could be observed. The ENDOR spectrum at this temperature shows a proton coupling of 0.88 MHz corresponding to a coupling constant of 0.032 mT. At 200 K the methyl (γ) proton coupling constant remained unchanged and that of the methine (β) proton decreases from 0.016 to less than 0.004 mT. This well-known behavior is characteristic for secondary alkyl substituents CHR_2 of π radicals;[15] it is attributed to the "locking" of the $C(\beta)$–$H(\beta)$ bond in the nodal plane of the π system at low temperatures (cf. the crystal structure of radical **1**) and thus vanishing π/σ hyperconjugative spin transfer. At 293 K application of the Heller–McConnell equation (eq 2) yields an average angle θ of the $C(\beta)$–$H(\beta)$ bond of about 7° relative to the π nodal plane. The

$$a = \varphi(B_0 + B_2 \cos^2 \theta)^{16} \qquad (2)$$

$$(\varphi = 0.2;\ B_0 = 0;\ B_2 = 5\ \text{mT}^{17})$$

pentamethylcyclopentadienyl radical with such an average angle

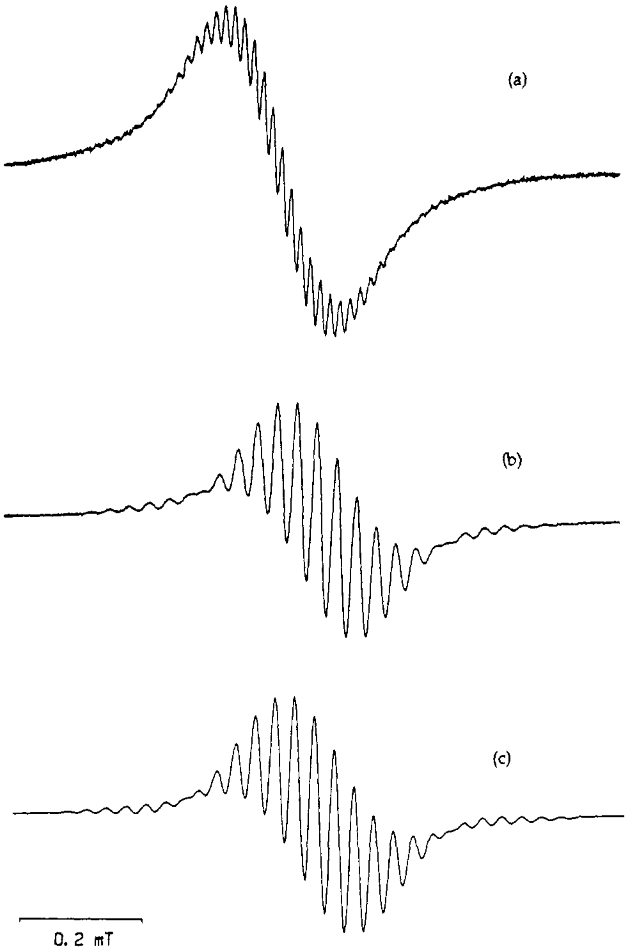


Figure 1. EPR spectra of $[C_5(i\text{-}Pr)_5]$ in toluene (a) at 293 K, (b) at 200 K, and (c) a computer simulation of b using $a_H(CH_3) = 0.0032$ mT, $a_{^{13}C}(CH_3) = 0.49$ mT, and a Gaussian line width of 0.025 mT.

of $\theta = 45°$ exhibits a much higher β proton coupling constant of 0.64 mT.[4] The considerable π/σ hyperconjugation from the cyclopentadienyl π system to the $C(\beta)$–$C(\gamma)$ bonds is nicely illustrated by the fairly intense ^{13}C doublet satellites, which are due to the coupling of the unpaired electron with one ^{13}C isotope within the manifold of 10 equivalent methyl carbon centers (Figure 1). Application of the Heller–McConnell equation with $\varphi = 0.2$, $B_0 = 0$, and $\theta = 60°$ yields a value of 2.0 mT for B_2, which is similar to the value of 2.5 mT for $B_2(^{29}Si)$ established for $\pi/C(\beta)$–$Si(\gamma)$ hyperconjugation in radical cations.[18] The coupling constant of the α carbon centers is calculated to about 0.2 mT using the Karplus–Fraenkel equation (eq 3) with $\varphi = 0.2$ and the optimized constants $Q_C = 3.56$ mT and $Q_{C'C} = -1.39$ mT;[19] the small value

$$a(^{13}C) = Q_C\varphi + Q_{C'C}\sum \varphi'_n{}^{19} \qquad (3)$$

$$(\varphi'_n\text{: spin population at neighboring } \pi \text{ centers})$$

of about 0.2 mT and the lower intensity for the satellites from only five equivalent carbon centers do not allow detection of corresponding EPR signals. There is no indication from EPR or ENDOR for conformational isomerism concerning the mutual orientation of isopropyl groups in radical **1**,[12] although the time

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[13] The color is reminiscent of diluted aqueous fluorescein solutions.

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scale of the EPR method is only about 10^{-7} s. If the rotation is fairly restricted at the EPR time scale, the different conformers will probably show very similar coupling constants, as the steric conditions for hyperconjugative spin transfer are probably identical.

Reactivity of Na[C_5(*i*-Pr)$_5$] in dichloromethane creates unidentified carbon-centered radicals with $a_{^{13}C} \sim 6$ mT.

