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Generation and Reaction of a Phenyl-Substituted Cyclopentadienyl Cation Annelated with Two Homoadamantene Frameworks

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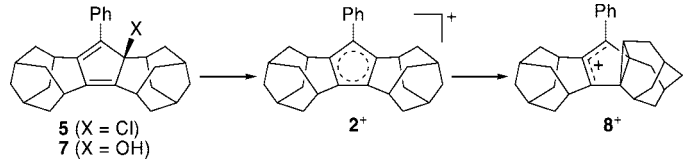

The generation of the title cation $\mathbf{2}^+$ and its reaction under solvolytic and non-nucleophilic conditions were investigated. When the precursor chlorocyclopentadiene **5** was reacted with silica gel that contained water or with anhydrous MeOH, the corresponding 5-hydroxy- and 5-methoxycyclopentadienes (**7** and **6**) were produced in 68 and 81% yields, respectively. This indicates that $\mathbf{2}^+$ is formed as an intermediate under solvolytic conditions and persists without any rearrangement of the homoadamantane frameworks, at least during the period before capture by the nucleophile. On the other hand, the abstraction of a chloride ion from **5** by Ag^+ in the absence of a nucleophile at −78 °C resulted in the quantitative formation of allyl cation $\mathbf{8}^+$, incorporated in a bicyclo[3.1.0]hexane framework, via the Wagner−Meerwein rearrangement of a homoadamantane framework. Cation $\mathbf{8}^+$ was isolated as the SbF_6^- salt, and its structure was determined by X-ray crystallography. Quenching this cation with MeOH afforded a methyl ether **14**, with a cyclopentadiene structure retained but one of the homoadamantane frameworks had undergone a structural change by a further Wagner−Meerwein rearrangement.

Introduction

The stability of a cyclopentadienyl (Cp) system is greatly dependent on its oxidation state, i.e., anion (aromatic), radical (nonaromatic), or cation (antiaromatic). A wide variety of theoretical and experimental approaches have been used in the investigations of these species.[1] In contrast to Cp anions, however, experimental studies of Cp radicals and cations are quite limited due to their thermal instability. In particular, Cp cations are highly labile species, as shown by the thermodynamic criteria described below, except for cations with several strongly electron-donating substituents[2] and those stabilized as cobalt complexes.[3] Several investigations have revealed the antiaromatic resonance destabilization of Cp cations due to the cyclic 4π systems. For example, the pK_R^+ value of the parent Cp cation, $C_5H_5^+$, was determined to be −40 by an electrochemical method (eq 1).[4] This value is remarkably low compared to that of the unsubstituted allyl cation ($pK_R^+ \approx -21$).[5] 5-Iodocyclopentadiene does not form the Cp cation, even with the assistance of silver ion (eq 2).[6] The rate of its solvolysis is at least 10^5 times slower than that of cyclopentyl iodide, the corresponding saturated analogue. Furthermore, the hydride affinity, as estimated by gas-phase ionization potential measurements, indicates that the Cp cation is destabilized by 1.37 eV (31.6 kcal/mol) with respect to the cyclopentenyl cation (eq 3).[7]

ESR and IR spectroscopy data, collected at low temperatures, demonstrated that several pentasubstituted Cp cation derivatives such as $C_5H_5^+$,[8] $C_5Cl_5^+$,[9,10] and $C_5(i\text{-}Pr)_5^+$[11] have C_5 or higher symmetry and a triplet ground state. On the other hand, pentaaryl

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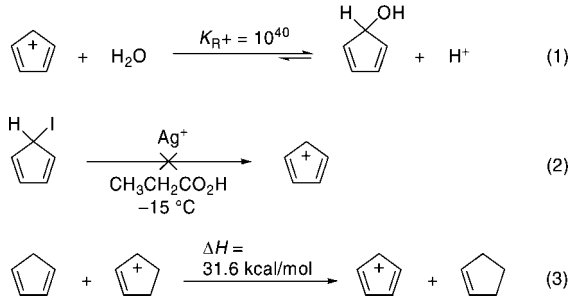
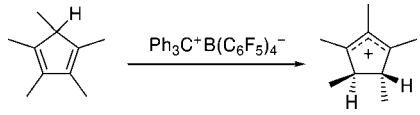
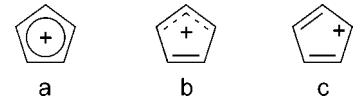


derivatives have an excited triplet state and persist as long-lived species at temperatures below −40 °C due to the substantial delocalization of the positive charge.[12] Trapping experiments for several derivatives under solvolytic conditions have been reported.[13] Reactions with nucleophiles, such as alcohols or amines, afforded the corresponding substitution products, suggesting the formation of a Cp cation as an intermediate. However, when a solution of the pentamethyl Cp cation, prepared at low temperature, is warmed and such nucleophiles are not present, polymers resulting from tetramethylpentafulvene generated by deprotonation are formed.[13a] These facts make investigations of the reaction behavior of Cp cation very difficult. More recently, the attempted hydride abstraction of pentamethylcyclopentadiene was reported to give a stable $B(C_6F_5)_4^-$ salt of $C_5Me_5^+$,[14] but it was subsequently proved to be the pentamethylcyclopentenyl cation.[15]

