JOURNAL OF
Materials
CHEMISTRY

Cu(I)-mediated regioselective tri-addition of Grignard reagent to [70]fullerene. Synthesis of indenyl-type metal ligand embedded into graphitic structure

Masaya Sawamura,† Motoki Toganoh, Hitoshi Iikura, Yutaka Matsuo, Atsushi Hirai‡ and Eiichi Nakamura*

Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033,
Japan. Tel: +81-3-5800-6889; Fax: +81-3-5800-6889;
E-mail: nakamura@chem.s.u-tokyo.ac.jp

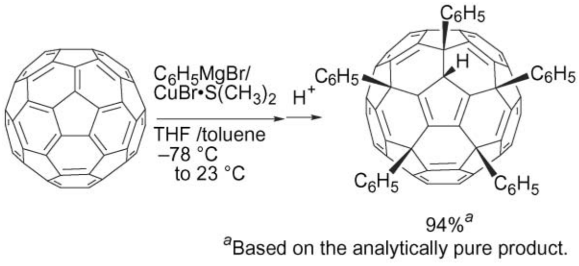
Received 28th February 2002, Accepted 24th April 2002
First published as an Advance Article on the web 10th May 2002

A variety of [70]fullerene derivatives bearing three organic groups $C_{70}R_3H$ (**1**, R = aryl, methyl) have been synthesized in 90–99% isolated yield by the reaction of [70]fullerene with a Grignard reagent in the presence of $CuBr{\cdot}S(CH_3)_2$. Deprotonation of $C_{70}R_3H$ with a metal alkoxide gave the corresponding metal complex $M(\eta^5\text{-}C_{70}R_3)$ [M = K (**2**), Tl (**3**)]. X-ray crystallographic analysis as well as theoretical study revealed the nature of the 68π-electron ligand, $C_{70}R_3^-$.

Introduction

Covalent functionalization of carbon clusters continues to attract the interest of synthetic and materials chemists.[1,2] With all the intense research activities in the area, the major problem still remains the poor yield of the synthetic transformations. In order for carbon cluster science to become truly useful core technology in the 21st century, the synthetic transformations must be quantitative based on the starting carbon cluster used for the reaction, and must be achieved in a simple and efficient procedure without production of noxious waste. Unfortunately, the current state of art is far from satisfactory. With virtually no exceptions, the reported synthetic transformations of carbon clusters produce the desired product together with over-reacted products, recovered starting material, regio- and stereoisomers, and therefore the product yield never approaches 100%.

Some time ago, we reported that [60]fullerene reacts with a phenyl Grignard reagent in the presence of a Cu(I) salt to form a penta-addition product $C_{60}(C_6H_5)_5H$ in 99% isolated yield based on the analytically pure product [(eqn. (1)].[3] The reaction can be easily performed on a 10 g scale in an ordinary chemical laboratory. This transformation represented, to our knowledge, the only chemical transformation at that time that enabled covalent functionalization of carbon clusters in quantitative yield. The reaction was proven to be applicable to the synthesis of variety of $C_{60}R_5H$ compounds (R = aryl, 1-alkenyl and methyl) often in quantitative yield.[3–5] The penta-adduct $C_{60}R_5H$ serves as a precursor to the pentahaptofullerene metalcomplexes $M(\eta^5\text{-}C_{60}R_5)$, which are useful for catalysis[6] and for construction of nanostructures in water and on the surface.[7]



(1)

^{a}Based on the analytically pure product.

With the intention of obtaining higher fullerene analogues of the penta-adduct, we examined the reaction of [70]fullerene with a Grignard reagent in the presence of a Cu(I) salt. The product was, however, not the expected penta-adduct (**4** or **5**) but a tri-adduct $C_{70}R_3H$ (**1**) (Scheme 1). Thus, the addition reaction took place 100% selectively on the side of the football-shaped fullerene rather than at the pointed end of the molecule, and stopped precisely after tri-addition. After considerable optimization of the reaction conditions, the tri-addition reaction was made to proceed in 90–99% isolated yield for methyl and aryl Grignard reagents. The tri-arylation reactions were essentially quantitative, while the tri-methylation reaction gave someside products. The reaction provided the second example of quantitative covalent functionalization reaction of carbon clusters,[8] which was followed later by the third example, quantitative tetra-amination reaction of [60]fullerene.[9]

The tri-adduct **1** was deprotonated with a metal alkoxide to obtain the corresponding metal complex $M(\eta^5\text{-}C_{70}R_3)$ [M = K (**2**), Tl (**3**)]. Single crystal X-ray crystallographic analysis of the Tl complex **3a** revealed that the compound possesses a metal η^5-indenyl structure flanked by three sp^3 carbons. The $C_{70}R_3$ anion ligand represents an unprecedented 68π-electron ligand to a metal cation. The synthetic route to this class of organofullerene is complementary to the stepwise synthesis of $C_{60}R^1{}_2R^2H$ from [60]fullerene,[10] and may acquire significant utility once the price of [70]fullerene goes downsignificantly. Brief mechanistic studies indicated that the premature

