

Electrophilic Addition of Polychloroalkanes to C₆₀: Direct Observation of Alkylfullerenyl Cation Intermediates

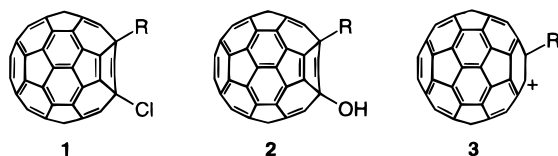
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On the basis of numerous reports on chemical reactions of buckminsterfullerene (C₆₀), it is now well accepted that C₆₀ generally behaves like an electron-deficient olefin.¹ For example, C₆₀ readily undergoes addition by a variety of nucleophiles. In contrast, examples of electrophilic addition to C₆₀ are limited to protonation^{1f} and nitration,² and the addition of carbon electrophiles to C₆₀ has not been reported. The absence of such reports leaves the impression that C₆₀ is totally inert to these reactions or that the addition is uncontrollable, if it proceeds at all. We now report that the addition of carbocations, generated from chloroform or 1,1,2,2-tetrachloroethane with aluminum trichloride, readily occurs. These addition reactions selectively give monoadducts in high yields. This observation represents the first example of a controlled electrophilic addition of a carbocationic species to C₆₀. The intermediate monosubstituted fullerenyl cations, evidence for the existence of which has not been observed to date, were generated in CF₃SO₃H from fullerol precursors and were directly observed by NMR spectroscopy. The only known carbocationic species that have a fullerene framework are the radical cations (C₆₀^{+•3} and C₇₆^{+•4}) and pentaaryl cations (Ar₅C₆₀⁺).⁵

Treatment of C₆₀ with AlCl₃ (100 equiv) in chloroform at 20 °C resulted in the addition of one molecule of chloroform, and the reaction reached completion in approximately 2 h. Chromatographic purification (SiO₂, quick elution with CS₂ at -20 °C; prolonged contact with silica gel caused hydrolysis, vide infra) gave the adduct, a dark brown powder, in 68% yield. A FAB mass spectrum of the adduct showed a molecular ion peak (M, m/z 838) and fragment peaks due to the consecutive elimination of chlorine atoms (M - Cl, 803; M - 2Cl, 768; M - 3Cl, 733). The adduct was shown to be isomerically pure and to have structure **1a** by the following spectral data.⁶ The ¹³C NMR



a: R = CHCl₂, b: R = CCl₂CH₂Cl

spectrum showed 58 distinct signals in the sp² region and three signals in the sp³ region. The ¹H NMR spectrum showed a single

(1) (a) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1138–1141. (b) Taylor, R.; Walton, D. R. M. *Nature* **1993**, 363, 685–693. (c) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: Stuttgart, 1994. (d) *The Chemistry of Fullerenes*; Taylor, R. Ed.; World Scientific: Singapore, 1995. (e) Diederich, F.; Thilgen, C. *Science* **1996**, 271, 317–323. (f) Olah, G. A.; Bucsi, I.; Ha, D. S.; Aniszfeld, R.; Lee, C. S.; Prakash, G. K. S. *Fullerene Sci. Technol.* **1997**, 5, 389–405.

(2) Chiang, L. Y.; Upasani, R. B.; Swirczewski, J. W. *J. Am. Chem. Soc.* **1992**, 114, 10154–10157.

(3) Isolation of a C₆₀^{+•} salt has been reported by C. A. Reed and co-workers; see Dagani, R. *Chem. Eng. News* **1998**, May 4, 49–54.

(4) Bolskar, R. D.; Mathur, R. S.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, 118, 13093–13094.

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resonance at δ 6.98. On the basis of PM3 calculations,⁷ the 1,2- and 1,4-adducts have the lowest heats of formation (771.7 and 772.1 kcal/mol, respectively) which are lower than those of other regioisomers by at least 11 kcal/mol. The obtained product was most likely the 1,4-adduct, since the number of ¹³C NMR signals rules out symmetrical molecules, such as the 1,2-adduct. UV-vis spectra in cyclohexane showed a broad absorption at 444 nm (ε 4620), which is typical of 1,4-adducts and is in contrast to the fact that 1,2-adducts generally exhibit a sharp absorption band at 430 nm.⁸

Likewise, 1,1,2,2-tetrachloroethane reacted with C₆₀ to form monoadduct **1b** in the presence of AlCl₃ (100 equiv), although heating (60 °C, 7 h) was required in order to complete the reaction. The ¹H NMR spectrum of the product showed an AB quartet (J = 12.2 Hz) at δ 5.02 and 5.09.⁶ A heteronuclear COSY measurement showed that these two protons are bound to the same carbon atom at δ 55.9. The signal corresponding to the other carbon in the addend appeared substantially downfield at δ 93.4. These results are consistent with structure **1b**, indicating that the initially formed cation, ⁺CHClCHCl₂ (or its complex with AlCl₄⁻), underwent a rapid hydride shift to form an isomeric cation, ⁺CCl₂CH₂Cl, which is stabilized by effective p(π) donation of unshared 3p electrons from two chlorine atoms.⁹

Compounds **1a** and **1b** were found to readily undergo hydrolysis in organic solvents in the presence of silica gel. Thus, treating a CS₂ solution with 230–400 mesh silica gel or passing a benzene solution through a silica gel column resulted in complete hydrolysis, giving the corresponding fullerols **2a** and **2b** regioselectively. The observation of 55–56 aromatic ¹³C signals⁶ and a broad absorption band at 438–439 nm suggest that they are 1,4-adducts.