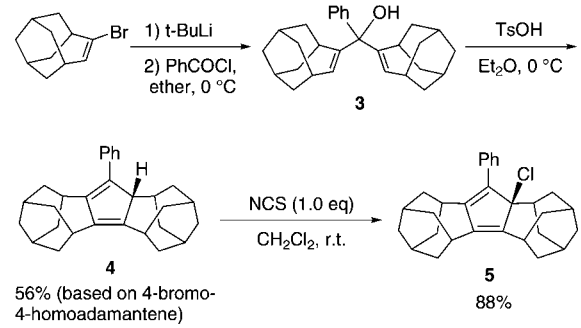


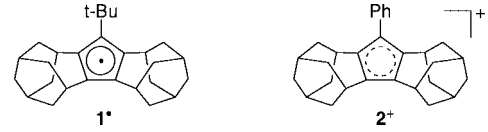
We recently reported on the isolation and X-ray structure of the cyclopentadienyl radical **1**•, annelated with two homoadamantene units.[16] Structural modification with rigid σ frameworks has been found to effectively stabilize the cyclic π-system by (i) $\sigma-\pi$ conjugation, i.e. C−C hyperconjugation, (ii) Bredt's rule protection, which avoids the elimination of hydrogen to form a bridgehead olefin, and (iii) steric protection by the bulkiness of the annelated structures.[17] When the cyclic π-system has a positive charge, additional stabilization would be expected due to inductive electron donation as a result of substitution with alkyl groups. Our attempted generation of the cation corresponding to **1**• at −78 °C, however, resulted in the formation of a complex mixture of unidentified compounds due to rearrangements initiated by methyl migration from the *tert*-butyl group to the five-membered ring.[18] We now wish to report on the generation and a new reaction of a phenyl-substituted Cp cation $\mathbf{2}^+$, in which a phenyl group has been introduced instead of a *tert*-butyl group to avoid alkyl migration.

SCHEME 1. Possible Charge Distribution in Cp Cations



SCHEME 2. Synthesis of Chlorocyclopentadiene 5





Structure $\mathbf{2}^+$ does not specify the degree of charge delocalization and potentially means one of the three possibilities indicated in Scheme 1, i.e., fully delocalized Cp cation (a), allyl-localized Cp cation (b), and localized Cp cation (c).

Results and Discussion

Synthesis of Chlorocyclopentadiene 5. Scheme 2 shows the synthetic route for preparing the homoadamantene-fused cyclopentadienes. The lithiation of 4-bromo-4-homoadamantene[16] followed by reaction with 0.5 equiv of benzoyl chloride afforded the tertiary alcohol **3**. The acid-catalyzed cyclization[16,19] of this alcohol using *p*-toluenesulfonic acid, followed by recrystallization from hexane, gave colorless crystals of cyclopentadiene **4** in 56% yield (based on 4-bromo-4-homoadamantene). The structure of **4** was determined by NMR, X-ray crystallography, and elemental analysis. The position of the hydrogen in the five-membered ring was confirmed by single-crystal X-ray analysis (see the Supporting Information).

Treatment of **4** with an equimolar amount of *N*-chlorosuccinimide in CH_2Cl_2 gave **5** as yellow crystals in 88% yield. The unsymmetrical structure of **5** was confirmed by NMR, elemental analysis, and X-ray crystallography (Figure 1a). A space-filling model (Figure 1b) shows that the bulky homoadamantane frameworks of **5** completely protects the backside of

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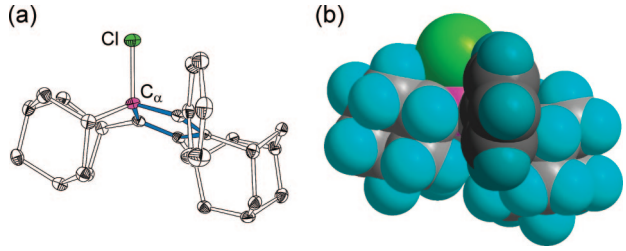
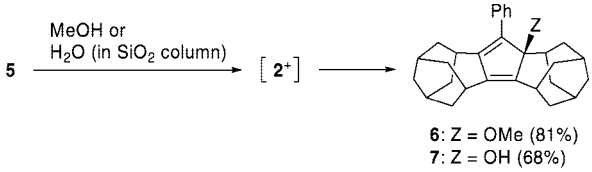


FIGURE 1. X-ray structures of **5**. The chlorine atom and the adjacent carbon atom (C_α) are shown in green and purple, respectively. The Cp ring is indicated in blue. (a) ORTEP drawing. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (b) Space-filling model viewed from the same direction. The carbon and hydrogen atoms of the phenyl groups are shown in dark colors. Note that the backside of the C_α−Cl bond is hidden by the homoadamantane frameworks.

SCHEME 3. Solvolytic Substitution of Chlorocyclopentadiene 5



the C_α−Cl bond from attack by nucleophiles. As a result, S_N2 type reactions at that bond are highly unlikely.

Reaction of Chloride 5 under Solvolytic Conditions. Chloride **5** was spontaneously converted to methyl ether **6** upon allowing it to stand in methanol at room temperature (Scheme 3). After 24 h, **6** was obtained in 81% isolated yield. Cyclopentadienol **7** was also obtained as colorless crystals in 68% isolated yield by passing chloride **5** through a silica gel column with CH_2Cl_2−hexane as the eluent. The structures of **6** and **7** were verified by NMR spectroscopy and elemental analysis. The position of the methoxy group in the five-membered ring of **6** was unambiguously confirmed by X-ray crystallography (see the Supporting Information). These findings suggest that the Cp cation $\mathbf{2}^+$ was generated from **5** under solvolytic conditions and then reacted with a solvent molecule to afford the corresponding methyl ether **6** or alcohol **7**.[20] It is also demonstrated that the cation $\mathbf{2}^+$ does not undergo rearrangement at room temperature, at least during the period prior to the nucleophilic attack.

The rate of methanolysis of **5** was determined by the conductometric method. The pseudo-first-order rate constant observed at 25 ± 0.1 °C, $k_1 = 1.33 \times 10^{-4}$ s^{-1}, is over 2 orders of magnitude greater than that of *tert*-butyl chloride under the same conditions ($k_1 = 7.53 \times 10^{-7}$ s^{-1}).[21] This indicates that annelation with two homoadamantene frameworks makes the formation of cation $\mathbf{2}^+$ easier than that of the *tert*-butyl cation.