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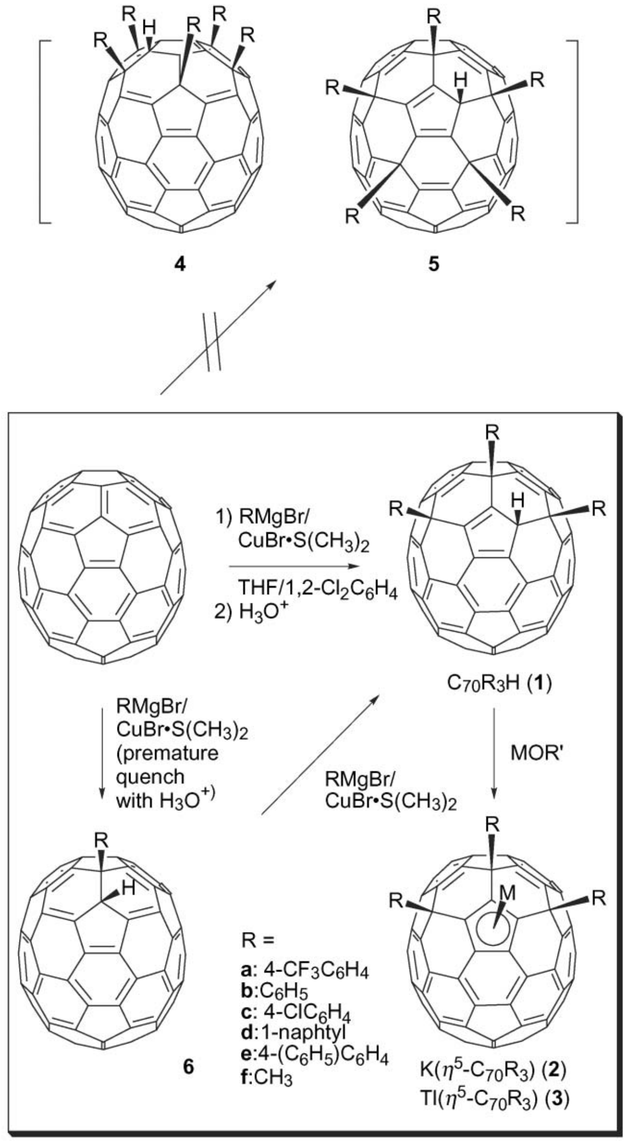
†Present address: Department of Chemistry, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. Fax: +81-11-706-4924; Tel: +81-11-706-4924; E-mail: sawamura@sci.hokudai.ac.jp

‡Present address: Department of Chemistry, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. Fax: +81-11-706-4920; Tel: +81-11-706-2716; E-mail: ahirai@sci.hokudai.ac.jp

DOI: 10.1039/b202130g

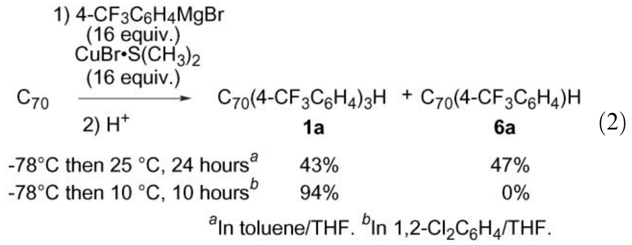


Scheme 1

quenching of the reaction gives a mono-adduct **6**, which could be converted further to the tri-adduct upon treatment with the same copper reagent. In this article, we report a full account of the synthesis of the $C_{70}R_3H$ compounds.

Results and discussion

Expecting the formation of the penta-adduct **4** or **5** in analogy with the formation of $C_{60}R_5H$ from [60]fullerene, we treated [70]fullerene with an organocopper reagent prepared *in situ* from a one-to-one mixture of $4\text{-}CF_3C_6H_4MgBr$ and $CuBr\cdot S(CH_3)_2$ under the conditions optimized for the [60]fullerene reaction [eqn. (2)].[3] A pre-cooled toluene solution of [70]fullerene at −78 °C was transferred through a cannula to a magnetically stirred mixture of the organocopper reagent (16 equiv.) in THF at −78 °C. The resulting black slurry was warmed to 25 °C. The reaction was monitored with HPLC, which indicated complete consumption of [70]fullerene after 24 hours, and wasstopped by addition of aq. NH_4Cl. After purification of the organic products with preparative HPLC, the tri-adduct $C_{70}(4\text{-}CF_3C_6H_4)_3H$ (**1a**) and the mono-adduct $C_{70}(4\text{-}CF_3C_6H_4)H$ (**6a**) were isolated in 43% yield and 47% yield, respectively. None of the expected penta-adducts **4** and **5** were detected in the mixture. Unlike [70]fullerene itself, the tri-addition product readily dissolves in toluene, carbon disulfide, and chloroform.