EI Mass Spectrum of 1.[20] The EI mass spectrum of radical **1** displays, in addition to the molecular ion peak (*m/z* 275.3), which is observed in neither the mass spectrum of 1,2,3,4,5-pentaisopropylcyclopentadiene nor that of tetraisopropylcyclopentadienone, oxygen-containing fragments, including the molecular ion of tetraisopropylcyclopentadienone. Striking here, in contrast to previously recorded EI mass spectra of isopropyl-substituted cyclopentadienes and their derivatives, is the absence of a C_3H_7 fragment. The isopropyl cation generated by fragmentation presumably combines with **1** to form a cation of mass 318.4. Exposure of **1** to dioxygen gives tetraisopropylcyclopentadienone **2**[21] as a stable end product, possibly generated from the initially formed oxidation product "$C_5(i\text{-Pr})_5O_2^{\bullet}$" by elimination of the isopropoxy radical. Evidence for this is provided by the peak at *m/z* 334.4, which might have arisen by combination of the isopropoxy radical with **1**. A 2:1 product of **1** and O_2 might be bis(pentaisopropylcyclopentadienyl) peroxide, whose symmetric cleavage product would be expected to give rise to the signal at *m/z* 291.3.

Structural Characterization of Radical 1.[22] Pentaisopropylcyclopentadienyl is the first cyclopentadienyl radical to be characterized by X-ray structure analysis. As already known from dynamic NMR investigations on [(C_5(*i*-Pr)$_5$)Mo(CO)$_3$(CH$_3$)][23] and [(C_5(*i*-Pr)$_5$)CoCp]$^+$[24] and from the crystal structure of hexaisopropylbenzene,[25] the isopropyl groups are arranged around the five- and six-membered rings in a paddlewheel-like fashion. Very recently, a similar situation has been found for the pentakis(dimethylsilyl)cyclopentadienyl complexes [{C_5(SiMe$_2$H)$_5$}Mn(CO)$_3$][26] and [{C_5(SiMe$_2$H)$_5$}Li·O═CPh$_2$].[27] In the crystal, half of the lattice sites are occupied by radicals with an opposite arrangement of the isopropyl groups, as confirmed by structure determinations on three different crystals, in part at higher temperatures. Superstructure reflections are not observed. The crystallographic mirror plane through C1, C5, and C6 perpendicular to the five-membered ring (Figure 2) is obtained by averaging over this disorder (cf. ref 25). The anisotropic displacement parameters (ADPs), especially of the ring C atoms, result from the overlap of oppositely oriented rings (Figure 3). A comparable disorder in the crystal has been discussed in detail for hexaisopropylbenzene.[25] Assuming that the differently oriented radicals differ little in their geometry, the C–C bond lengths in the ring are not affected by the disorder and are somewhat larger (C1–C2 1.412(2) Å, C2–C3 1.401(1) Å) than the C–C distances in the cyclopentadienyl anion (calculated value, 1.393 Å;[28] average value in NaC$_5$Me$_5$·TMEDA, 1.377 Å[29]) and are in good agreement with the values of coordinated C_5H_5 ligands (average value in ferrocene, 1.406 Å[30]). The five-membered ring is planar, as shown by the internal ring angles at C1, C2, and C3 (107.5(2), 108.1(2), and 108.1(1)°, respectively) and the sum of the angles (539.9°). According to the Jahn–Teller theorem, stabilization of the cyclopentadienyl radical is expected to occur through distortion of the D_{5h} geometry; ab initio calculations predict a stabilization of 7–8 kcal mol^{-1}.[31] ESR spectroscopic investigations of the pentafluorocyclopentadienyl radical in a hexafluorobenzene single-crystal matrix indicate that

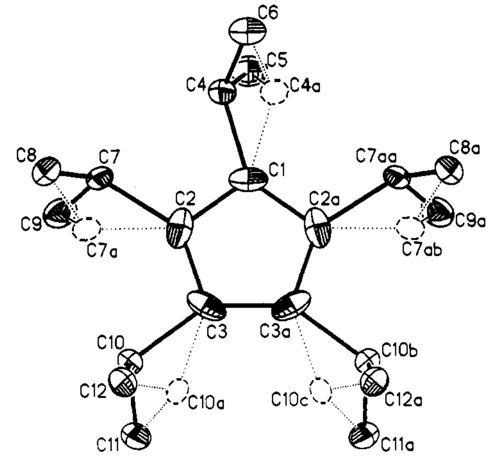

Figure 2. Molecular structure of **1**. For important bond lengths and angles, see text. Two sets of methine C atoms (C7, C4a, C10c and C7a, C4, C7aa, C10b, C10a) appear, owing to the disorder of radicals with opposite orientation of the isopropyl groups; see Figure 3.

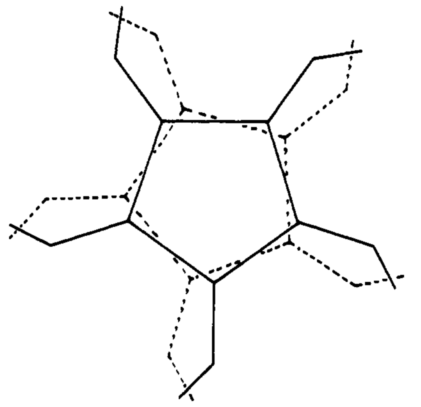

Figure 3. Overlapping of the two possible orientations of **1** in the crystal.

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(20) EI-MS of **1** (30 eV): *m/z* 334.3 ([M + OC$_3$H$_7$]$^+$, 6%); 318.4 ([M + C$_3$H$_7$]$^+$, 12%); 291.3 ([M + O]$^+$, 31%); 276.3 ([M + H]$^+$, 59%); 275.3 (M$^+$, 35%); 249.2 (C$_5{}^i$Pr$_4$OH$^+$, 60%); 248.2 (C$_5{}^i$Pr$_4$O$^+$, 100%); 233.1 (C$_5{}^i$Pr$_4$H$^+$, 61%); 191.1 (C$_5{}^i$Pr$_3$H$_2{}^+$, 39%); 148.9 (C$_5{}^i$Pr$_2$H$_3{}^+$, 85%); 106.8 (C$_5{}^i$PrH$_4{}^+$, 26%).