Theoretical Calculations of Cp Cation $\mathbf{2}^+$. Theoretical calculations at the (U)MP2/6-311+G(d,p)//(U)B3LYP/6-31+G(d,p) level predicted that Cp cation $\mathbf{2}^+$ has a singlet ground state, with the energy of the corresponding triplet state being 3.0 kcal/mol higher in energy. The nucleus-independent chemical shift (NICS) values in the center of the five-membered ring

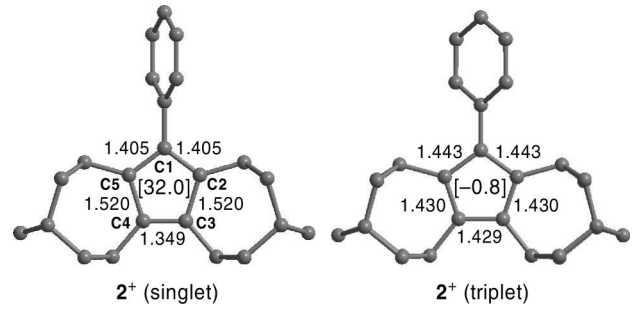
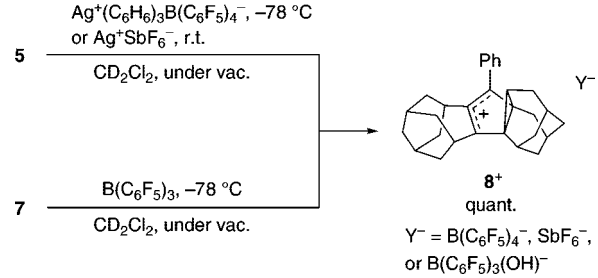
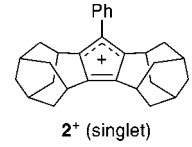


FIGURE 2. Structures of singlet and triplet states of $\mathbf{2}^+$ optimized at the B3LYP/6-31+G(d,p) and the UB3LYP/6-31+G(d,p) levels, respectively. Selected bond lengths are indicated, together with the NICS values calculated at the (U)B3LYP/6-311+G(d,p)//(U)B3LYP/6-31+G(d,p) level in brackets.

SCHEME 4. Formation of Cation $\mathbf{8}^+$



for singlet and triplet states are +32.0 and −0.8, exhibiting anti- and nonaromatic characteristics, respectively. The optimized structure of singlet $\mathbf{2}^+$ shows a pronounced bond alternation in the five-membered ring and indicates that the cation has an allyl-like moiety at C2−C1−C5 with a C3=C4 double bond, whereas that of triplet $\mathbf{2}^+$ possesses less bond alternation [ΔR(C−C) ≤ 0.014 Å], as shown in Figure 2. These results, as well as the absence of triplet signals in the ESR spectra of $\mathbf{2}^+$ (vide infra), suggest that $\mathbf{2}^+$ exists as a singlet state, which would be best illustrated as below:



Generation and Reaction of the Cation $\mathbf{2}^+$ in the Absence of Nucleophiles. In an attempt to directly observe $\mathbf{2}^+$, the abstraction of the chloride ion from **5** with Ag^+ was conducted under weakly nucleophilic conditions. When chloride **5** was treated with $Ag^+(C_6H_6)_3B(C_6F_5)_4^-$[22] in vacuum-degassed CD_2Cl_2 at −78 °C, the color of the solution changed from yellow to intense reddish orange over a period of 30 min. Monitoring this reaction by ^{1}H and ^{13}C NMR spectra at −80 °C showed an almost quantitative conversion of **5** to a new, C_1-symmetrical carbocation $\mathbf{8}^+$, in which the structure of one of the homoadamantane frameworks changed by a skeletal rearrangement (Scheme 4). Treatment of **5** with $AgSbF_6$ under the same conditions afforded the SbF_6^- salt of the identical cation $\mathbf{8}^+$, which was isolated as reddish orange crystals. The reaction of alcohol **7** with $B(C_6F_5)_3$ in CD_2Cl_2 at −78 °C also

(20) Although the S_N2 process is unlikely, some S_N2'-like nucleophilic assistance of the solvent molecule upon ionization might be possible. We appreciate a comment of one of the reviewers that the solvolysis process would be further elucidated by examining the product obtained from the reaction in the presence of an added strong nucleophile, such as N_3^-.

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(23) The assignment of this signal is based on DEPT and H−C COSY measurements and the result of GIAO calculations (Figure 3).

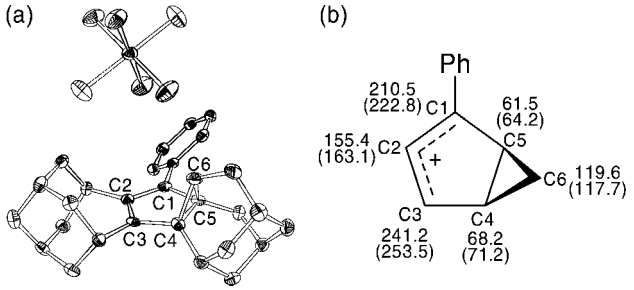


FIGURE 3. (a) ORTEP drawing of $\mathbf{8}^{+}SbF_6^{-}$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): C1−C2 = 1.404(5), C2−C3 = 1.398(5), C3−C4 = 1.450(5), C4−C5 = 1.490(5), C1−C5 = 1.478(5), C4−C6 = 1.580(5), C5−C6 = 1.539(5). (b) ^{13}C NMR chemical shifts (δ) of $\mathbf{8}^{+}SbF_6^{-}$ in CD_2Cl_2 at ambient temperature. Values obtained by the GIAO method [B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d,p)] are shown in parentheses.