Initial optimization was carried out for the copper reagent (16 equiv.) derived from $4\text{-}CF_3C_6H_4MgBr$ and $CuBr\cdot(CH_3)_2$. When $1,2\text{-}Cl_2C_6H_4$ was used instead of toluene, the reaction was faster but low-yielding (7–32%) to produce numerous side products as detected by HPLC. However, by lowering the reaction temperature from 25 °C to 10 °C, the desired product **1a** was obtained in 94% isolated yield without being accompanied by the mono-adduct **6a**. Thus, a $1,2\text{-}Cl_2C_6H_4$ solution of [70]fullerene was added to an aryl copper reagent (16 equiv.) and the reaction mixture was stirred for an hour at −78 °C then for 10 hours at 10 °C (Method A). After aqueous work-up, the desired product was extractedwith toluene and purified by precipitation.

For yet unknown reasons, some organocopper reagents afforded the tri-adduct in better yield (*e.g.*, less side products) if the fullerene and the copper reagent were mixed at room temperature rather than at –78 °C, and the reaction mixture was let stand further at that temperature (Method B). Because of a competing thermal homocoupling reaction of the copper reagent, further excess of the copper reagent (20–30 equiv.) is needed. As in the reaction of [60]fullerene,[5] the reaction of the methyl copper reagent necessitates the use of 1,3-dimethyl-2-imidazolidinone in order to obtain a maximum product yield (90% yield).

Table 1 summarizes the results of the tri-addition of various Grignard reagents to [70]fullerene in the presence of $CuBr\cdot S(CH_3)_2$. Method A was applied for the cases of R = $4\text{-}CF_3C_6H_4$, C_6H_5, $4\text{-}ClC_6H_4$ and 1-naphthyl (entries 1–4). The products were obtained in 93–95% isolated yield. When applicable, Method B afforded the product of better purity because of less side products derived from the fullerene (entries 5–7). For instance, the biphenyl adduct was obtained in 99% yield. Tri-addition of CH_3MgBr afforded, in 90% yield, $C_{70}(CH_3)_3H$, which is much less sterically hindered than $C_{70}Ar_3H$ and will serve as a useful ligand for transition metal organometallics.

The structural identification of the unexpected tri-adduct initially rested on spectroscopic analyses. The mass spectrum of the tri-adduct **1a** exhibits a parent peak at *m*/*z* = 1276 (FAB-MS, M^+) that corresponds to the molecular formula $C_{70}(4\text{-}CF_3C_6H_4)_3H$. In the ^1H NMR analysis, six doublet peaks in the aromatic proton region appeared (δ = 7.92, 7.84, 7.71, 7.66, 7.58–7.52: two doublets overlap on each other and

Table 1 Three-fold organocopper addition to [70]fullerene with a variety of Grignard reagents

Entry	R	Method	Yield[a]
1	$4\text{-}CF_3C_6H_4$	A	94% (**1a**)
2	C_6H_5	A	93% (**1b**)
3	$4\text{-}ClC_6H_4$	A	94% (**1c**)
4	1-naphthyl	A	95% (**1d**)
5	C_6H_5	B	95% (**1b**)
6	$4\text{-}(C_6H_5)C_6H_4$	B	99% (**1e**)
7[b]	CH_3	B	90% (**1f**)

[a] The present yields were calculated on the basis of the purity of the product and that of the starting [70]fullerene. [b] 1,3-Dimethyl-2-imidazolidinone was used as additive.

integrated twice as much.) indicating the existence of three non-equivalent aryl groups. The proton directly attached to the fullerene core appears at δ = 4.40 ppm as a singlet. The ^{13}C NMR and 2D HMBC NMR spectra of **1a** are also consistent with the assigned C_1 structure.

Deprotonation of **1a** with $KOC(CH_3)_3$ afforded a potassium complex $K[C_{70}(4\text{-}CF_3C_6H_4)_3]$ (**2a**). The singlet peak at δ = 4.40 ppm disappeared. The ^{13}C NMR and ^{1}H NMR spectra became dramatically simplified, indicating much higher symmetry of the potassium compound. The structure of **1a** was unequivocally determined by X-ray crystallographic analysis of the corresponding thallium complex $Tl[C_{70}(4\text{-}CF_3C_6H_4)_3]$ (**3a**) as described later.

Once the structure of **1a** was solved, the structure of the mono-adduct **6** followed, since **1a** and **6** can be chemically correlated. When the isolated $C_{70}(4\text{-}CF_3C_6H_4)H$ (**6a**) was treated again with the copper reagent, it was further converted to the tri-adduct **1a** whose structure was known from the crystal structure of the corresponding thallium complex **3a** (*vide infra*).

