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Stepwise Synthesis of Fullerene Cyclopentadienide $R_5C_{60}^-$ and Indenide $R_3C_{60}^-$. An Approach to Fully Unsymmetrically Substituted Derivatives

Masaya Sawamura,*,[†] Motoki Toganoh, Kazuhiro Suzuki, Atsushi Hirai, Hitoshi Iikura, and Eiichi Nakamura*

Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku,
Tokyo 113-0033, Japan

nakamura@chem.s.u-tokyo.ac.jp

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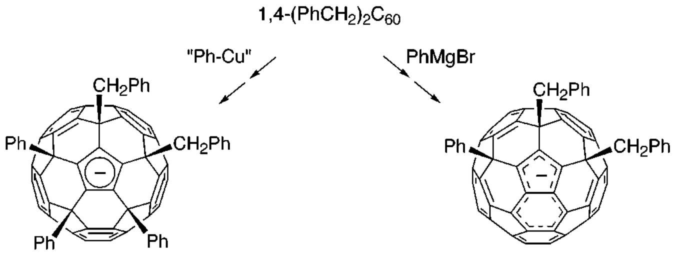
ABSTRACT



Fullerene cyclopentadienide $(PhCH_2)_2Ph_3C_{60}^-$ and indenide $(PhCH_2)_2PhC_{60}^-$, each bearing two different organic groups, were efficiently synthesized through regioselective reactions of 1,4-$(PhCH_2)_2C_{60}$ with an organocopper reagent ($PhMgBr/CuBr{\cdot}SMe_2$) or a Grignard reagent (PhMgBr) followed by deprotonation with KO^{t}Bu.

We reported earlier the synthesis of cyclopentadienes (R_5HC_{60}; R = Ar, Me) and cyclopentadienides ($R_5C_{60}^-$) embedded in C_{60} through quantitative 5-fold organocopper addition to C_{60}.[1] The pentakis addition is so effective that a variety of $R_5C_{60}^-$ compounds have been prepared, in many cases, in a quantitative yield; nonetheless, the method is totally unsuitable for the synthesis of compounds bearing different R groups or for the synthesis of C_{60} derivatives bearing fewer than five substituents. Here we report strategies for the installation of two different R groups totaling three and five in number as demonstrated through synthesis of new cyclopentadienide and indenides, $K^+[(PhCH_2)_2Ph_3C_{60}]^-$ (**3**) and $K^+[(PhCH_2)_2PhC_{60}]^-$ (**5**).

We are currently postulating that the 5-fold organocopper addition to C_{60} proceeds through a sequential addition/oxidation process involving nucleophilic attacks of R_2Cu^- species and one-electron oxidation by a Cu(I) salt. Formation of a 1,4-diorgano-1,4-dihydro[60]fullerene (1,4-R_2C_{60})[2] and 1,4,11,30-tetraorgano-1,4,11,30-tetrahydro-[60]fullerene (1,4,11,30-R_4C_{60})[3] as transient intermediates are being postulated. Along such a line of reasoning, we considered that the reaction of 1,4-R_2C_{60} with an organocopper reagent

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[†] E-mail: sawamura@chem.s.u-tokyo.ac.jp.

(1) (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850−12851. (b) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599*, 32−36. (c) Sawamura, M.; Toganoh, M.; Kuninobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett.* **2000**, 262−263. (d) Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 8285−8286.

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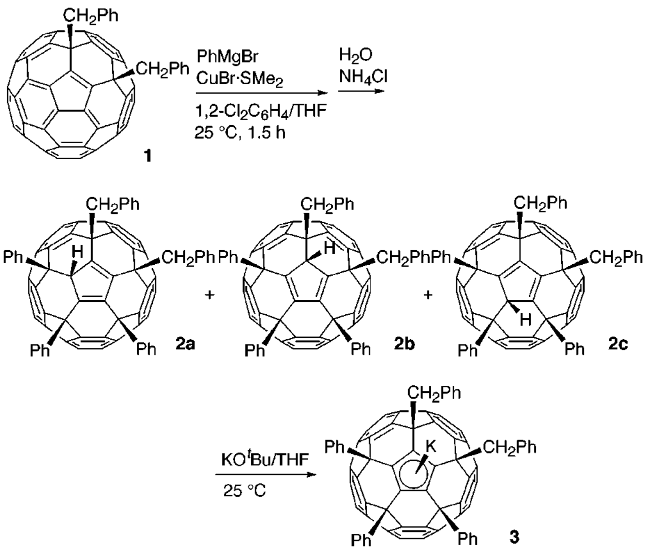
R'_2Cu^- would afford the mixed organohydrofullerene $R_2R'_3HC_{60}$. We have chosen $(PhCH_2)_2C_{60}$ (**1**)[2b,c,f] as a starting material of the present studies because of its availability and the high solubility in organic solvent. To our satisfaction, the reaction of **1** (1,2-dichlorobenzene/THF, 25 °C, 2 h) with an excess amount of an organocopper reagent prepared from PhMgBr (15 equiv) and $CuBr{\cdot}SMe_2$ (15 equiv) (after quenching with aqueous NH_4Cl) gave $(PhCH_2)_2Ph_3H$ (**2a**−**c**) quantitatively as a mixture of three isomers (Scheme 1).