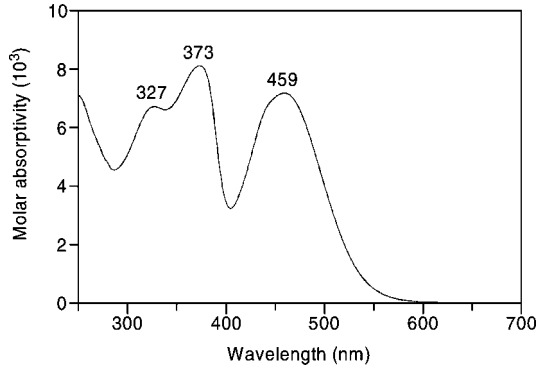


FIGURE 4. UV−vis spectrum of $\mathbf{8}^{+}SbF_6^{-}$ in CH_2Cl_2 at room temperature.

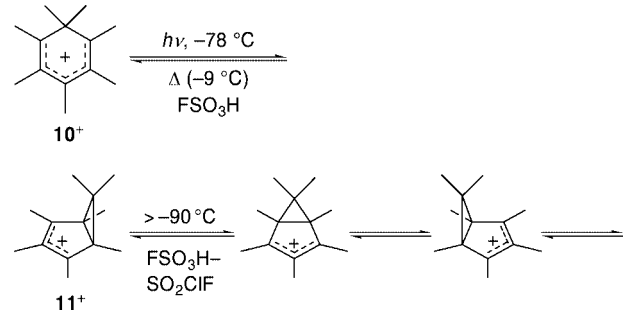
afforded the same cation $\mathbf{8}^{+}$ quantitatively, which was observed by NMR spectroscopy.

The molecular structure of $\mathbf{8}^{+}SbF_6^{-}$ was determined by X-ray crystallography (Figure 3a), which revealed $\mathbf{8}^{+}$ to be a bicyclo[3.1.0]hexenyl cation. To the best of our knowledge, $\mathbf{8}^{+}SbF_6^{-}$ is the first bicyclo[3.1.0]hexenyl cation salt to be analyzed by X-ray crystallography. The phenyl ring is twisted by 38.8°, and the cyclopropane ring is fixed at an angle of 102.8° with respect to the planar five-membered ring. The five membered ring is nearly planar (the sum of the internal angles is 539.9°). The C1−C2 [1.404(5) Å] and C2−C3 [1.398(5) Å] bond lengths in the allyl cation moiety are comparable to those of the pentamethylcyclopentenyl cation [1.396(3) and 1.385(3) Å].[15b]

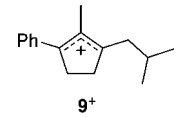
Two bonds of the cyclopropane ring external to the five membered ring, C4−C6 and C5−C6, are significantly elongated, the former [1.580(5) Å] being much longer than the other [1.539(5) Å]. The positive charge on the allyl cation moiety (C1−C2−C3) is not equally distributed over the C1 and C3 carbons, as indicated by the ^{13}C NMR chemical shifts (241.2 and 210.5 ppm, respectively) (Figure 3b). These findings demonstrates more effective $\sigma-\pi$ conjugation between the 2p orbital of the C3 carbon and the C4−C6 σ bond. The signal for the C6 atom was at a considerably low field (δ 119.6[23]), which indicates the distribution of positive charge on this carbon through hyperconjugation.

The UV−vis spectrum of $\mathbf{8}^{+}SbF_6^{-}$ (Figure 4), measured in CH_2Cl_2 at room temperature, shows absorption maxima at 459 (ϵ 7170) and 373 (ϵ 8090) nm, which were assigned to

SCHEME 5. Generation and Rearrangement of $\mathbf{11}^{+}$



HOMO→LUMO (460 nm, 2.70 eV) and HOMO–2→LUMO (371 nm, 3.34 eV) transitions with oscillator strengths f = 0.1468 and 0.1693, respectively, based on theoretical calculations [TD-B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d,p)]. The longest wavelength absorption is red-shifted compared with that of the related cyclopentenyl cation $\mathbf{9}^{+}$ (λ_{max} 394 nm in 96% H_2SO_4[24]) due to the $\sigma-\pi$ conjugation between the cationic p orbitals and the cyclopropane ring.



$\mathbf{9}^{+}$

It has been reported that bicyclo[3.1.0]hexenyl cation derivatives can be generated by irradiation of the corresponding benzenium ion in FSO_3H at −78 °C (Scheme 5).[25] They are thermally unstable and readily isomerize back to the benzenium ion via cleavage of the cyclopropane ring. The dimethylmethylene carbon of the heptamethylbicyclo[3.1.0]hexenyl cation ($\mathbf{11}^{+}$), formed from heptamethylbenzenium ion $\mathbf{10}^{+}$, was reported to undergo migration around the five-membered ring, which can be observed by NMR at temperatures above −90 °C.[25b,c] In contrast, cation $\mathbf{8}^{+}$ does not undergo decomposition or isomerization to a benzenium ion even at room temperature for over 3 months in solution in a tube sealed under vacuum. The ring-opening reaction is suppressed because the cyclopropane ring is incorporated into a rigid polycyclic σ-framework.

A possible mechanism for the formation of $\mathbf{8}^{+}$ is shown in Scheme 6. The Cp cation $\mathbf{2}^{+}$, formed by abstraction of a chloride or a hydroxide ion from **5** and **7**, respectively, is unstable due to the absence of aromatic stabilization. As a result, a Wagner−Meerwein rearrangement readily takes place in the homoadamantane framework to give a secondary cyclopentadienylmethyl cation $\mathbf{12}^{+}$ (path a),[26] followed by cyclopropanation to form a more stable cation, $\mathbf{8}^{+}$. This rearrangement does not appear to be concerted with the formation $\mathbf{2}^{+}$, since no rearranged products such as **14** were detected under solvolytic conditions. DFT calculations [MP2/6-311+G(d,p)//B3LYP/6-31+G(d,p)] predict that cation $\mathbf{8}^{+}$ is 24.2 kcal/mol more stable