The tri-adduct **1a** was converted to the thallium complex $Tl[C_{70}(4\text{-}CF_3C_6H_4)_3]$ (**3a**) and recrystallized from 1,2-$Cl_2C_6H_4$–hexane to obtain crystals suitable for X-ray crystallographic analysis. While the data from a sample used in the preliminary report[8] did not successfully converge, we recently were able to obtain reasonable data for a deep red single crystal of **3a**·(1,2-$Cl_2C_6H_4)_2$. The crystal structure of **3a** with a space group $P2_1/n$ 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 (Fig. 1). This structure was fully consistent with the result of *ab initio* study described below. One aryl ring of the three $4\text{-}CF_3C_6H_4$ groups is oriented perpendicular to another aryl ring. In the light of the short distance of C(*ortho*)–H···C(*ipso*) [2.77 Å], these two aryl group may have weak C–H···π interaction with each other. The third aryl ring is free from intramolecular interactions. The lengths of the five thallium–carbon bonds are nearly equal to each other [2.88–2.93 Å, av. 2.91 Å] and the complex is judged to be an η^5-bonded Tl complex. These bond lengths are comparable with those of $Tl[\eta^5\text{-}C_{60}(C_6H_5)_5]$ [2.83–2.90 Å, av. 2.87 Å] that we previously reported.[3]The structural data therefore indicate that the [70]fullerene tri-adduct is a member of new indenyl-type ligand incorporated into a graphitic structure.

Theoretical study was performed on model compounds $K(C_{70}H_3)$ and $Li(C_{70}H_3)$.[11] The optimized structures were analyzed in some detail, since the X-ray analyses are not good enough to discuss the C–C bond lengths. Molecular orbitals of the optimized structure were also examined.

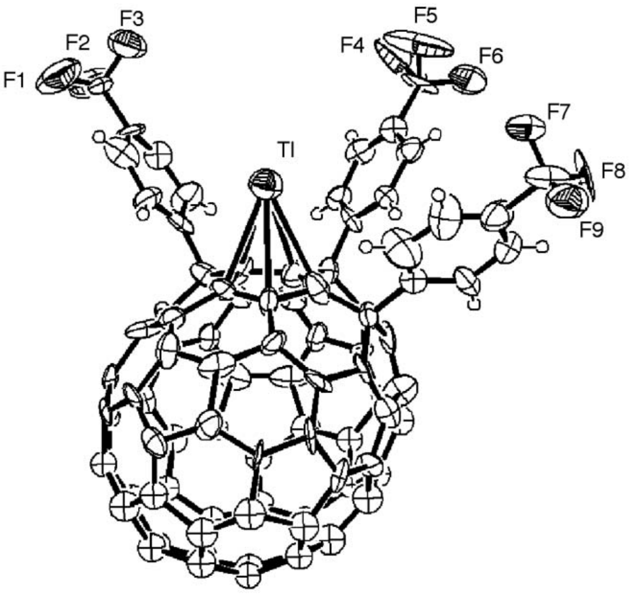


Fig. 1 Molecular structure of **3a**·(1,2-$Cl_2C_6H_4)_2$. Solvent molecules are omitted for clarity.

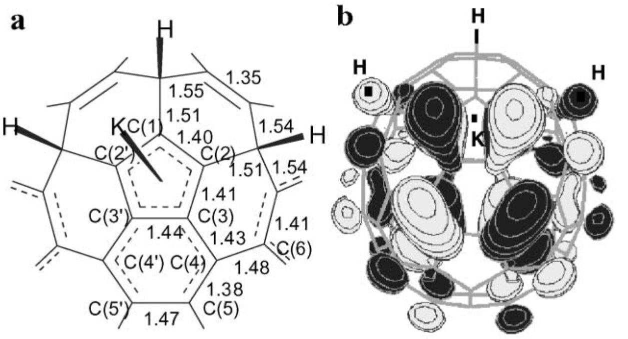


Fig. 2 (a) A part of the optimized structure of $K(C_{70}H_3)$ at the HF/3-21G(*) level. Bond lengths are in Å. K–C bond lengths: K–C(1), 3.06; K–C(2), 2.99; K–C(3), 2.92. (b) HOMO surface of $K(C_{70}H_3)$.

As the potassium complex **2** did not give X-ray quality crystals, we examined the structure of the model compound $K(C_{70}H_3)$ as optimized at the HF/3-21G(*) level[12] under C_s symmetry (total energy = −3233.615841 hartree,[8] Fig. 2). The potassium atom is bonded to the [70]fullerene sphere in an η^5 coordination mode. The η^5-moiety of the complex shows relatively long C–C bond length of the [5,6] junction [C(3)–C(3′); 1.44 Å] and adjacent six-membered ring C–C bonds [C(3)–C(4) and C(3′)–C(4′); 1.43 Å], which are the features commonly observed for metal indenyl complexes (*videinfra*). The molecular orbitals of the complex are essentially a hybrid of an indenyl anion and [70]fullerene. As shown in Fig. 2b, the HOMO (A″, −6.66 eV) of $K(C_{70}H_3)$ is localized mainly at the indenyl moiety but extends also over the whole fullerene cage.

