J. Am. Chem. Soc. **1998,** *120,* 8285−8286

Synthesis of π-Indenyl-type Fullerene Ligand and Its Metal Complexes via Quantitative Trisarylation of C$_{70}$

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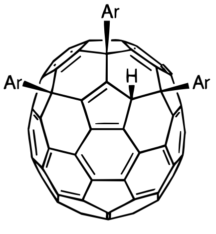
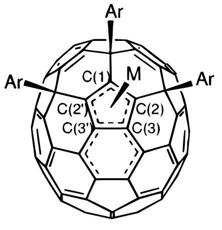
Received April 14, 1998

We reported earlier that C$_{60}$ reacts with an organocopper reagent prepared from arylmagnesium bromide and CuBr·SMe$_2$ to form a pentakis addition product C$_{60}$Ar$_5$H in a quantitative yield.[1] The pentakis adduct was used as a precursor to the pentahaptofullerene metal complexes M[η^5-C$_{60}$(C$_6$H$_5$)$_5$]. With an intention to obtain a higher fullerene analogue of the pentakis adduct, we have examined the reaction of C$_{70}$ with the organocopper reagent. The compound that we obtained was, however, not the expected pentakis adduct but a tris adduct C$_{70}$Ar$_3$H (**1**)[2] with an indene-like substructure flanked by the three sp^3 carbons. The tris adduct **1** was deprotonated with metal alkoxides to form the corresponding metal complexes C$_{70}$Ar$_3$M [M = K (**2**), Tl (**3**)]. The ab initio MO studies (HF/3-21G$^{(*)}$) suggested that the fullerene group C$_{70}$Ar$_3$$^-$ coordinates to the metal as an η^5-indenylide rather than a η^3-ligand in **2** and **3**. The X-ray diffraction study of the thallium complex **3**·(1,2-Cl$_2$-C$_6$H$_4$) not only confirmed the η^5-coordination but indicated the presence of two-dimensional cage-to-cage van der Waals contacts in crystal packing.



C$_{70}$(4-CF$_3$-C$_6$H$_4$)$_3$H (**1**)

Ar = 4-CF$_3$-C$_6$H$_4$



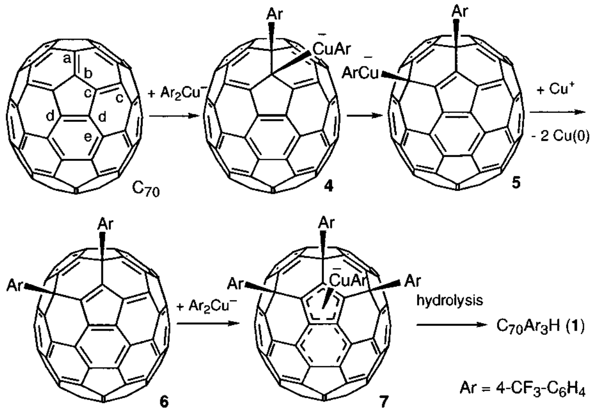
M[η^5-C$_{70}$(4-CF$_3$-C$_6$H$_4$)$_3$]
[M = K (**2**), Tl (**3**)]

The organocopper tris addition to C$_{70}$ is very clean under the optimized conditions using 4-CF$_3$-C$_6$H$_4$MgBr (16 equiv) and CuBr·SMe$_2$ (16 equiv) in 1,2-Cl$_2$-C$_6$H$_4$ (eq 1). The C_1 symmetric tris adduct C$_{70}$(4-CF$_3$-C$_6$H$_4$)$_3$H (**1**)[3] of 96% purity on HPLC has been obtained in 96% isolated yield after aqueous workup.

$$\mathrm{C_{70}} \xrightarrow[\substack{\text{1,2-Cl}_2\text{-C}_6\text{H}_4 \\ -78\ ^\circ\text{C} \longrightarrow 10\ ^\circ\text{C}}]{\substack{\text{4-CF}_3\text{-C}_6\text{H}_4\text{MgBr (16 equiv)} \\ \text{CuBr·SMe}_2\text{ (16 equiv)}}} \underset{96\%}{\mathrm{C_{70}(4\text{-}CF_3\text{-}C_6H_4)_3H}\ (\mathbf{1})} \qquad (1)$$

In contrast to C$_{60}$, the higher fullerene C$_{70}$ has two areas of different reactivities. One is the inert equator area, and the other is more reactive C$_{60}$-like region near the poles.[4] The latter possesses two different kinds of double bonds ($C_a{=}C_b \times 10$ and $C_c{=}C_c \times 10$, see Scheme 1). The first step of the tris addition (Scheme 1) is likely to be the regioselective carbocupration[5] of the most reactive double bond $C_a{=}C_b$ with one molecule of (4-CF$_3$-C$_6$H$_4$)$_2$Cu$^-$ giving the metalated fullerene **4**, which may equilibrate with the 1,4-addition product **5**. This species (**5**) decomposes to form the 1,4-bisarylation product **6**, Cu(0), and one electron, which is given to the Cu(I) species that exists in excess in the solution. The third aryl group adds to $C_c{=}C_c$ to form the stable copper(I) species with three aryl groups (**7**) (see below for the ligand hapticity), which gives C$_{70}$(4-CF$_3$-C$_6$H$_4$)$_3$H (**1**) upon hydrolysis.