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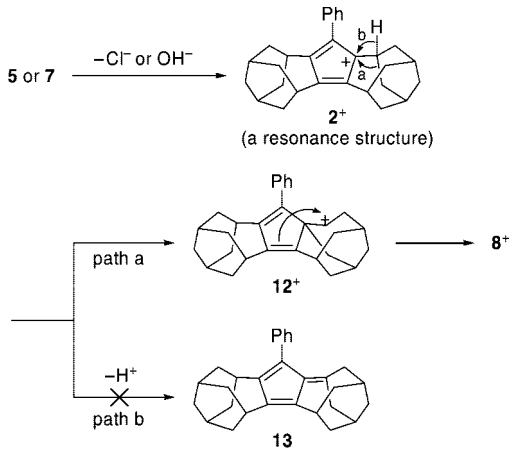
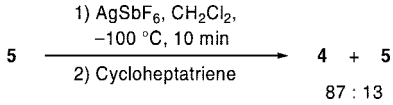
(26) The 2-homoadamantyl cation, generated under the solvolysis conditions, has been reported to readily undergo a Wagner−Meerwein rearrangement: (a) Kitagawa, T.; Okazaki, T.; Komatsu, K.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 7891. (b) Okazaki, T.; Kitagawa, T.; Takeuchi, K. *J. Phys. Org. Chem.* **1994**, *7*, 485. Although $\mathbf{12}^{+}$ might be higher in energy than $\mathbf{2}^{+}$, the equilibrium $\mathbf{2}^{+} \rightleftarrows \mathbf{12}^{+}$ can be shifted to the right if $\mathbf{12}^{+}$ is consumed by conversion to $\mathbf{8}^{+}$, thus enabling overall transformation from $\mathbf{2}^{+}$ to $\mathbf{8}^{+}$.

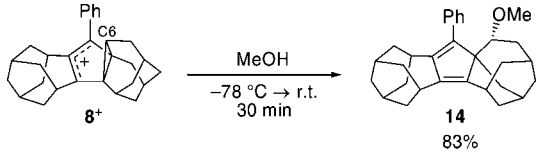
SCHEME 6. Mechanism for the Formation of 8^+



SCHEME 7. Trapping of 2^+ with Cycloheptatriene



SCHEME 8. Reaction of 8^+ with MeOH



than singlet 2^+. Unlike the case of the pentamethyl Cp cation,[13a] 2^+ cannot be transformed into fulvene **13** (path b), a highly strained bridgehead olefin. Thus, the formation of 8^+ can be taken not only as evidence of the generation of the Cp cation 2^+ but also as a result of a novel rearrangement of the alkyl-substituted Cp cation.

Trapping and Attempted ESR Measurement of 2^+. To confirm the formation of 2^+ prior to rearrangement, **5** was treated with $AgSbF_6$ in CH_2Cl_2 at −100 °C for 10 min, and the subsequent addition of excess cycloheptatriene as a hydride donor at −100 °C afforded a mixture of the original cyclopentadiene **4** and unchanged **5** (87:13), which strongly supports the formation of singlet 2^+ as an intermediate (Scheme 7).

The ESR spectral measurement conducted for the product of the chloride ion abstraction of **5** with $Ag^+(C_6H_6)_3B(C_6F_5)_4^-$ or with SbF_5 in frozen CH_2Cl_2 at −100 °C showed a single line at approximately $g = 2.0$. In both cases, the signal for a $\Delta m = 2$ transition and the *xy*- and *z*-components of the $\Delta m = 1$ transition, expected for a triplet biradical, were not observed even at −223 °C. The observed ESR signal is most probably due to a residual amount of paramagnetic species.

Reaction of 8^+ with MeOH. On quenching a CH_2Cl_2 solution of $8^+SbF_6^-$ with MeOH, another rearrangement of the polycycloalkane framework took place to give an ether **14** in 83% isolated yield as colorless crystals (Scheme 8). The molecular structure of **14** was confirmed by X-ray crystallography and spectral data (see the Supporting Information). The formation of **14** can be rationalized by assuming a nucleophilic attack of MeOH on the cyclopropane carbon C6 of 8^+. This is consistent with the significant positive charge located on this carbon, as suggested by the X-ray structure and the unusual low field shift of this carbon in ^{13}C NMR (Figure 3b). Theoretical calculations indicated that this carbon has a considerably large coefficient in LUMO (Figure 5), supporting this assumption. It should be noted that **14** was not formed by the methanolysis of **5** (Scheme 3), confirming that the intermediate 2^+ underwent a nucleophilic attack without rearranging to 8^+ under solvolytic conditions.

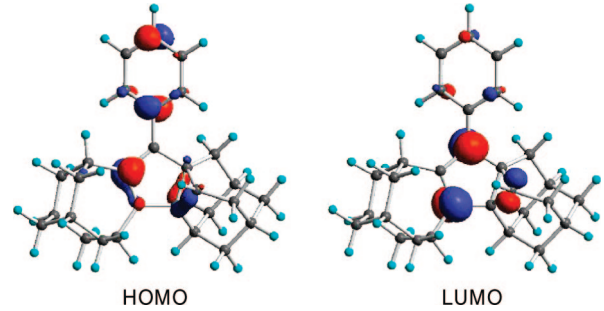


FIGURE 5. Pictorial presentation of HOMO and LUMO in 8^+ calculated at the B3LYP/6-31+G(d,p) level.