The structure of the model compound $Li(C_{70}H_3)$ was also optimized at the HF/3-21G(*) level under C_s symmetry (total energy = −2644.860708 hartree,[8] Fig. 3). The lithium atom is bonded to the [70]fullerene sphere in an η^5 coordination mode. The indenyl moiety of $Li(C_{70}H_3)$ shows striking resemblance to the X-ray crystal structure of Li(η^5-indenyl)(temda).[13]

In view of the very nature of the reaction, the mechanism likely involves a radical species or a radical-like species (*e.g.*, organocopper(II) species). In the light of the mechanistic correlation between the mono- and tri-adduct described above, and the parallel studies carried out on the formation of $C_{60}R_5H$ from C_{60},[10] we can draw a possible reaction pathway from [70]fullerene to $C_{70}R_3H$ under assumption of an organometallic mechanism (Scheme 2). The initial addition of an anionic R group in a putative diorganocuprate species takes place at the most strained sp^2 carbon center indicated as A, which generates a 1,2-adduct **7**. The 1,2-adduct **7** may equilibrate to **8** *via*1,3-metal shift. Removal of one electron from the copper atom in **8** (possibly by a Cu(I) specied, fullerene or a fullerene

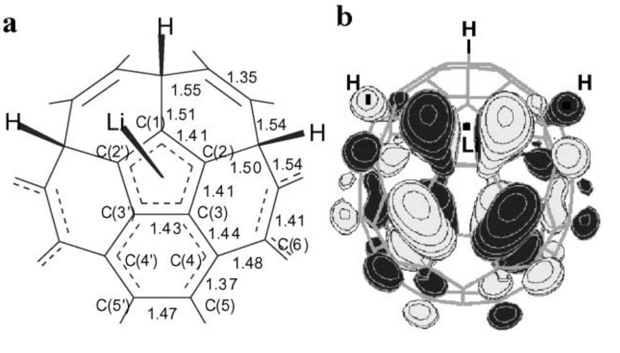
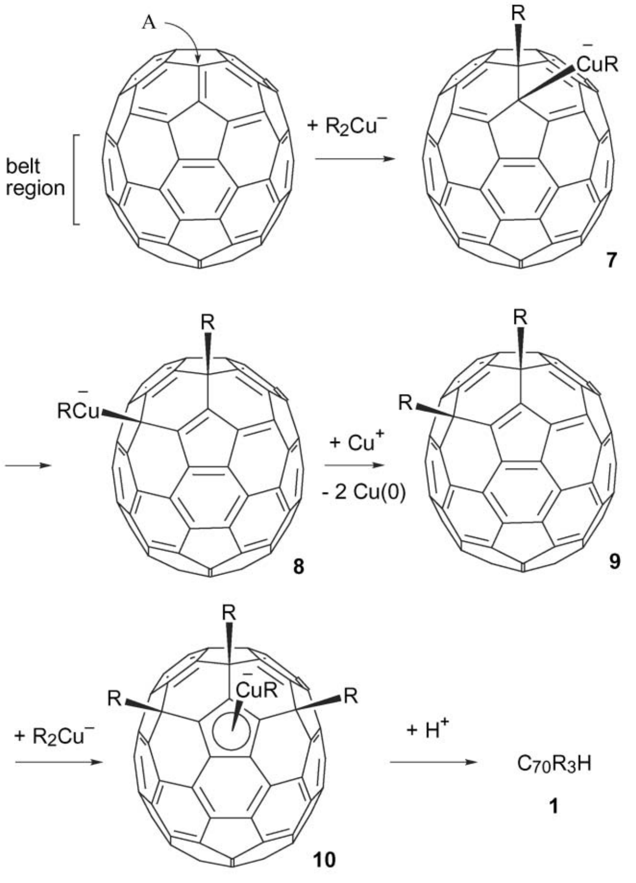


Fig. 3 (a) A part of the optimized structure of $Li(C_{70}H_3)$ at the HF/3-21G(*) level. Bond lengths are in Å. Li–C bond lengths (Å): Li–C(1), 2.24; Li–C(2), 2.20; Li–C(3), 2.18. (b) HOMO surface of $Li(C_{70}H_3)$.



Scheme 2

derivative) generates a transient Cu(II) species, which decomposes to give **9** and Cu(0). Experimentally, the formation of metallic copper (sometimes as copper mirror) was observed. The addition of the third R anion generates a stable cyclopentadienide **10**, which gives **1** upon protonation. The cyclopentadienide anion in **10** is located at the flat, strain-free belt region of [70]fullerene, and hence is stable so that further decomposition does not take place. In the case of [60]fullerene, the equivalent cyclopentadienide copper complex is still strained and undergoesfurther reactions. Though this organometallic mechanism appears to be reasonable, involvement of an organic radical species cannot be discounted at this time.

