7912 J. Org. Chem. 1997, 62, 7912−7913

Endohedral Homoconjugation in Cyclopentadiene Embedded in C_{60}. Theoretical and Electrochemical Evidence

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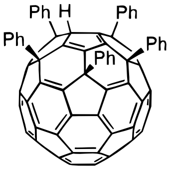
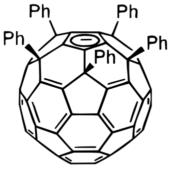
Received June 9, 1997

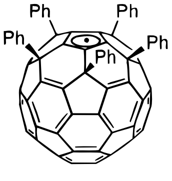
The pentaphenylated fullerene anion $C_{60}Ph_5^-$ (**2**) and its metal complexes represent a new class of cyclopentadiene derivatives,[1] which can be prepared through deprotonation of the parent compound $C_{60}Ph_5H$ (**1**).[2] One out of 12 pentagons in C_{60} is isolated from the remaining 50 sp^2 carbon atoms of the C_{60} molecule by five surrounding sp^3 carbon atoms, each bearing a phenyl group. The previous X-ray crystallographic studies[1] revealed the highly unique cavity structure formed around the cyclopentadienyl (Cp) moiety by the five phenyl groups but failed to give us information on the electronic properties of these unique molecules. We report herein theoretical and experimental evidence that there is endohedral homoconjugation, that is, an electronic interaction between the upper Cp and the lower C_{50} moiety in **1** and **2** through inside of the C_{60} cage. We also found a chemical reaction on the Cp moiety can be induced by reduction of the bottom half of the molecule. No such cyclopentadienes have been recorded previously in the literature.



$C_{60}Ph_5H$ (**1**)

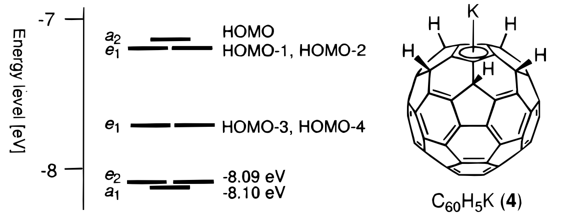


$C_{60}Ph_5^-$ (**2**)



$C_{60}Ph_5^\bullet$ (**3**)

We first present the results of the *ab initio* molecular orbital (MO) calculations performed on $C_{60}H_5K$ [**4**, $K(\eta^5\text{-}C_{60}H_5)$],[3] a model of $K^+\cdot$**2**, at the Hartree−Fock level using the 3-21G(*) basis set.[4,5] An MO diagram for top eight occupied orbitals is shown in Figure 1. While HOMO (a_2, −7.13 eV) is localized at the C_{50} moiety (equatorial belt region of the fullerene sphere), two pairs of doubly degenerate orbitals (e_1) next to HOMO (HOMO-1 to HOMO-4) are fully delocalized over the Cp moiety and the C_{50} bottom half as visualized in Figure 2. In-phase interactions between the upper and lower halves can be seen in the lower energy MO pair (HOMO-3, HOMO-4, −7.69 eV) and out-of-phase ones in the higher energy pair (HOMO-1 and HOMO-2, −7.19 eV). These theoretical data fully corroborate the presence of strong endohedral homoconjugation,[6] $\pi-\pi$ orbital interactions inside the C_{60} cage. Note that the Cp-related occupied orbitals are remarkably stabilized and found at the much lower energy levels compared with HOMOs (e_1, −5.82 eV, HF/3-21G$^{(*)}$) of $C_5(Me)_5K$ (Cp*K). The total natural atomic charge[7] on the Cp carbons in Cp*K is −3.27, while that in $C_{60}H_5K$ (**4**) is only −0.82, indicating that a considerable amount of negative charge on the Cp is delocalized toward the C_{50} moiety through homoconjugation.



$C_{60}H_5K$ (**4**)

Figure 1. Molecular orbital diagram for the top eight occupied orbitals of $C_{60}H_5K$ (**4**).