Experimental Section

1,1-Bis(4-homoadamanten-4-yl)-1-phenylmethanol (3). To a stirred solution of 4-bromo-4-homoadamantene[16] (2.85 g, 12.5 mmol) in ethyl ether (100 mL), cooled at 0 °C, was added a solution of *tert*-butyllithium (1.60 M) in pentane (15.0 mL, 24.0 mmol) dropwise over 15 min. After the mixture was stirred at 0 °C for 15 min, benzoyl chloride (0.72 mL, 6.2 mmol) was added at 0 °C over a 5 min period. The mixture was gradually warmed to room temperature over 1 h and then stirred for an additional 13 h. The reaction mixture was quenched by adding water (100 mL) and extracted with ethyl ether, and the organic layer was washed with 10% NaCl and dried ($MgSO_4$). Evaporation of the solvent gave a pale yellow oil (2.61 g). This oil was analyzed by ^1H and ^{13}C NMR, which confirmed **3** as the major product, and was used in the next step without further purification: ^1H NMR (300 MHz, C_6D_6) δ 7.57 (dd, $J = 8.4$, 1.2 Hz, 2H), 7.27−7.04 (m, 3H), 5.96 (dd, $J = 9.2$, 1.7 Hz, 2H), 2.63 (br s, 2H), 2.23 (br s, 2H), 2.02 (br s, 4H), 1.84−1.58 (m, 20H); ^{13}C NMR (75 MHz, C_6D_6) δ 152.7, 144.6, 135.5, 128.5, 127.9, 127.2, 87.3, 37.7, 35.5, 35.1, 35.0, 34.6, 33.8, 32.5, 30.41, 30.35.

Cyclopentadiene 4. To a solution of crude **3** (2.61 g) in ethyl ether (100 mL), cooled to 0 °C, was added dropwise a solution of *p*-toluenesulfonic acid monohydrate (0.517 g, 2.72 mmol) in ethyl ether (20 mL). The mixture was gradually warmed to room temperature over 6 h and stirred for an additional 6 h. The mixture was quenched by adding H_2O and extracted with ethyl ether. The organic layer was washed with 5% $NaHCO_3$ and 10% NaCl and dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by chromatography on SiO_2 followed by recrystallization from hexane to give **4** (1.35 g, 56% based on 4-bromo-4-homoadamantene) as colorless crystals: mp 187−188 °C; ^1H NMR (300 MHz, C_6D_6) δ 7.26 (d, $J = 4.8$ Hz, 4H), 7.12−7.05 (m, 1H), 3.58 (s, 1H), 3.39 (t, $J = 5.3$ Hz, 1H), 3.20 (br s, 1H), 2.96 (t, $J = 5.4$ Hz, 1H), 2.16 (t, $J = 5.4$ Hz, 1H), 2.11−1.33 (m, 23H), 0.98 (d, $J = 13.8$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 150.8, 149.1, 145.8, 138.6, 138.4, 129.5 (2C), 128.9 (2C), 126.0, 64.1, 43.2, 42.3, 38.0, 37.6 (2C), 37.1, 36.7, 36.6, 34.5, 32.4, 31.3, 31.1, 30.1 (2C), 29.1, 29.0, 28.6, 27.7; IR (KBr, cm^{-1}) 2894, 2842, 1595, 1560, 1488, 1440, 1352, 1085, 947, 779, 754, 700. Anal. Calcd for $C_{29}H_{34}$: C, 91.04; H, 8.96. Found: C, 91.18; H, 8.99.

Chlorocyclopentadiene 5. *N*-Chlorosuccinimide (95.2 mg, 0.71 mmol) was added to a solution of cyclopentadiene **4** (0.267 g, 0.70 mmol) in CH_2Cl_2 (10 mL) under argon at room temperature. The mixture was stirred for 14 h and quenched with water (100 mL). The mixture was extracted with CH_2Cl_2, and the organic layer was washed with 10% NaCl and dried ($MgSO_4$). The solvent was evaporated, and the residue was recrystallized from CH_2Cl_2−MeCN

to afford **5** (0.256 g, 88%) as pale yellow crystals: mp 153−154 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 7.60 (d, J = 7.5 Hz, 2H), 7.31−7.23 (m, 2H), 3.16 (br s, 1H), 2.94−2.82 (m, 2H), 2.77 (br s, 1H), 2.64 (d, J = 13.8 Hz, 1H), 2.37 (t, J = 5.9 Hz, 1H), 1.94−1.38 (m, 20H), 1.32 (d, J = 12.3 Hz, 1H), 1.11 (d, J = 14.4 Hz, 1H), one of the phenyl proton signals was overlapped with the solvent peak; ^{13}C NMR (75 MHz, C_6D_6) δ 150.6, 147.7, 146.0, 140.2, 136.7, 130.9 (2C), 128.8 (2C), 127.6, 89.0, 44.7, 38.3, 37.8, 37.2, 36.4, 36.3, 36.13, 36.07, 33.8, 32.7, 31.6, 30.9 (2C), 30.2, 28.6, 28.5, 28.2, 27.8; IR (KBr, cm^{-1}) 2906, 2848, 1489, 1465, 1440, 1084, 946, 823, 781, 695. Anal. Calcd for $C_{29}H_{33}Cl$: C, 83.52; H, 7.98. Found: C, 83.59; H, 7.95.

Methoxycyclopentadiene 6. A solution of chlorocyclopentadiene **5** (14.1 mg, 0.034 mmol) in MeOH (2 mL) was stirred under N_2 for 24 h. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 5% $NaHCO_3$ and 10% NaCl and dried ($MgSO_4$). The solvent was evaporated, and the residue purified by column chromatography on SiO_2 using CH_2Cl−hexane as the eluent to afford **6** (11.4 mg, 81%) as pale yellow crystals (prisms): mp 179−180 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 7.55 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 3.32−3.24 (m, 1H), 3.27 (s, 3H), 3.10−2.94 (m, 2H), 2.82 (t, J = 5.7 Hz, 1H), 2.32 (t, J = 5.6 Hz, 1H), 2.21 (d, J = 13.5 Hz, 1H), 2.04−1.44 (m, 20H), 1.39 (d, J = 12.0 Hz, 1H), 1.16 (d, J = 13.5 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) 152.7, 147.9, 142.6, 137.6, 135.5, 128.9 (2C), 128.8 (2C), 126.8, 95.8, 49.9, 44.2, 38.6, 38.5, 37.8, 37.6, 36.3, 36.1, 34.0, 32.7, 32.6, 31.5, 31.02, 30.99, 30.95, 29.3, 28.5, 28.3, 28.2; IR (KBr, cm^{-1}) 2898, 2843, 1598, 1489, 1464, 1442, 1073, 942, 762, 700. Anal. Calcd for $C_{30}H_{36}O$: C, 87.33; H, 8.79. Found: C, 87.08; H, 8.79.