In summary, we have discovered that various Grignard reagents undergo completely regioselective tri-addition to [70]fullerene in the presence of $CuBr{\cdot}S(CH_3)_2$ under mild reaction conditions. The experimental procedure is simple and requires only the skill of undergraduate organic experiments. Most importantly, the product yields are excellent and often quantitative, which is unique among the methods known for covalent functionalization of carbon clusters. Together with the results of penta-addition to [60]fullerene, the present results suggest that the multi-addition of organocopper reagents will be applicable to higher fullerenes and possibly also to carbon nanotubes. The structural and theoretical data indicate that the cyclopentadienyl anion of the [70]fullerene tri-adduct involves 68π-electrons and represents a member of new indenyl-type ligand incorporated into a graphitic structure.

Experimental

General

All reactions were performed in an oven-dried reaction vessel under argon or nitrogen using standard Schlenk technique or in a glove box. The reactions were monitored with HPLC (column: Buckyprep, 4.6 × 250 mm, Nacalai tesque; flow rate: 1.0 to 3.0 ml min^{-1}; eluent: toluene/2-propanol = 7 : 3; detector: SPD-M10Avp, Shimadzu). Purity of products was determined by integrated area ratios at 350 nm absorption on HPLC analysis. The present yields were calculated on the basis of this purity and the purity of the starting [70]fullerene. Common organic solvents as well as aqueous solutions were deoxygenated by freeze-thaw cycles (over three times) or by bubbling nitrogen (over 30 min).

All ^1H NMR spectra were taken at 400 MHz (JEOL EX-400) or 500 MHz (JEOL α-500), and ^{13}C NMR spectra at 100 MHz (JEOL EX-400) or 125 MHz (JEOL α-500). Spectra are reported in parts per million from internal tetramethylsilane or the residual proton of the deuterated solvent. Mass spectra were measured with Shimadzu LCMS-QP8000 (APCI mode) equipped with Buckyprep column or JEOL JMS SX102 (FAB mode). Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene/2-propanol = 7 : 3 as eluent (flow rate 12 to 20 ml min^{-1}, detected at 350 nm with a UV spectrophotometric detector, Shimadzu SPD-6A).

Solvents

Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical Co., Inc. (free from stabilizer). Toluene and 1,2-$Cl_2C_6H_4$ were distilled under reduced pressure from CaH_2 and dried over molecular sieves 4A. The water content of the solvent was determined with a Karl-Fisher Moisture Titrator (MK-210, Kyoto Electronics Company) to be less than 20 ppm.

Materials

All commercially available reagents unless noted below were distilled or recrystallized before use. $KOC(CH_3)_3$ in THF and $TlOC_2H_5$ were purchased from Aldrich Inc. and used as received. [70]Fullerene (98% purity) was received from Hoechst Japan and used as received. $CuBr{\cdot}S(CH_3)_2$ was freshly prepared from CuBr (washed with methanol prior to use) and $(CH_3)_2S$ and reprecipitated twice from $(CH_3)_2S$ and pentane.[14]

Synthesis and characterization of 2,5,10-tris(4-trifluoromethylphenyl)-2,5,6,10-tetrahydro[70]fullerene (1a) and 2-(4-trifluoromethylphenyl)-1,2-dihydro[70]fullerene (6a)