(21) **2**: IR (cyclohexane) $\tilde{\nu}$[cm^{-1}] = 1708 (C═O). ^{1}H-NMR (200 MHz, C$_6$D$_6$, δ): 2.78 (sept, J = 7.0 Hz, 2 H, CH), 2.69 (sept, J = 7.2 Hz, 2 H, CH), 1.28 (d, J = 7.0 Hz, 12 H, CH$_3$), 1.06 (d, J = 7.2 Hz, 12 H, CH$_3$). Anal. Calcd for C$_{17}$H$_{28}$O: C, 82.20; H, 11.36; O, 6.44. Found: C, 82.00; H, 11.40; O, 6.35. X-ray structure analysis of **2**: A single crystal with dimensions of 0.38 × 0.25 × 0.19 mm^3 was used to obtain 2041 unique reflections at 103 K on a Nicolet R3m/V X-ray four-circle diffractometer with Mo Kα radiation and graphite monochromator in the angle range $3 \leq 2\theta \leq 45°$, according to the method of Wyckoff; 1718 with $F_o \leq 4\sigma(F)$ were observed reflections. On the basis of the diffractometer angles of 50 reflections, the cell was determined to be monoclinic in the space group $P1$, a = 6.000(1) Å, b = 8.192(1) Å, c = 17.0003(2) Å, α = 95.32(2)°, β = 90.22(1)°, γ = 110.37(1)°, V = 779.5(2) Å^3, Z = 2. The structure was solved using the program SHELXTL-PLUS; all atoms except for hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically as rigid groups (C–H = 0.96 Å, C–C–H and H–C–H = 109.5°); 118 parameters; R = 0.044, R_w = 0.054.

(22) X-ray structural analysis of **1**: A single crystal with dimensions of 0.41 × 0.30 × 0.28 mm^3, obtained by vacuum sublimation in a sealed ampule, was used for structure determination. A total of 1263 unique reflections were collected at 110 K on a Nicolet R3m/V X-ray four-circle diffractometer with Mo Kα radiation and graphite monochromator in the angle range $3 \leq 2\theta \leq 45°$, according to the method of Wyckoff, 1040 with $F_o \leq 4\sigma(F)$ were observed reflections. On the basis of the diffractometer angles of 26 reflections, the cell was determined to be monoclinic in the space group $P2_1/m$, a = 6.337(2) Å, b = 16.225(5) Å, c = 9.257(3) Å, β = 101.94(2)°, V = 931.2(5) Å^3, Z = 2. The structure was solved using the program SHELXTL-PLUS; all atoms except for hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically as rigid groups (C–H = 0.96 Å, C–C–H and H–C–H = 109.5°); 118 parameters; R = 0.044, R_w = 0.054.

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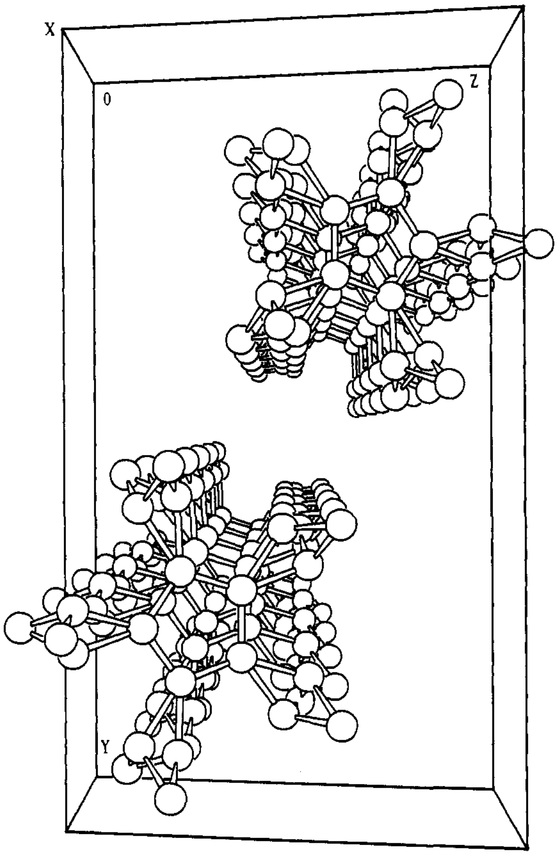

Figure 4. Stacking of **1** in the crystal. See text for explanation.

a permanent Jahn–Teller distortion is present only below 8 K.[3] For neither the unsubstituted nor the deuterated cyclopentadienyl radical did LIF down to 0.6 K reveal evidence of a permanent distortion.[5] The slight distortions from the ideal geometry of a five-membered ring could be due to crystal packing forces or to symmetry lowering as a consequence of steric crowding in **1**. Along the crystallographic *x* axis, **1** forms stacks of eclipsing, equally spaced, planar five-membered rings, whereby the ring planes adopt an angle of 23° with respect to the stack axis (Figure 4) (compare the stacking of Si_5^{6-} rings in the silicides $Li_{12}Si_7$[32a] and Li_8MgSi_6[32b]). The rings are 5.82 Å apart, owing to the bulky isopropyl substituents. This interplanar distance is apparently too large for a stable coordination of two pentaisopropylcyclopentadienyl ligands to an iron center. Possibly, other sterically encumbered cyclopentadienyl ligands will also fail to form ferrocenes, but instead afford cyclopentadienyl radicals, if their dimerization or disproportionation is hindered by steric or electronic effects.