Cyclopentadienol 7. Crude chloride **5**, prepared from cyclopentadiene **4** (0.372 g, 0.97 mmol) and *N*-chlorosuccinimide (0.142 g, 1.06 mmol) by the method described above, was passed through a silica gel column using hexane−CH_2Cl_2 as an eluent. The solvent was removed by evaporation, and the residue was recrystallized from CH_2Cl_2−MeCN (1:1) to afford **7** (0.261 g, 67% based on **4**) as colorless crystals: mp 192−193 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 7.59 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 3.13 (t, J = 5.3 Hz, 1H), 3.05 (br s, 1H), 2.91 (d, J = 13.2 Hz, 1H), 2.78 (t, J = 5.6 Hz, 1H), 2.46−2.28 (m, 2H), 2.04−1.45 (m, 20H), 1.38 (d, J = 10.5 Hz, 1H), 1.32 (s, 1H), 1.13 (d, J = 14.1 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 150.0, 147.7, 145.3, 140.8, 137.6, 129.5 (2C), 126.9, 91.7, 44.2, 38.3, 38.0, 37.9, 37.0, 36.6, 36.2, 33.2, 32.8, 32.6, 31.33, 31.27, 30.9, 30.8, 29.0, 28.5, 28.3, 28.2, one of the phenyl carbon signals was overlapped with the solvent peak; IR (KBr, cm^{-1}) 2903, 2841, 1491, 1440, 1348, 991, 943, 701. Anal. Calcd for $C_{29}H_{34}O$: C, 87.39; H, 8.60. Found: C, 87.30; H, 8.65.

Preparation and Characterization of Cation 8^+. (A) Preparation with Chloride 5 and $AgSbF_6$. An NMR sample tube containing chloride **5** (16.6 mg, 0.040 mmol) and $AgSbF_6$ (14.4 mg, 0.042 mmol) was evacuated with a vacuum line. CD_2Cl_2 (0.75 mL), dried over CaH_2 and degassed by repeated freeze−pump−thaw cycles, was vacuum-transferred to the NMR sample tube, which was then sealed under vacuum. The reaction mixture was warmed to room temperature and monitored by ^{1}H and ^{13}C NMR, which showed the quantitative formation of cation $\mathbf{8}^+$. Reddish orange crystals of $\mathbf{8}^+SbF_6^-$ suitable for X-ray analysis were obtained by allowing the reaction mixture to stand at room temperature for 1 week: mp 240 °C dec; ^{1}H NMR (300 MHz, CD_2Cl_2, rt) δ 7.72 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 6.9 Hz, 2H), 4.15 (d, J = 5.4 Hz, 1H), 3.54 (t, J = 5.6 Hz, 1H), 3.30 (t, J = 5.7 Hz, 1H), 3.13 (br s, 1H), 2.50 (dtd, J = 18.5, 6.5, 1.7 Hz, 1H), 2.40−1.55 (m, 22H), 1.42 (d, J = 13.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, rt) δ 241.2, 210.5, 155.4, 135.4, 132.6, 130.3 (2C), 129.9 (2C), 119.6, 68.2, 61.5, 40.0, 38.03, 37.99, 36.5, 35.0, 34.3, 33.2 (2C), 32.4, 32.3, 30.8, 30.2, 28.8, 28.3, 27.3, 26.7, 26.5; IR (KBr, cm^{-1}) 2903, 1456, 1449, 1437, 1232, 937, 657; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 327 (6720), 373 (8090), 459 (7170).

(B) Preparation with Chloride 5 and $Ag^+(C_6H_6)_3B(C_6F_5)_4^-$. An NMR sample tube containing chloride **5** (23.5 mg, 0.056 mmol) and $Ag^+(C_6H_6)_3B(C_6F_5)_4^-$ [22] (58.4 mg, 0.057 mmol) was evacuated with a vacuum line. CD_2Cl_2 (0.75 mL), dried over CaH_2 and degassed by repeated freeze−pump−thaw cycles, was vacuum-transferred to the NMR sample tube, which was then sealed under vacuum. The reaction mixture was monitored at −80 °C by ^{1}H and ^{13}C NMR, which showed the quantitative formation of cation $\mathbf{8}^+$.

(C) Preparation with Cyclopentadienol 7 and $B(C_6F_5)_3$. An NMR sample tube containing alcohol **7** (38.2 mg, 0.096 mmol) and $B(C_6F_5)_3$ (51.5 mg, 0.101 mmol) was evacuated with a vacuum line. CD_2Cl_2 (0.75 mL), dried over CaH_2 and degassed by repeated freeze−pump−thaw cycles, was vacuum-transferred to an NMR sample tube, which was then sealed under vacuum. The reaction mixture was stirred at −78 °C for 30 min and monitored at −90 °C by ^{1}H and ^{13}C NMR, which showed the quantitative formation of the cation $\mathbf{8}^+$.