$4\text{-}CF_3C_6H_4MgBr$ was freshly prepared by addition of a THF solution (6.00 ml) of $4\text{-}CF_3C_6H_4Br$ (1.13 g, 5.00 mmol) to Mg turnings (130 mg, 5.30 mmol). A solution of 65.0 mg (77 μmol) of C_{70} in 50.0 ml of toluene was cooled to −78 °C and transferred through a cannula over 15 minutes to a magnetically stirred solution of an organocopper reagent prepared from $4\text{-}CF_3C_6H_4MgBr$ (1.87 ml) and $CuBr{\cdot}S(CH_3)_2$ (274 mg, 1.33 mmol) at −78 °C. The resulting dark green suspension was gradually warmed to −20 °C over 3 hours. The mixture was then allowed to warm to 25 °C. While stirring was continued at this temperature, the reaction was monitored by HPLC. After stirring for 3 hour at this temperature, the color of the solid became dark brown, and the color of the supernatantbecame dark brown-red. The reaction completed in 1 day and was quenched with saturated NH_4Cl solution. The mixture was separated into two phases, and the aqueous phase was extracted with toluene three times. The combined organic extracts were washed with brine, dried by passing through a pad of Na_2SO_4, and evaporated. The residual powder was washed with hexane four times to obtain the dark-brown solid. Further purification was achieved by HPLC to give $C_{70}(4\text{-}CF_3C_6H_4)_3H$ (**1a**, 40.2 mg, 31.5 μmol, 43%) and $C_{70}(4\text{-}CF_3C_6H_4)H$ (**6a**, 33.6 mg, 34.1 μmol, 47%). **1a**: ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.92 (d, J = 6.50 Hz, 2H), 7.84 (d, J = 6.50 Hz, 2H), 7.71(d, J = 6.50 Hz, 2H), 7.66 (d, J = 6.50 Hz, 2H), 7.58–7.52 (m, 4H), 4.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 159.26, 155.03, 154.07, 153.45, 152.19, 152.10, 151.94, 150.26, 149.91, 149.66, 149.16, 148.98, 148.77, 148.59, 148.36, 148.29, 148.25, 147.96, 147.88, 147.86, 147.81, 147.73, 147.54, 147.27, 147.04, 147.02, 146.69, 146.66, 146.49, 146.20, 145.90, 145.75, 145.44, 145.38, 144.98, 144.94, 144.91, 144.89, 144.73, 144.71, 144.53, 144.12, 143.74, 143.40, 143.24, 143.06, 142.57, 142.43, 142.35, 141.94, 140.43, 140.07, 139.44, 137.19, 133.05, 132.85, 131.86, 131.83, 131.66, 131.53, 130.61, 127.58, 127.31, 127.22, 126.86, 126.20, 126.08–126.00 (m), 125.84 (q, $J_{C\text{–}F}$ = 3.70 Hz), 59.54, 55.87, 55.72, 55.17 (Six quartetsignals corresponding to CF_3 and CF_3–C carbons were not detected because of their low intensities.); FAB-MS *m*/*z* 1276 (M^+). **6a**: ^{1}H NMR (400 MHz, $CDCl_3$–CS_2) δ 8.23 (d, *J* = 8.19 Hz, 2H), 7.91 (d, *J* = 8.19 Hz, 2H), 4.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$–CS_2) δ 156.86, 154.36, 151.67, 150.92, 150.47, 150.38, 149.76, 149.38, 149.21, 148.60, 148.53, 146.97, 146.89, 146.76, 146.65, 146.47, 146.03, 145.69, 143.40, 142.93, 142.81, 142.65, 142.44, 140.42, 140.04, 137.52, 133.63, 131.16, 130.94, 130.75, 130.19, 130.14, 127.37, 126.52 (q, $J_{C\text{–}F}$ = 4.15 Hz), 59.40, 56.00, two quartet signals corresponding to CF_3 andCF_3–C carbons were not detected because of their low intensities.

Optimized procedures of the three-fold organocopper addition to [70]fullerene

Method A. *2,5,10-Tris(4-trifluoromethylphenyl)-2,5,6,10-tetrahydro[70]fullerene (**1a**).* 4-$CF_3C_6H_4MgBr$ was freshly prepared by addition of a THF solution (8.00 ml) of 4-$CF_3C_6H_4Br$ (0.930 ml, 1.90 mmol) to Mg turnings (173 mg). A solution of 100 mg (0.119 mmol) of C_{70} in 100 ml of 1,2-$Cl_2C_6H_4$ was cooled to −78 °C and cannulated over 15 minutes to a magnetically stirred solution of an organocopper reagent prepared from 4-$CF_3C_6H_4MgBr$ (2.68 ml) and $CuBr\cdot S(CH_3)_2$ (392 mg, 1.90 mmol) at −78 °C. The resulting dark green suspension was stirred at this temperature over an hour. The mixture was then allowed to warm to 10 °C.After an hour stirring at this temperature, the color of the solid became dark brown, and the color of the supernatant became dark brown-red. While stirring was continued at this temperature, progress of the reaction was monitored by HPLC. The reaction completed in 10 hours and was quenched with a saturated NH_4Cl solution. The mixture was separated into two phases, and the aqueous phase was extracted with toluene three times. The combined organic extracts were washed with brine, dried by passing through a pad of Na_2SO_4, and evaporated. The residual powder was washed with hexane four times to remove biaryl (91%, 158 mg) and dried *in vacuo* to obtain 140 mg (94% yield, 96% purity) of $C_{70}(4\text{-}CF_3C_6H_4)_3H$.

*2,5,10-Triphenyl-2,5,6,10-tetrahydro[70]fullerene (**1b**).* This compound was synthesized by Method A. Starting with 100 mg (119 µmol) of C_{70}, we obtained 127 mg (93% yield, 92% purity) of $C_{70}(C_6H_5)_3H$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2H), 7.74–7.70 (m, 2H), 7.61–7.57 (m, 3H), 7.39–7.23 (m, 8H), 4.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$–CS_2) δ 160.70, 155.67, 155.07, 153.80, 152.62, 153.14, 152.62, 152.19, 150.16, 149.87, 149.57, 149.42, 149.39, 149.17, 149.08, 148.95, 148.82, 148.68, 148.59, 148.30, 148.21, 148.09, 147.92, 147.88, 147.77, 147.68, 147.18, 147.06, 147.00, 146.65, 146.61, 146.44, 146.23, 146.18, 145.84, 145.64,145.51, 145.32, 145.06, 145.03, 144.92, 144.88, 144.74, 144.48, 144.15, 143.97, 143.43, 142.99, 142.81, 142.21, 142.18, 140.50, 140.40, 139.54, 139.20, 138.33, 136.87, 133.08, 131.96, 131.93, 131.82, 131.72, 131.59, 131.43, 131.41, 130.65, 128.96, 128.88, 128.78, 128.16, 128.04, 127.71, 127.60, 127.47, 127.27, 127.15, 126.70, 126.42, 56.23, 56.19, 55.5; APCI-MS *m*/*z* 1072 [(M − H)$^-$].