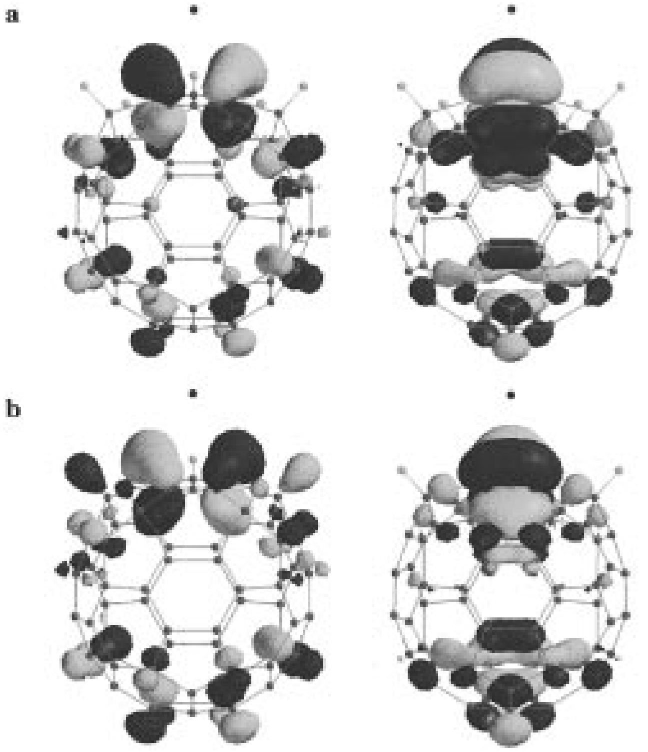


Figure 2. Molecular orbitals of $C_{60}H_5K$ (**4**) at the HF/3-21G(*) level. (a) HOMO-1 and HOMO-2 (e_1). (b) HOMO-3 and HOMO-4 (e_1).

Cyclic voltammetry (CV) measurements (−3.0 to +1.0 V vs Fc/Fc^+) on $C_{60}Ph_5H$ (**1**) and its anion $C_{60}Ph_5^-$ (**2**)[8] at −78 °C in THF showed that these molecules accept electrons with exceptional ease.[9] The neutral compound **1** showed two reversible reduction events at −1.45 and −2.10 V ($E_{1/2}$) (Figure 3a, eq 1). In light of the fact that C_5Me_5H cannot be reduced with such ease, these reduction events must be due to the presence of the C_{50} moiety.

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(1) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850.

(2) Avent, A. G.; Birkett, P. R.; Crane, J. D.; Darwish, A. D.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1463.

(3) Optimized under C_{5v} symmetry; total energy = −2858.211673 hartree. Comparison of the structural parameters (C−C bonds in the C_{60} core and the distances between the top Cp moiety and the bottom pentagon) in the calculated $C_{60}H_5K$ structures with the X-ray structure of $Tl(\eta^5\text{-}C_{60}Ph_5)$ (ref 1) revealed close matching of these three structures (<1% deviation with exceptionally large 2.0% deviation for the bonds around the sp^3 carbon atoms).

(4) (a) 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1986**, *7*, 359. (b) 3-21G$^{(*)}$: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(5) For semiempirical calculations on $C_{60}H_5^-$ and $C_{60}H_5M$ (M = SiCp, etc.), see: Chistyakov, A. L.; Stankevich, I. V. *Russ. Chem. Bull.* **1996**, *45*. 2294.

(6) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283.

(7) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(8) Note that the potassium cation has most likely been replaced by Bu_4N^+ contained in the supporting electrolyte.