MeOH Quenching of $\mathbf{8}^+SbF_6^-$ to Form 14. Chloride **5** (35.6 mg, 0.085 mmol) was allowed to react with $AgSbF_6$ (31.4 mg, 0.091 mmol) in dry CH_2Cl_2 (1.5 mL) for 10 min at −78 °C and for a further 30 min at room temperature. The solution was cooled again to −78 °C, and dry MeOH (1.0 mL) was added dropwise over 5 min. The mixture was warmed to room temperature, stirred for 30 min, and filtered through a PTFE membrane filter to remove the AgCl. Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and evaporated. The residue was purified by chromatography on SiO_2 to give **14** (29.2 mg, 83% based on **5**) as colorless crystals: mp 139−140 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 7.34 (d, J = 8.3 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 3.29 (dt, J = 12.6, 2.6 Hz, 1H), 3.12−2.97 (m, 4H), 2.55 (s, 3H), 2.14−1.36 (m, 23H), one of the phenyl proton signals was overlapped with the solvent peak; ^{13}C NMR (75 MHz, C_6D_6) δ 148.5, 147.1, 145.5, 143.2, 140.5, 130.5, 128.0, 126.2, 82.2, 65.5, 55.8, 42.4, 41.9, 39.7, 38.2, 38.0, 37.8, 37.5, 37.0, 36.5, 34.9, 32.2, 31.8, 30.82, 30.77, 29.6, 29.0, 28.4; IR (KBr, cm^{-1}) 2907, 2876, 2843, 1493, 1441, 1092, 1077, 1064, 959, 934, 799, 754, 744, 700. HRMS (EI+) m/z calcd for $C_{30}H_{36}O$ (M^+) 412.2766, found 412.2774.

X-ray Crystal Structure Analysis. Intensity data were collected at 100 K on a Bruker SMART APEX diffractometer with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. The structures were solved by direct method (SHELXTL) and refined by the full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed using AFIX instructions and refined isotropically.

4: $C_{29}H_{34}$; FW = 382.56, crystal size 0.10 × 0.10 × 0.10 mm^3, monoclinic, $P2(1)/n$, a = 6.3533(12) Å, b = 17.527(3) Å, c = 18.820(4) Å, β = 96.512(4)°, V = 2082.2(7) Å^3, Z = 4, D_c = 1.220 g cm^{-3}. The refinement converged to R_1 = 0.0528, wR_2 = 0.1067 ($I > 2\sigma(I)$), GOF = 1.013.

5: $C_{29}H_{33}Cl$; FW = 417.00, crystal size 0.20 × 0.20 × 0.20 mm^3, triclinic, $P-1$, a = 6.5347(13) Å, b = 10.784(2) Å, c = 15.777(3) Å, α = 74.790(4)°, β = 82.116(4)°, γ = 81.619(4)°, V = 1055.7(4) Å^3, Z = 2, D_c = 1.312 g cm^{-3}. The refinement converged to R_1 = 0.0406, wR_2 = 0.0869 ($I > 2\sigma(I)$), GOF = 1.082.

6: $C_{30}H_{36}O$; FW = 412.59, crystal size 0.20 × 0.20 × 0.20 mm^3, monoclinic, $C2/c$, a = 11.0557(16) Å, b = 17.650(3) Å, c = 22.609(3) Å, β = 97.847(3)°, V = 4370.6(11) Å^3, Z = 8, D_c = 1.254 g cm^{-3}. The refinement converged to R_1 = 0.0429, wR_2 = 0.0857 ($I > 2\sigma(I)$), GOF = 1.012.

$\mathbf{8}^+SbF_6^-$: $C_{29}H_{33}F_6Sb$; FW = 617.30, crystal size 0.10 × 0.10 × 0.10 mm^3, monoclinic, $P2(1)/n$, a = 10.0120(13) Å, b = 21.486(3) Å, c = 11.6831(16) Å, β = 100.848(2)°, V = 2468.3(6) Å^3, Z = 4, D_c = 1.661 g cm^{-3}. The refinement converged to R_1 = 0.0378, wR_2 = 0.0726 ($I > 2\sigma(I)$), GOF = 1.061.

14: $C_{30}H_{36}O$; FW = 412.59, crystal size 0.10 × 0.10 × 0.10 mm^3, monoclinic, $P2(1)/c$, a = 16.001(2) Å, b = 9.9744(14) Å, c = 14.124(2) Å, β = 95.655(3)°, V = 2243.3(6) Å^3, Z = 4, D_c =

1.222 g cm^{-3}. The refinement converged to $R_1 = 0.0441$, $wR_2 = 0.0798$ ($I > 2\sigma(I)$), GOF = 1.012.

Kinetic Measurement for the Methanolysis of 5. The reaction was conducted at 25.0 ± 0.1 °C using a 1.9×10^{-4} M solution of **5** in MeOH in the presence of 2.3×10^{-4} M 2,6-lutidine. The progress of the reaction, monitored by conductometry, was fitted to the first-order rate equation, yielding a rate constant of $k_1 = 1.33 \times 10^{-4}$ s^{-1}.

Calculations. Molecular structures of singlet $\mathbf{2}^+$, triplet $\mathbf{2}^+$, and $\mathbf{8}^+$ were optimized by DFT calculations at the (U)B3LYP/6-31+G(d,p) levels, using the Gaussian-98 program.[27] The energies were computed at the (U)MP2/6-311+G(d,p) level with the single-point calculations using the (U)B3LYP/6-31+G(d,p) geometries. Frequency calculations were performed at the 6−31G(d) level, which gave optimized structures similar to those obtained by B3LYP/6-31+G(d,p), to reduce computational time. The absence of a negative frequency was confirmed for all structures.

Quenching of $\mathbf{2}^+$ with Cycloheptatriene. To a stirred solution of chlorocyclopentadiene **5** (21.4 mg, 0.051 mmol) in CH_2Cl_2 (3 mL), cooled at −100 °C under argon, was added $AgSbF_6$ (21.3 mg, 0.062 mmol), and the mixture was stirred at −100 °C for 10 min. Cycloheptatriene (0.18 mg, 2.0 mmol) was added, and the temperature was raised to −85 °C over a period of 1.5 h and then to room temperature. Water (10 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 10% NaCl, dried ($MgSO_4$), and evaporated to dryness. Analysis by ^{1}H NMR indicated that the residue (24 mg) consisted of cyclopentadiene **4** and unchanged **5** in a molar ratio of 87:13.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds and crystallographic data (table and CIF file) for **4**, **5**, **6**, $\mathbf{8}^+$, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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