The above hydrolysis would be expected to proceed via a cationic intermediate R-C₆₀⁺, which is formed by ejection of a chloride ion and which has the same structure as the intermediate of the AlCl₃-catalyzed addition of chloroform and 1,1,2,2-tetrachloroethane. The facile hydrolysis led to the expectation that it might be possible to observe the cations as long-lived species. Such an experiment was performed by dissolving fullerols **2a** and **2b** in CF₃SO₃H. The resulting reddish purple solutions had characteristic absorption maxima at around 500, 790, and 1200 nm (Figure 1).

The ¹³C NMR spectrum of the cation generated from **2a** showed 29 aromatic signals at δ 137–154 (Figure 2), indicating a change in symmetry from C₁ to C_s by the loss of a hydroxyl group. In this cation, **3a**, the cationic center and the sp³ carbon on the C₆₀ sphere have chemical shifts of δ 175.6 and 68.3, respectively. The proton and the carbon in the CHCl₂ group appeared at δ 6.44 and 72.7, respectively. The cationic center is considerably more shielded than for ordinary carbenium ions;¹⁰ the coordination of a chlorine atom to the cationic center to form a four-membered, chloronium ion-like structure (Figure 3, upper right) is suggested.¹¹

(6) ¹H (CS₂-CDCl₃ 4:1) and ¹³C (1,2-dichlorobenzene-C₆D₆ 19:1, 100 MHz) NMR data. **1a**: ¹H NMR (270 MHz) δ 6.98 (s). ¹³C NMR δ 149.8–137.7 (58 peaks), 75.3, 65.1, 61.2. **1b**: ¹H NMR (270 MHz) δ 5.02 and 5.09 (AB quartet, J = 12.2 Hz). ¹³C NMR δ 149.9–137.3 (56 peaks), 93.4, 68.0, 61.5, 55.9. **2a**: ¹H NMR (400 MHz) δ 6.96 (s, 1H), 4.01 (s, 1H). ¹³C NMR δ 150.8–138.4 (56 peaks), 75.9, 75.8, 64.7. **2b**: ¹H NMR (400 MHz) δ 5.00 and 5.06 (AB quartet, J = 12.2 Hz, 2H), 4.07 (s, 1H). ¹³C NMR δ 150.2–138.3 (55 peaks), 93.3, 75.6, 67.5, 55.5.

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(9) (a) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, 118, 3580–3583. (b) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmaier, H. *J. Am. Chem. Soc.* **1997**, 119, 6648–6655.

(10) For example, 9-phenylfluorenyl cation shows a resonance at δ 224.2: Olah, G. A.; Prakash, G. K. S.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, 102, 4485–4492.

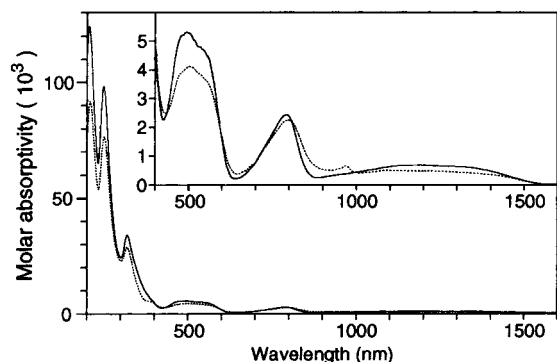


Figure 1. The UV-vis-NIR absorption spectra of **3a** (solid line) and **3b** (dotted line) in $\text{CF}_3\text{SO}_3\text{H}$ at room temperature. The inset shows the absorptions in the vis-NIR region.

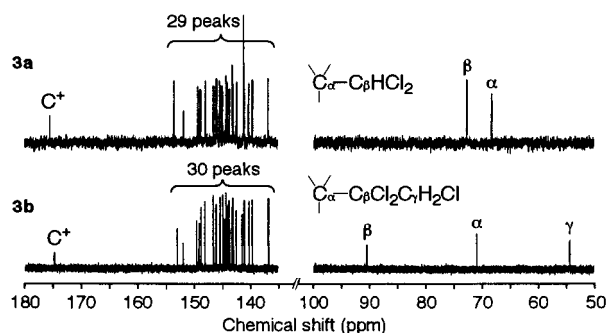


Figure 2. ^{13}C NMR spectra of **3a** and **3b** (rt, 100 MHz, in $\text{CF}_3\text{SO}_3\text{H}$; cyclohexane- d_{12} was used as an external standard and deuterium lock).