Electrochemistry of 1. In acetonitrile the wave for $[C_5(i\text{-}Pr)_5]^-$/$[C_5(i\text{-}Pr)_5]^0$ is observed at −1.91 V vs ferrocene/ferrocenium (ΔE_{pp} = 85 mV, i_{pa}/i_{pc} = 1.0). In agreement with the stability and isolability of $Na[C_5(i\text{-}Pr)_5]$ and its one-electron oxidation product **1**, the corresponding cyclovoltammetric wave is fully reversible. The rather negative value of −1.91 vs ferrocene/ferrocenium explains the oxidation of $Na[C_5(i\text{-}Pr)_5]$ by $FeCl_2$ (which produces Fe) in the unsuccessful attempt to prepare decaisopropylferrocene.[12a] Further oxidation of the neutral radical to the 4-π electron cation $[C_5(i\text{-}Pr)_5]^+$ occurs quasi-reversibly at an anodic peak potential of +0.58 V, i.e. at a relatively low potential.

Photoelectron Spectrum of Radical 1. Photoelectron spectroscopy (PES), well suited to characterize short-lived molecules by their ionization pattern in real time and to optimize their generation under close to unimolecular conditions in a gas flow,[33] has been applied to numerous radicals.[34] The He(I) PE spectrum of the yellow-green $[C_5(i\text{-}Pr)_5]^{\bullet}$ radical **1** (Figure 5) is satisfactorily resolved (cf. Experimental Section) with respect to its 40 C_{2p} and 35 H_{1s} valence electrons. According to the tentative overall assignment based on Koopman's correlation, $IE^{\nu}_{\eta} = -\epsilon_J^{MNDO}$, with open-shell MNDO eigenvalues, the π-type ionizations from the doublet ground state of pentaisopropylcyclopentadienyl radical **1** at about 7.1 and 9.1 eV are followed by many overlapping bands at higher energy, which can be classified according to their dominant M^+ contribution[35] as σ_{ring} between 9.5 and 10.5 eV, σ_{CC2} of the isopropyl substituents between 10.5 and 12 eV, and σ_{CH} between 12 and 16 eV as well as those with increasing C_{2s} character above 16 eV. This rather crude generalization, however, is reflected by the ratios of the relative band intensities, amounting approximately to 1(7.1 eV):1(9.1 eV):5(9.9 eV):16(11.5 eV):20(13.3 + 14.5 eV).

Actually, the ionization processes $M^{\bullet} \rightarrow M^+ + e^-$ from a radical in a quasi-degenerate doublet ground state into its cation states of both triplet and singlet variety are considerably more complex. This is exemplified by a detailed assignment of the first PES ionization band (Figure 6) with its maximum at 7.15 eV and distinguishable shoulders at 7.02, 7.30, and 7.42 eV, which due to their irregular spacings between 0.12 and 0.14 eV are assumed not to be members of a distinct vibrational series. Based on a MNDO/CI calculation starting from the (modified) crystallographic structural data of **1** and including 4225 π-type configurations (cf. Experimental Section), the results obtained (Figure 6) are a considerably closer approximation to the still more complicated reality. To begin with, the Jahn–Teller distortion in the doublet ground state of the parent $C_5H_5^{\bullet}$ radical has been both experimentally[36a,b] and theoretically[36c,d] investigated and the conclusion reached that the effect, although observable, is too weak to permanently distort the D_{5h} symmetry of its $\tilde{X}(^2E_1'')$ state to no longer degenerate C_{2v} symmetric $^2A_2$ + $^2B_1$ states; in addition, pseudorotation possibly is activated at higher vibrational energies.[36d] The partly geometry-optimized structural parameters for the sterically overcrowded pentaisopropyl derivative suggest that the local C_5 axis vanishes and C_s symmetry results. The MNDO/CI approximation predicts a total energy difference of 0.12 eV = 12 kJ mol^{-1} between the two radical doublet states, $\tilde{X}(^2B_1)$ and $\tilde{A}(^2A_2)$, as characterized by their local ring symmetry. Ionization from both of them can generate the pentaisopropyl-substituted cation, which according to the MNDO/CI calculations (cf. ref 36d) will undergo another Jahn–Teller distortion, changing the ring symmetry from D_{5h} to C_{2v} and, therefore, produces a nondegenerate triplet ground state $\tilde{X}(^3B_2)$ as well as the higher

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(32) (a) Böhm, M. C.; Ramirez, R.; Nesper, R.; von Schnering, H. G. *Phys. Rev.* **1984**, *B30*, 4870. (b) Ramirez, R.; Nesper, R.; von Schnering, H. G. *Chem. Phys.* **1985**, *95*, 17.

(33) Bock, H.; Solouki, B.; Aygen, S.; Bankmann, M.; Breuer, O.; Dammel, R.; Dörr, J; Haun, M.; Hirabayashi, T.; Jaculi, D.; Mintzer, J.; Mohmand, S.; Müller, H.; Rosmus, P.; Roth, B.; Wittmann, J.; Wolf, H.-P. *J. Mol. Spectrosc.* **1988**, *173*, 31 and literature cited. See also: Bock, H.; Solouki, B. *Angew. Chem.* **1981**, *93*, 425; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427 and literature cited.

(34) (a) Alkyl radicals, cf.: Bock, H.; Berkner, B. *Z. Naturforsch.* **1992**, *B47*, 1551 and the literature reviewed, e.g. Schultz, J. C.; Honle, F. A.; Beauchamp, B. *J. Am. Chem. Soc.* **1984**, *106*, 7336. Koenig, T.; Chang, J. *Ibid.* **1978**, *100*, 2240; or Dyke, J. M.; Jonathan, N. B. H.; Lee, E. P.; Morris, A. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1385, as well as Wentrup, C. *Reactive Molecules*; Wiley Interscience: New York, 1984 and literature cited. (b) Radicals of unsaturated hydrocarbons, cf.: Blush, J. A.; Clanberg, H.; Kohn, D. W.; Minsek, D. W.; Zhang, X.; Chen, P. *Acc. Chem Res.* **1992**, *25*, 385 and literature quoted therein. (c) Heterocyclic five-membered ring radical, cf.: Boere, R. T.; Oakley, R. T.; Reed, R. W.; Westwood, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1180 and literature cited. (d) Di- to tetraatomic radicals, cf.: Dyke, J. M.; Jonathan, N.; Morris, A. *Int. Rev. Phys. Chem.* **1982**, *2*, 3 and literature reviewed.