Scheme 1



When a THF-d_8 solution of **1** was treated with 1 equiv of metal alkoxide (KO^{t}Bu, TlOEt) at 25 °C, the color of the solution changed from reddish brown to dark red, and the ^{1}H and ^{13}C NMR spectra showed quantitative formation of a C_s-symmetric metal complex formulated as C$_{70}$(4-CF$_3$-C$_6$H$_4$)$_3$M [M = K (**2**), Tl (**3**)]. Contrary to the isolated 6π cyclopentadienyl anion in the pentakis-arylated fullerene ligand C$_{60}$Ph$_5$$^-$,[1] the corresponding five-membered ring of the present C$_{70}$ analogue is directly conjugated with the remaining polyene moiety of the C$_{70}$ cage. Therefore, various structures are conceivable for the complex **2** and **3** as to the position of the metal binding site. Among those the most probable ones are η^3- and η^5-complexes, in which the metal atom is coordinated to the three or five sp^2 carbon atoms flanked by the three sp^3 carbon atoms. Such a consideration is a reasonable one since the pyramidarization at the three sp^3 carbons makes the adjacent three sp^2 carbons [C(1), C(2), C(2′)] more planar, and this planarity should favor the interaction with the metal atom.[6] The C_s symmetry observed in the NMR spectra of **2** and **3** is consistent with both the η^3- and η^5-structures. The hapticity issue was examined first by theory and then by X-ray crystallographic analysis.

In the optimized structure of model compound C$_{70}$H$_3$Li (**8**) (HF/3-21G$^{(*)}$, C_s symmetry, total energy = −3233.615841 hartree, Figure 1a),[7,8] the lithium atom is bonded to the fullerene in an η^5-coordination mode. The part structure of the indenyl moiety of **8** shows striking resemblance to the X-ray crystal structure of Li(η^5-indenyl)(tmeda).[8b] Relatively long C−C bond lengths of [5,6] junction [C(3)−C(3′); 1.43 Å in **8**] and adjacent six-membered ring C−C bonds [C(3)−C(4) and C(3′)-C(4′); 1.44 Å

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(1) (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850. (b) Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912.

(2) While we studied mainly this compound because of its reasonable solubility in organic solvents, the reaction with other arylmagnesium bromides such as C$_6$H$_5$MgBr, 4-Cl-C$_6$H$_4$MgBr, and 1-NpMgBr gave similar results. Full details will be described elsewhere.

(3) The gross structure including the positions of the aryl groups was determined by the X-ray crystal structure analysis of **3**. The HMBC 2D NMR spectrum was consistent with the location of the hydrogen atom indicated in **1**.

(4) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber*. **1993**, *126*, 1061.

(5) Nakamura, E.; Mori, S.; Nakamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 4887.

(6) Haddon, R. C. *J. Comput. Chem.* **1998**, *19*, 139.

(7) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(8) For theoretical calculation of Cp and indenyllithium complexes, see: (a) Alexandratos, S.; Streitwieser, A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 7959. (b) Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 737.

S0002-7863(98)01256-6 CCC: $15.00

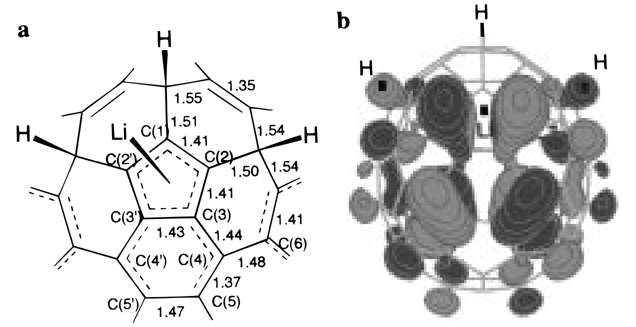

Figure 1. (a) A part of the optimized structure of **8** at the HF/3-21G(*) level. C−C bond lengths (Å) are affixed to the respective bonds. Li−C bond lengths (Å): Li−C(1), 2.24; Li−C(2), 2.20; Li−C(3), 2.18. (b) HOMO surface of **8**.

in **8**] are common features of the both systems. Characteristics of **8** can be seen in rather long bond length of [5,6] junction C(5)−C(5′) and the shorter distance between the lithium atom and C(3)/C(3′) atoms. As shown in Figure 1b, the HOMO (A″, −7.18 eV) of **8** is localized mainly at the indenyl moiety and substantially delocalized over most of the fullerene cage. The calculations on the potassium and thallium complexes gave optimized structures very similar to that of **8** except for the metal carbon bond lengths (data not shown).