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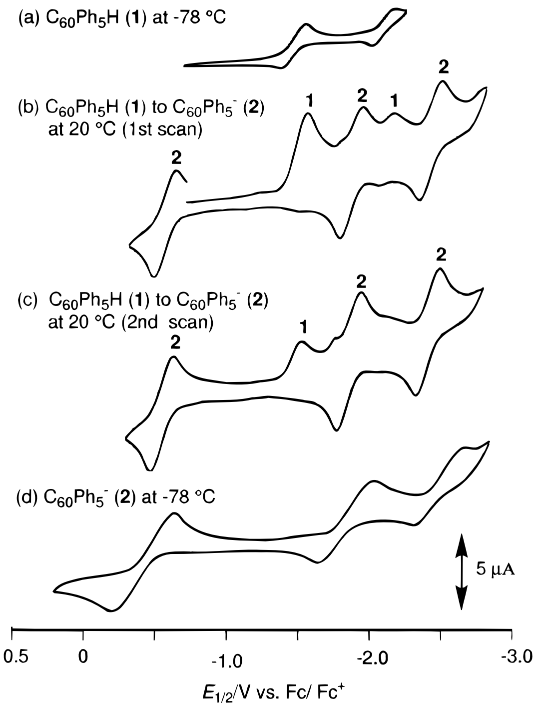


Figure 3. Cyclic voltammograms of $C_{60}Ph_5H$ (**1**) and $C_{60}Ph_5^-$ (**2**). 0.1 M Bu_4NClO_4 in THF with Pt working and counter electrodes. Scan rate: 100 mV/s. The peak-to-peak separation values for the Fc/Fc^+ couple (4.1 mM) were 0.93 and 0.68 V at −78 and +20 °C, respectively: (a) 1.0 mM **1** at −78 °C, $E_{1/2}^{red1} = -1.45$ V, $E_{1/2}^{red2} = -2.10$ V; (b) first scan for 1.0 mM **1** at 20 °C; (c) second scan for 1.0 mM **1** at 20 °C; (d) 5.0 mM **2** at −78 °C, $E_{1/2}^{ox} = -0.43$ V, $E_{1/2}^{red1} = -1.84$ V, $E_{1/2}^{red2} = -2.52$ V.

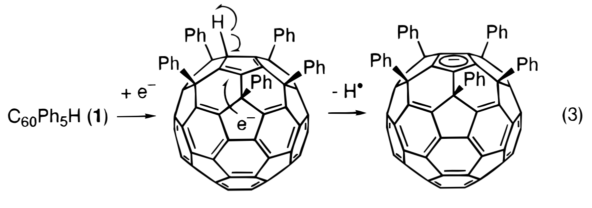
Compound **1** could not be oxidized within the potential range studied (<+1.0 V). On the other hand, the anionic compound **2** showed an oxidation event at −0.43 V ($E_{1/2}$) in a reversible manner as well as two reduction events at −1.84 and −2.52 V ($E_{1/2}$) (Figure 3d, eq 2). The product of the oxidation of anion **2** can be depicted as a cyclopentadienyl radical **3**.

$$\mathrm{C_{60}Ph_5H}\ (\mathbf{1}) \underset{\substack{-\,e^- \\ E_{1/2}^{\mathrm{red1}}}}{\overset{+\,e^-}{\rightleftharpoons}} \mathrm{C_{60}Ph_5H}^{\bullet\,-} \underset{\substack{-\,e^- \\ E_{1/2}^{\mathrm{red2}}}}{\overset{+\,e^-}{\rightleftharpoons}} \mathrm{C_{60}Ph_5H}^{2-} \tag{1}$$

$$\mathrm{C_{60}Ph_5}^{\bullet}\ (\mathbf{3}) \underset{\substack{-\,e^- \\ E_{1/2}^{\mathrm{ox}}}}{\overset{+\,e^-}{\rightleftharpoons}} \mathrm{C_{60}Ph_5}^{-}\ (\mathbf{2}) \underset{\substack{-\,e^- \\ E_{1/2}^{\mathrm{red1}}}}{\overset{+\,e^-}{\rightleftharpoons}} [\mathrm{C_{60}Ph_5}^{-}]^{\bullet\,-} \underset{\substack{-\,e^- \\ E_{1/2}^{\mathrm{red2}}}}{\overset{+\,e^-}{\rightleftharpoons}} [\mathrm{C_{60}Ph_5}^{-}]^{2-} \tag{2}$$