(35) For molecular orbital presentations, cf. $C_5H_5^-$ (D_{5h}) in the following: Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 237–239.

(36) A CAS on-line search for both $C_5H_5^{\bullet}$ and $C_5(CH_3)_5^{\bullet}$ of January 1992 revealed no entry for PE spectroscopic investigations. For other spectroscopic studies, cf. e.g. (a) electron affinity measurement (Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1977**, *67*, 1412); (b) electronic spectrum[5] and numerous theoretical studies such as on (c) the vibronic states[22b] and on (d) the Jahn–Teller effects, especially in $C_5H_5^+$ [22a].

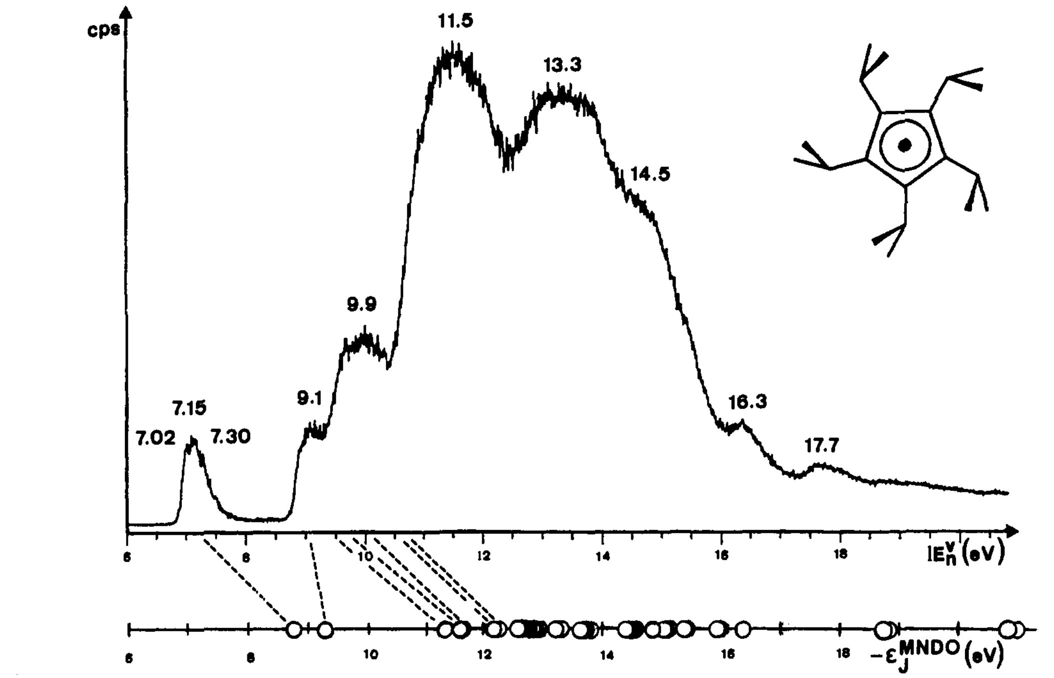

Figure 5. He(I) photoelectron spectrum of the pentaisopropylcyclopentadienyl radical with tentative assignment of characteristic radical cation states by Koopman's correlation, $IE_n = -\varepsilon_J^{MNDO}$, with MNDO eigenvalues from a geometry-optimized open-shell UHF-MNDO calculation. For the discussion of the eight low-energy $M^{\bullet+}$ states based on MNDO/CI calculations, see Figure 6 and text.

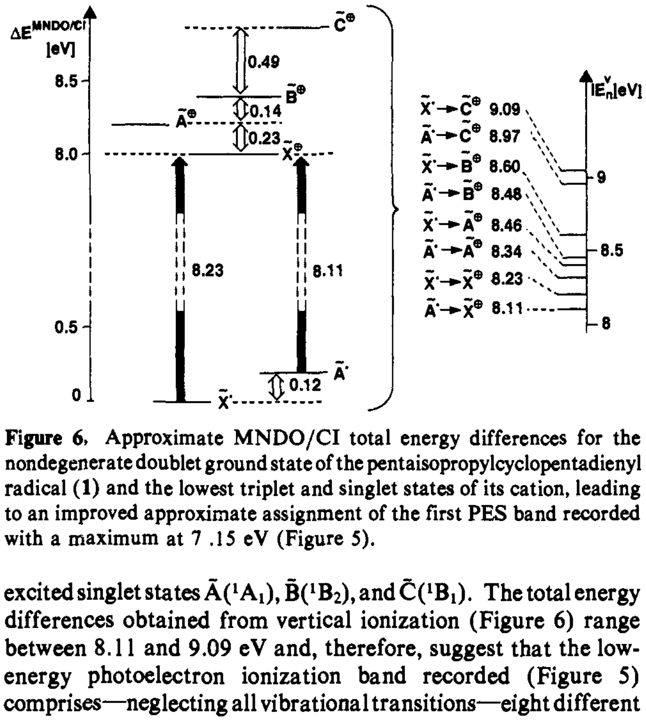

Figure 6. Approximate MNDO/CI total energy differences for the nondegenerate doublet ground state of the pentaisopropylcyclopentadienyl radical (1) and the lowest triplet and singlet states of its cation, leading to an improved approximate assignment of the first PES band recorded with a maximum at 7 .15 eV (Figure 5).

excited singlet states $\tilde{A}(^1A_1)$, $\tilde{B}(^1B_2)$, and $\tilde{C}(^1B_1)$. The total energy differences obtained from vertical ionization (Figure 6) range between 8.11 and 9.09 eV and, therefore, suggest that the low-energy photoelectron ionization band recorded (Figure 5) comprises—neglecting all vibrational transitions—eight different valence electron expulsion processes.