Deep red single crystals of the thallium complex with composition **3**·(1,2-Cl_2-C_6H_4) were obtained by recrystallization through slow diffusion of hexane into a solution of **3** in 1,2-Cl_2-C_6H_4 and analyzed by X-ray diffraction.[9] The crystal structure shows that the thallium atom is located equidistant from the three aryl groups and bonded to the pentagon flanked by the three sp^3 carbons. The crystal packing (Figure 2) shows columnar stacking of **3** along the *a* axis through van der Waals contacts between neighboring fullerene cages. The columns have additional cage-to-cage contacts to form a sheet structure on the *a*,*b* plane. Lattice solvent 1,2-Cl_2-C_6H_4 occupies the columnar cavities formed between the sheets on the *a*,*b* plane. The thallium atom has intermolecular contacts only with two chlorine atoms of 1,2-Cl_2-C_6H_4.

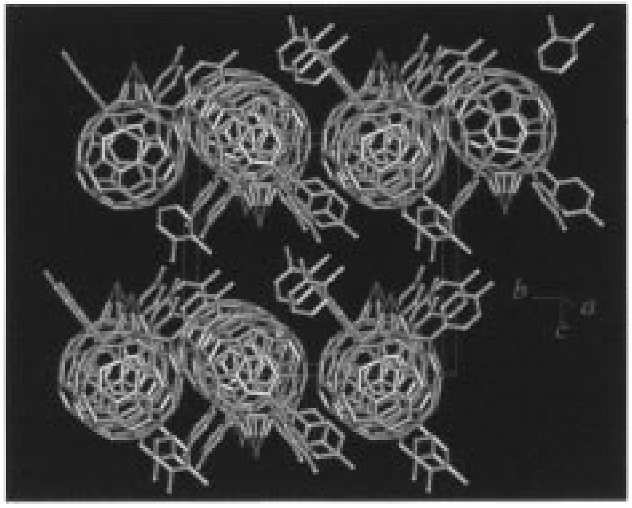

Figure 2. Crystal packing of **3**·(1.2-Cl_2−C_6H_4). All fluorine and hydrogen atoms are omitted for clarity.

In summary, the tris-arylated fullerene $C_{70}Ar_3H$ has been synthesized in a quantitative yield through 3-fold addition of an organocopper reagent to C_{70} and has been shown to act as a π-indenyl-type ligand in the metal complexes M(η^5-$C_{70}Ar_3$) (M = K, Tl) as shown by the ab initio molecular orbital calculations and the X-ray crystal structure analysis. Although only a η^5-coordination mode has been revealed in this study, the $C_{70}Ar_3$ ligand will show different coordinating property such as η^3-coordination toward a different kind of metal fragment, as seen in the case of the simple Cp and indenyl-type ligands.[10]

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research from Monbusho, Japan. Generous allotment of computational time from Intelligent Modeling Laboratory, University of Tokyo, is gratefully acknowledged. H.I. thanks JSPS for a predoctral fellowship.

Supporting Information Available: Experimental procedure for the preparation of **1**, spectral and analytical data for compounds **1**−**3**, Cartesian coordinates of **8**, and summary of the X-ray crystal structure determination of **3**·(1.2-Cl_2-C_6H_4) (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(9) Diffraction study was carried out by an imaging plate method with MacScience DIP-2030 diffractometer: monoclinic, $P2_1$ (No. 4); $a = 11.282(2)$, $b = 17.576(4)$, and $c = 15.993(4)$ Å, $\beta = 97.07(1)°$, $V = 3147.2(4)$ Å^3; $Z = 2$; $^{\mu}$ (Mo Kα) = 2.645 mm^{-1}; λ (Mo Kα) = 0.71073 Å; $T = 298$ K; 5558 reflections measured, 3085 observed ($I > 2.00\sigma(I)$); $\theta_{max} = 25.24°$; 891 parameters; $R = 0.085$; $Rw = 0.102$; $S = 8.275$. The refinement has not converged appropriately ($(\Delta/\sigma)_{max} = 2.9775$) due to insufficiency of the number of wide-angle reflections.

(10) For a review concerning ring slippage of this type of ligands, see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.