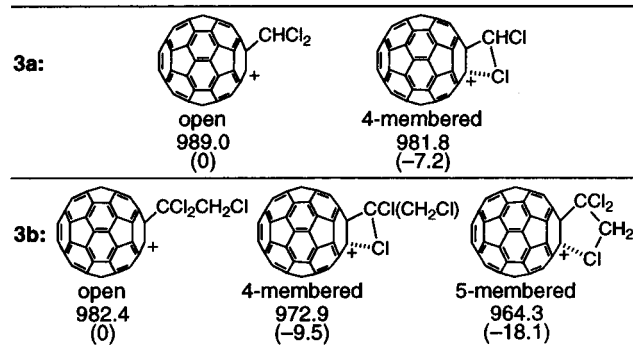
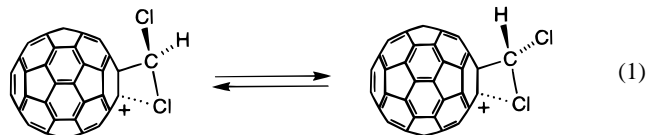


Figure 3. Possible structures for cations **3a** and **3b** and their heats of formation (kcal/mol) calculated by the PM3 method (values relative to that for open structure are shown in parentheses).

PM3 calculations predicted that the coordinated structure is more stable than the open structure by 7.2 kcal/mol. The cyclic structure is also supported by the C-H coupling constant (J_{CH}) of the CHCl_2 group, 189 Hz, a value considerably larger than would be expected for the open structure, in which the methylene carbon has a normal sp^3 hybridization; for comparison, the CHCl_2 group in compound **1a** has a J_{CH} of 182 Hz. The observed large J_{CH} can be attributed to an increase in the s-character of the carbon atom due to the formation of a four-membered ring¹² and development of positive charge on the adjacent chlorine atom.¹³

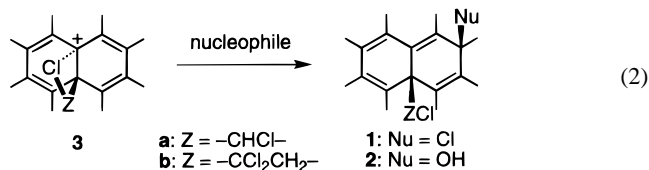
(11) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985; pp 193-207.

It should be noted that if the coordination of the chlorine atom to the C_{60} skeleton is tight, the molecule would be expected to be nonsymmetrical owing to the presence of a chiral carbon atom. The apparent C_s symmetry observed by ^{13}C NMR indicates that the coordination is rather weak and that a pair of enantiomers is in rapid equilibrium with each other. The interconversion is so fast that no line broadening was observed in the ^{13}C NMR spectrum at -45°C .



Fullerol **2b** also gave a reddish purple cation, **3b**, when dissolved in $\text{CF}_3\text{SO}_3\text{H}$, and showed a ^{13}C NMR spectrum (Figure 2) with a signal for the cationic center at δ 174.9. Four- and five-membered structures (Figure 3) are conceivable, but the latter possibility is more likely because the J_{CH} value for the methylene group, 156 Hz, is greater than that of **1b** by only 3 Hz.¹² This is consistent with the results of PM3 calculations, which indicated that the five-membered structure is more stable than the open and the four-membered structures (Figure 3).

Cations **3a** and **3b** are remarkably stable, showing little or no decomposition over several weeks in $\text{CF}_3\text{SO}_3\text{H}$ solution at room temperature. The observed exclusive formation of 1,4-adducts **1a**, **1b**, **2a**, and **2b** is adequately explained by an $\text{S}_{\text{N}}2'$ -type attack of



chloride ion or water on the proposed coordinated structures. Quenching $\text{CF}_3\text{SO}_3\text{H}$ solutions of cations **3a** and **3b** with methanol also yielded a single isomer of methyl ether $\text{MeO}-\text{C}_{60}-\text{R}$ ($\text{R} = \text{CHCl}_2$ or $\text{CCl}_2\text{CH}_2\text{Cl}$) which appears to be the 1,4-isomer, based on NMR and UV-vis spectra (see Supporting Information).

In conclusion, we have shown that C_{60} is sufficiently nucleophilic to undergo electrophilic attack of carbenium ions, which gives a stable monoalkylfullerenyl cation intermediate. This finding suggests potential utility of electrophilic addition as a new carbon-carbon bond forming reaction for the derivatization of C_{60} .

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 10146226) from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Spectroscopic data for **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, $\text{MeO}-\text{C}_{60}-\text{CHCl}_2$, and $\text{MeO}-\text{C}_{60}-\text{CCl}_2\text{CH}_2\text{Cl}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) For example, $(\text{CH}_3)_3\text{S}^+$ has a J_{CH} which is 8 Hz greater than that for $(\text{CH}_3)_2\text{S}$: Haake, P.; Miller, W. B.; Tyssee, D. A. *J. Am. Chem. Soc.* **1964**, *86*, 3577-3578.