As concerns the adiabatic oxidation of the pentaisopropylcyclopentadienyl radical (**1**) to its cation in solution, the most elegant single electron transfer reagents, $AlCl_3$ or $SbCl_5$ in H_2CCl_2,[37] which neither contain any oxygen component nor, therefore, produce any water in the system, and which have been applied worldwide to generate numerous radical cations, are well suited; their redox potentials of about +1.7 V correspond to a vertical ionization energy below 8 eV.[37]

As another promising approach to pentaisopropylcyclopentadienyl cation generation, the reaction of pentaisopropylcyclopentadienyl halides with a suitable Lewis acid has been considered. Compared to **1**, such halides should be less air-sensitive educts and thus facilitate the preparation of uncontaminated EPR samples. 5-Bromo-1,2,3,4,5-pentaisopropylcyclopenta-1,3-diene (**3**) could be synthesized in close analogy to the corresponding bromo[38] and iodo derivatives[39] of pentamethylcyclopentadiene from pentaisopropylcyclopentadienylsodium and bromine in pentane at low temperature (eq 4). After removal of unsoluble

$$\mathrm{Na[C_5(\mathit{i}\text{-}Pr)_5] + Br_2 \xrightarrow{\text{pentane, }-78\ {}^{\circ}\mathrm{C}} BrC_5(\mathit{i}\text{-}Pr)_5 + NaBr} \quad (4)$$

products the bromide **3** is isolated as a yellow solid in 63% yield, which can be sublimed in vacuo or recrystallized from pentane or diethyl ether. The lemon yellow crystals are air and moisture sensitive and even under inert gas undergo slow decomposition at room temperature with accompanying color changes to blue-green and evolution of hydrogen bromide. The compound can be stored for weeks at −30 °C.

Chlorination of pentaisopropylcyclopentadienylsodium with hexachloroethane in pentane gives a 72% yield of light yellow 5-chloro-1,2,3,4,5-pentaisopropylcyclopenta-1,3-diene (**4**) (eq 5), which can be handled in air and is thermally stable. Proton NMR

$$\mathrm{Na[C_5(\mathit{i}\text{-}Pr)_5] + C_2Cl_6 \xrightarrow{\text{pentane, }0\ {}^{\circ}\mathrm{C}} ClC_5(\mathit{i}\text{-}Pr)_5 + NaCl + C_2Cl_4} \quad (5)$$

spectra of both halides at temperatures up to 353 K show no signs of halogen migration around the five-membered ring.

EPR of the Triplet State of the Pentaisopropylcyclopentadienyl Cation and the ENDOR Spectrum of its Decomposition Product. At 180 K methylene chloride solutions of **3** and **4** react immediately with $SbCl_5$ with concomitant color change from yellow to red-brown (eq 6). EPR spectra of the frozen sample recorded at 115 K (Figure 7) exhibit triplet features for the chemically generated

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[37] (a) Bock, H.; Lechner-Knoblauch, U. *J. Organomet. Chem.* **1985**, *294*, 295. Examples for applications to compounds containing (b) carbon: Bock, H.; Roth, B.; Maier, G. *Chem. Ber.* **1984**, *117*, 172; (c) silicon: Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *7*, 9; (d) nitrogen: Bock, H; Kaim, W.; Nöth, H.; Semkow, A. *J. Am. Chem. Soc.* **1980**, *102*, 4421; (e) p hosphorus: Kaim, W.; Bock, H.; Nöth, H. *Chem. Ber.* **1978**, *111*, 3276; (f) sulfur: Bock, H.; Stein, U.; Semkow, A. *Chem. Ber.* **1980**, *113*, 3206.

[38] C_5Me_5Br from LiC_5Me_5 and BrCN: Schwartzen, K.-H.; Jutzi, P. *Zh. Org. Khim.* **1988**, *24*, 1109.

[39] C_5Me_5Br from LiC_5Me_5 and I_2: Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

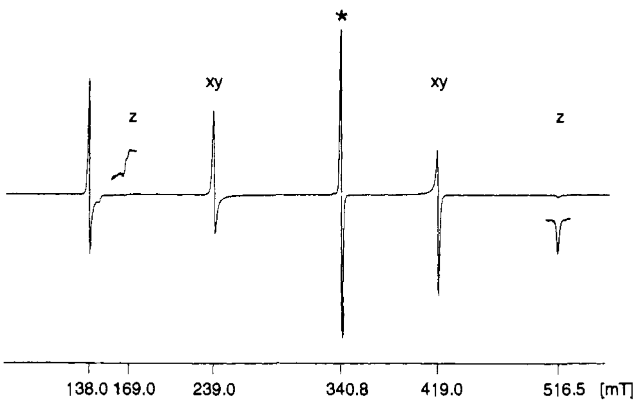

Figure 7. EPR triplet spectrum of $[C_5(i\text{-}Pr)_5]^+$ in dichloromethane at 115 K with a microwave frequency of 9.558 GHz. The signal (*) is assigned to the doublet radical cation of the follow-up product.