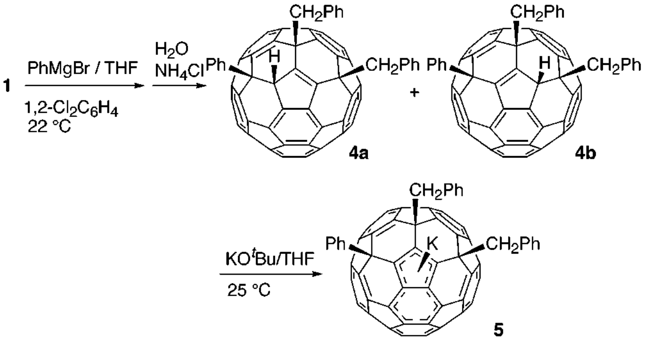
Scheme 1



Purification by HPLC (Bucky Prep, Nacalai Tesque Co.) afforded an analytically pure material in 86% yield. Treatment of the solution of the isomeric mixture of **2** in THF with an excess KO^{t}Bu (1.2 equiv) at 20 °C caused immediate color change from dark red to very dark brown. The ^{1}H and ^{13}C NMR (THF-d_8) showed that the isomeric mixture converged into a single cyclopentadienide $K^+[(PhCH_2)_2Ph_3C_{60}]^-$ (**3**) with C_s symmetry. This result indicates that the isomerism in **2** arises from the positional isomers of the cyclopentadiene moiety as shown for **2a**−**c** and, therefore, that the three phenyl groups were regioselectively installed in such a manner that one of the C_{60} pentagons became isolated from the remainder of the C_{60} core to form a cyclopentadiene.

It is known that a Grignard reagent reacts with C_{60} in a 1,2-monoaddition manner.[4] We have conjectured that the reaction of 1,4-R_2C_{60} with a Grignard reagent will take place only once to give a triorganomonohydrofullerene. In light of our previous knowledge on a regioselectivity in the 3-fold addition reaction of C_{70}, we considered that the reaction would give **5**. According to this scenario, we have carried out the reaction of 1,4-$(PhCH_2)_2C_{60}$ (**1**) with PhMgBr. The reaction of **1** proceeded smoothly in 1,2-dichlorobenzene at 22 °C in the presence of 3.6 equiv of PhMgBr (1 M in THF) and, after hydrolysis with aqueous NH_4Cl and HPLC purification (Bucky Prep), gave $(PhCH_2)_2PhHC_{60}$ (**4a**,**b**) in 72% yield as a mixture of two isomers (100% conversion of C_{60}). The structure of $(PhCH_2)_2PhHC_{60}$ was assigned in the manner similar to the one employed for **2**; namely, deprotonation with KO^{t}Bu formed a single C_1 symmetric potassium salt $K^+[(PhCH_2)_2PhC_{60}]^-$ (**5**) (Scheme 2).

Scheme 2



Optimized structure of a C_s symmetric model compound $C_{60}H_3K$ (**6**) (HF/3-21G$^{(*)}$, total energy = −2857.00417344 hartree, Figure 1a)[5] shares some important features with that of its C_{70} analogue, $C_{70}H_3Li$ reported previously.[1d] Thus, the fully delocalized 10-π indenyl framework is separated from the remaining 48-π electron system by the seven surrounding C−C bonds of rather long bond lengths (1.47−1.52 Å).[6] The pentagon of the indenyl moiety coordinates to the metal center in an η^5-fashion. The HOMO surface of **6** depicted in Figure 1b represents a typical indenyl HOMO and shows remarkable resemblance to that of $C_{70}H_3Li$. Such an effective π electron delocalization within the indenyl framework of **6**

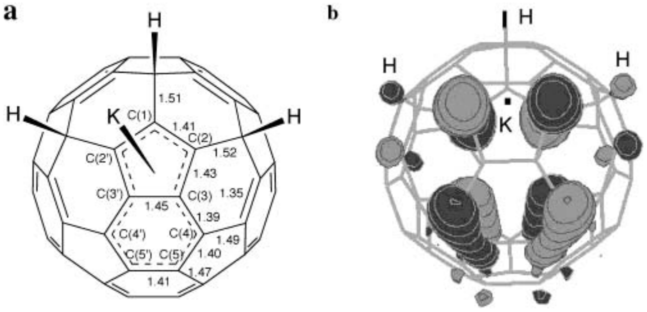


Figure 1. (a) Part of the optimized structure of **6** at the HF/3-21G(*) level. C−C bond lengths (Å) are affixed to the respective bonds. K−C bond lengths (Å): K−C(1), 3.08; K−C(2), 2.98; K−C(3), 2.93. (b) HOMO surface of **6**.

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[6] The most obvious difference is found in the shorter C(3)−C(4) bond length (1.39 Å) of **6**.

[7] Note that the indenyl plane of $C_{70}H_3Li$ is rather flat due to the decreased degree of curvature in the equatorial belt region of C_{70} cage.

is surprising if one consider the highly bent structure of the indenyl plane.[7]

In conclusion, we have shown that the cyclopentadiene ($R^1{}_2R^2{}_3HC_{60}$, $R^1{}_2R^2HC_{60}$) and cyclopentadienide ($R^1{}_2R^2{}_3C_{60}{}^-$, $R^1{}_2R^2C_{60}{}^-$) bearing two different organic substituents can efficiently be synthesized by stepwise methods by way of 1,4-diorganofullerene.[2] Since unsymmetrical 1,4-diorganofullerene $RR'C_{60}$ of various combination of R and R′ can be prepared through trapping of $RC_{60}{}^-$ with an electrophile,[2d−f] we can fully expect that one can now synthesize a wide variety of analogues of R_5HC_{60} and R_3HC_{60} bearing various different organic substituents. The structure diversity thus created on a spherical platform will open new opportunities on application of the densely functionalized, geometrically well-defined compounds in various fields.

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Supporting Information Available: Experimental procedures and characterization for compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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