Comparison of Figure 1a and d shows that the first and the second reduction potentials of the anion **2** are systematically shifted (by −0.39 and −0.42 V, respectively) as compared with the corresponding ones of neutral compound **1**. Evidently, the conversion of **1** to its monoanion (**2**) much reduces the electron-accepting ability of the C_{50} moiety. These results are in good agreement with the theoretical conclusion that the top Cp^- moiety in the anion **2** supplies substantial negative charge to the C_{50} bottom through endohedral homoconjugation.[10]

We have found evidence of dynamic electronic communication between the top and the bottom halves upon electrochemical measurement of the neutral compound **1** at temperatures above 0 °C. While the cyclic voltammogram at 20 °C for the anion **2** was essentially the same as the one at −78 °C (shifted by <±0.11 V, data not shown), the electrochemistry of **1** at 20 °C was found to be different from that at −78 °C. Thus, in the first reduction/oxidation cycle (Figure 1b), the reduction and oxidation waves due to **2** emerged in addition to those of **1**. In the second cycle (Figure 1c) and afterward, most of **1** disappeared and **2** became a predominant species detectable by electrochemical measurement.[11,12] This result can be rationalized by considering the limiting structure **A** for $C_{60}Ph_5H^{\bullet-}$, wherein the added electron is localized at the bottom half. The electron is transmitted to the top CpH moiety through the homoconjugated system, causing expulsion of $H^\bullet$ and formation of a Cp anion species **2**.[13]



A ($C_{60}Ph_5H^{\bullet-}$) $C_{60}Ph_5^-$ (**2**) (3)

In summary, we have demonstrated unique electronic properties of the fullerene−cyclopentadiene derivatives $C_{60}Ph_5H$ (**1**) and $C_{60}Ph_5^-$ (**2**). The Cp structure embedded in the fullerene core offered us a prospect that the properties of the Cp chemistry may be tunable with external electronic field.[14] The intense UV/vis absorption of these molecules[1] suggests a further perspective toward phototuning of the Cp properties, which will be the subject of future studies.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (B) No. 09440238 from Monbusho and the Sumitomo Foundation and by a generous supply of C_{60} from Hoechst Japan Ltd. We thank Prof. T. Saito and Prof. H. Nishihara at the University of Tokyo for the help and discussion on the cyclic voltammetry measurement. H.I. and S.M. thank JSPS for predoctoral fellowships. We thank the Institute for Molecular Science, Japan, for the computational time.

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(9) (a) The first and second reduction potentials −0.86 and −1.44 V ($E_{1/2}$) of C_{60} may provide reference points: Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807. (b) For CV measurements of organofullerenes, see: Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364. Cardullo, F.; Isaacs, L.; Diederich, F.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *J. Chem. Soc., Chem. Commun.* **1996**, 797. Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077.

(10) Although we show the limiting structures such as **2** and **3** for the ease of understanding, they are an incorrect representation of the reality, where the two systems actually form a single π-electronic system. The seeming presence of Coulombic interactions between the upper and the lower halves must therefore be interpreted in terms of a delocalized electron system rather than the localized pictures of **2** and **3**.

(11) After the second cycle until the seventh scan, the voltammogram remains identical showing the presence of a small amount of **1**, since a steady state was reached for the material exchange between the vicinity of the electrode and the bulk solution where excess **1** is present.

(12) The same conclusion was reached when a narrower scan range (−0.70 to −1.95 V) or different scan rates (10 and 1000 mV/s) were employed.

(13) A reviewer suggested the possibility that the anion **2** was formed through deprotonation of **1** with an electrochemically generated base. Indeed, if a strong base were generated in situ, it would have deprotonated **1**. However, we did not observe any CV indications of side reactions other than the irreversible conversion of **1** to **2** and their reversible CV behavior, and hence, there was no sign of direct electrochemical generation of a strong base. Indirect formation of a base through the radical anion **A** is not likely either, since the radical anions of C_{60} and its derivatives have not be reported to be very basic (ref 9).

(14) For our previous work on a C_{60}-based metal ligand system, see: Yamago, S.; Yanagawa, M.; Mukai, H.; Nakamura, E. *Tetrahedron* **1996**, *52*, 5091.