cation $[C_5(i\text{-}Pr)_5]^+$ (**5**) rather similar to the ones reported for other cyclopentadienyl cations.[9,10,40] The signal for the $\delta m = 2$ transition at 138.3 mT, the *xy* components of $\delta m = 1$ transitions at 239.0 and 419.0 mT, and the very weak *z* components of $\delta m = 1$ transitions at 170.0 and 516.9 mT prove the presence of a triplet state with a zero field splitting parameter *D* of 0.1615(4) cm^{-1} and $E < 0.003$ cm^{-1}.[41] The coincidence of the *x* and *y* lines and, therefore, the very small value of *E* indicate only minor distortions of the regular polygonal symmetry.[42] This is consistent with results for other penta-substituted[10,40] and unsubstituted[9] cyclopentadienyl cations. From the *D* value of cation **5** (0.1615

$$[C_5(i\text{-}Pr)_5]X + SbCl_5 \rightarrow [C_5(i\text{-}Pr)_5]^+[SbCl_5X]^- \quad (6)$$
$$X = Br\ (\mathbf{3}),\ Cl\ (\mathbf{4})$$

cm^{-1}), which reflects the interaction of the two unpaired electrons, a mean separation $R = 2.525$ Å between these electrons can be calculated.[43] These values place **5** close to the parent compound $C_5H_5^+$ ($D = 0.1868$ cm^{-1}; $R = 2.406$ Å[9]), compared to $C_5Cl_5^+$ ($D = 0.1495$ cm^{-1}; $R = 2.591$ Å[10]) and $C_5Ph_5^+$ ($D = 0.1050$ cm^{-1}; $R = 2.915$ Å[40]).

Assuming an axial symmetry, the *g* values of $[C_5(i\text{-}Pr)_5]^+$ were calculated from the position of the observed satellites[42] to be $g_\parallel = g_z = 1.992(5)$ and $g_\perp = 2.007(7)$. The same spectrum was obtained for both the bromo- and chloropentaisopropylcyclopentadiene (**3** and **4**) as starting materials, and variation of the solvent had no influence on the spectrum.

In addition to the EPR signals for $[C_5(i\text{-}Pr)_5]^+$, we observed a strong signal of a doublet radical at $g = 2.0024$, which we assign to the radical cation of a follow-up product. After the sample had been warmed up to 263 K and cooled down back to 110 K, the triplet signals had disappeared and only the very strong signal of the follow-up product was observed. Further examination of this radical by EPR and ENDOR spectroscopy (Figure 8) at 180 K enabled us to determine the coupling constants of six different kinds of protons: $a_1 = 0.842$ mT, $a_2 = 0.087$ mT, $a_3 = 0.072$ mT, $a_4 = 0.057$ mT, $a_5 = 0.048$ mT, $a_6 = 0.030$ mT. The EPR spectrum only shows a doublet with a coupling constant of 0.84 mT and a line width of 0.26 mT. The assumed combination of rearrangement and hydrogen abstraction from the solvent which presumably gives rise to formation of a radical cation of another pentaisopropylcyclopentadiene isomer has not been clearly established yet.

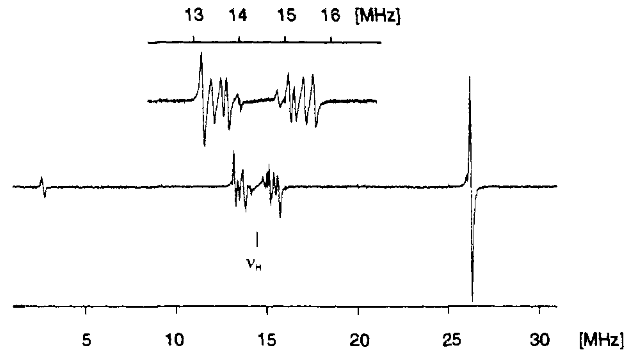

Figure 8. ENDOR spectrum of the radical cation of the follow-up product in dichloromethane at 180 K (microwave power = 125 mW, modulation depth = 70 kH) with an enlarged central part (modulation depth = 25 kHz). The ENDOR resonance condition is $\nu = \nu_H \pm a/2$ where ν_H is the "free" NMR frequency for a hydrogen at the applied field (in this experiment 14.43 MHz) and *a* is the hyperfine coupling constant in MHz.

Experimental Section

Materials. All procedures required an inert atmosphere and degassed dry solvents. Acetonitrile and dichloromethane were dried over calcium hydride, pentane, toluene, THF, and diethyl ether over Na/K alloy. After degassing, the solvents were saturated with argon. Pentaisopropylcyclopentadienylsodium was prepared as reported.[12c] Antimony pentachloride (Merck) was used without further purification.

Instrumentation. NMR: Bruker AM 400, 400 MHz, and Bruker WP 200, 200 MHz; C_6D_6, δ (C_6D_5H) = 7.159, as internal standard or $CDCl_3$, δ ($CHCl_3$) = 7.270, as internal standard.

EI-MS: MAT 90 (Finnigan MAT GmbH).

EPR, ENDOR. EPR and ENDOR spectra were recorded in the X band on a Bruker ESP 300 system, equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter, and a HP 5350B microwave counter.

Cyclovoltammetry. Cyclic voltammetry was carried out using a three-electrode configuration (GCE, Ag/AgCl, Pt), a PAR 273 potentiostat, and function generator. The cyclovoltammograms of $Na[C_5(i\text{-}Pr)_5]$ were recorded at room temperature in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. All potentials given are vs ferrocene/ferrocenium pair (internal standard) at a scan rate of 200 mV s^{-1}.

He(I) Photoelectron Spectrum. PE spectra were recorded in 10^{-5} mbar pressure using a high-performance spectrometer Leybold Heraeus UPG 200, equipped with a heated inlet system ($T = 320$ K) and an internal short-pathway pyrolysis oven ($T = 350$ K, cf. ref 29) with about 1000 counts s^{-1} and calibrated by both the $^2P_{3/2}$ ionization needles of Xe (12.13 eV) and Ar (15.76 eV).

MNDO/CI Calculations. The calculations were performed on an IBM RISC 320 workstation with the SCAMP program (T. Clark, Erlangen). The experimental structure of $[C_5(i\text{-}Pr))_5]^\bullet$ has been used for both the UHF-SCF and the MNDO/CI calculations. Further details: UHF-SCF calculation was carried out with annihilation of higher spin contamination and yielded the enthalpy of formation $\Delta H_f^{MNDO} = 193$ kJ mol^{-1}. As concerns the orbital energies, the corresponding pairs of α and β spin orbital eigenvalues are averaged (Figure 6). The MNDO/CI calculations included six unoccupied and six occupied MOs in the CI expansion and yielded $\Delta H_f^{CI}(M^\bullet) = 169$ kJ mol^{-1} and $\Delta H_f^{CI}(M^+) = 972$ kJ mol^{-1}. The ground state of $M^\bullet$ was calculated to be a doublet and that of M^+ a triplet, and thus eight lowest ionization energies between $M^\bullet$ doublets and M^+ triplet as well as lowest singlets result (Figure 6).

Preparation of Pentaisopropylcyclopentadienyl (1). To a suspension of 0.57 g (1.91 mmol) of pentaisopropylcyclopentadienylsodium in 20 mL of pentane was added 0.14 g (0.88 mmol) of Br_2 at -78 °C. The yellow solution was allowed to warm to room temperature and stirred for another 30 min. Removal of the solvent in vacuo and sublimation of the residue (65 °C, 0.05 mbar) gave 0.34 g (1.23 mmol; 70.5%) of yellow-green crystals of **1**.

5-Bromo-1,2,3,4,5-pentaisopropylcyclopenta-1,3-diene (3). To a suspension of 0.97 g (3.25 mmol) of pentaisopropylcyclopentadienylsodium in 30 mL of pentane was added 0.52 g (1.62 mmol) of Br_2 at -78 °C. The orange-colored suspension was stirred for 1 h at that temperature, then allowed to warm to room temperature, and filtered through a glass frit (D3). Removal of the solvent and traces of bromine in vacuo yielded

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(41) De Groot, M. S.; van der Waals, J. H. *Mol. Phys.* **1960**, *3*, 190.

(42) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(43) Simons, M. *Chemical and Biological Aspects of Electron Spin Resonance*; Van Nostrand Reinhold, New York, 1978.

0.73 g (2.05 mmol; 63%) of light yellow **3**, mp 57–58 °C: ^{1}H-NMR ($CDCl_3$, 263 K, δ) 3.15 (sept, J = 7.4 Hz, 1 H, CHMe$_2$), 3.08 (br, 1 H, CHMe$_2$), 2.91 (sept, J = 7.3 Hz, 1 H, CHMe$_2$), 2.70 (sept, J = 7.2 Hz, 1 H, CHMe$_2$), 2.36 (br, 1 H, CHMe$_2$), 1.32 (d, J = 7.2 Hz, 6 H, CH_3), 1.23–1.11 (m, 18 H, CH_3), 0.80 (d, J = 5.6 Hz, 6 H, CH_3. Anal. Calcd for $C_{20}H_{35}Br$: C, 67.59; H, 9.93. Found: C, 67.40; H, 9.90.

5-Chloro-1,2,3,4,5-pentaisopropylcyclopenta-1,3-diene (4). To a magnetically stirred suspension of 4.48 g (15.0 mmol) of pentaisopropylcyclopentadienylsodium in 25 mL of pentane at 0 °C was added dropwise a solution of 3.50 g (14.8 mmol) of hexachloroethane in 25 mL of pentane. The mixture was allowed to warm to room temperature and stirred for another 30 min. After centrifugation and extraction of the insoluble products with 20 mL of pentane, the combined organic solutions were evaporated to yield 3.33 g (10.7 mmol; 72%) of **4** as a light yellow solid, mp 66–67 °C: ^{1}H-NMR ($CDCl_3$, 278 K, δ) 3.08 (br, 2 H, CHMe$_2$), 2.93 (sept, J = 7.2 Hz, 1 H, CHMe$_2$), 2.72 (sept, J = 7.2 Hz, 1 H, CHMe$_2$), 2.41 (sept, J = 6.8 Hz, 1 H, CHMe$_2$), 1.33 (d, J = 7.2 Hz, 6 H, CH_3), 1.24–1.17 (m, 18 H, CH_3), 0.84 (d, J = 6.7 Hz, 6 H, CH_3). Anal. Calcd for $C_{20}H_{35}Cl$: C, 77.25; H, 11.35. Found: C, 77.50; H, 11.40.

Generation of $[C_5(i\text{-}Pr)_5]^+$. In a typical experiment, a solution of 5-chloro-1,2,3,4,5-pentaisopropylcyclopenta-1,3-diene (**4**) was cooled to 180 K in an EPR quartz tube. After addition of a few drops of a precooled solution of $SbCl_5$ in CH_2Cl_2 an immediate change of color from yellow to red-brown was observed. The tube was sealed and the reaction mixture quickly cooled to 77 K in liquid nitrogen to obtain a frozen solution. This method was also used to prepare $[C_5(i\text{-}Pr)_5]^+$ in toluene solution or from $C_5(i\text{-}Pr)_5Br$ as starting material.

Conclusion and Outlook

High stability and potential 5-fold symmetry are characteristics of the pentaisopropylcyclopentadienyl system, which gains from its substituents full steric protection with a minimum of electron-delocalizing properties. Radical **1** could therefore well be a component for the preparation of charge-transfer complexes with organic electron acceptors with interesting magnetic properties. Whether steric shielding alone is enough to isolate reasonably stable salts of the corresponding cation **5** from solution remains to be seen.

Acknowledgment. This work was funded by the Deutsche Forschungsgemeinschaft (Grant Si 366/4-1). H.S. and T.D. thank Professor O. J. Scherer for generous support and helpful discussions.

Supplementary Material Available: X-ray crystallographic data for compounds **1** and **2**, atomic coordinates, isotropic and anisotropic displacement coefficients, bond lengths and angles, and ^{1}H-NMR spectrum of **1** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.