*2,5,10-Tris(4-chlorophenyl)-2,5,6,10-tetrahydro[70]fullerene (**1c**).* This compound was synthesized by Method A. Starting with 50 mg (60 µmol) of C_{70}, we obtained 67 mg (94% yield, 98% purity) of $C_{70}(4\text{-}ClC_6H_4)_3H$. ^{1}H NMR (500 MHz, $CDCl_3$–CS_2) δ 7.73 (d, *J* = 6.50 Hz, 2H), 7.63 (d, *J* = 6.50 Hz, 2H), 7.50 (d, *J* = 6.50 Hz, 2H), 7.38 (d, *J* = 6.00 Hz, 2H), 7.27–7.21 (m, 4H), 4.34 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$–CS_2) δ 160.22, 155.60, 154.74, 153.97, 152.73, 152.59, 152.52, 150.53, 150.22, 149.96, 149.50, 149.47, 149.34, 149.12, 148.94, 148.90, 148.63,148.57, 148.34, 148.21, 148.13, 148.11, 148.04, 147.96, 147.55, 147.36, 147.01, 146.97, 146.79, 146.53, 146.21, 146.19, 145.76, 145.73, 145.67, 145.31, 145.22, 145.12, 145.05, 144.85, 144.38, 144.27, 143.98, 143.66, 143.27, 143.01, 124.65, 124.61, 140.81, 140.05, 139.81, 140.00, 137.38, 136.92, 134.74, 134.60, 134.19, 133.40, 133.25, 132.22, 132.02, 131.88, 130.85, 130.55, 129.57, 129.53, 129.3, 128.96, 128.68, 128.25, 127.68, 127.60, 126.63, 59.60, 55.93, 55.81, 55.67; Anal. calcd for $C_{88}H_{13}Cl_3$: C 89.85; H 1.11%. Found: C 89.55; H 1.02%.

*2,5,10-Tris(1-naphthyl)-2,5,6,10-tetrahydro[70]fullerene (**1d**).* This compound was synthesized by Method A (Reaction time: 10 °C for 16 hours, then 15 °C for 10 hours). Starting with 50 mg (60 µmol) of C_{70}, we obtained 69 mg (95% yield, 97% purity) of C_{70}(1-naphthyl)$_3$H. ^{1}H NMR (500 MHz, $CDCl_3$/CS_2) δ 9.65 (d, *J* = 8.54 Hz, 1H), 9.54 (d, *J* = 9.77 Hz, 1H), 8.92 (d, *J* = 8.85 Hz, 1H), 8.26 (d, *J* = 7.02Hz, 1H), 8.09 (d, *J* = 7.63 Hz, 1H), 7.89–7.45 (m, 5H), 7.40 (m, 1H), 7.36 (m, 1H), 7.30–7.23 (m, 7H), 6.96 (m, 1H), 6.86 (m, 1H) 4.90 (s,1H); ^{13}C NMR (125 MHz, $CDCl_3$/CS_2) δ 161.34, 158.16, 157.43, 155.83, 154.51, 153.22, 152.61, 150.79, 150.26, 150.20, 150.13, 149.95, 149.60, 149.26, 149.19, 149.16, 148.55, 148.39, 148.35, 148.28, 147.94, 147.86, 147.60, 147.49, 147.26, 147.18, 147.02, 146.96, 146.86, 146.71, 146.65, 146.28, 146.09, 145.90, 145.73, 145.36, 145.31, 145.17, 145.10, 144.93, 144.81, 144.52, 144.20, 143.59, 143.45, 142.93, 142.01, 141.86, 141.26, 141.09, 139.86, 139.54, 136.71, 135.40, 134.93, 134.81, 134.75, 133.63, 133.58, 132.56, 132.47, 132.19, 131.98, 131.58, 130.84, 129.83, 129.70, 129.54, 129.48, 129.42, 129.21, 128.94, 128.43, 128.30, 128.15, 127.03, 126.56, 126.36, 126.33, 126.19, 125.76, 125.73, 125.47, 125.40, 125.19, 125.00, 124.85, 124.61, 121.48, 61.24, 57.58, 57.31, 54.22; APCI-MS *m*/*z* 1221 [(M − H)$^-$].

Method B. *2,5,10-Triphenyl-2,5,6,10-tetrahydro[70]fullerene (**1b**).* To a suspension of $CuBr\cdot S(CH_3)_2$ (374 mg, 1.82 mmol, 30 equiv.) in THF (23.0 ml) was added a THF solution of C_6H_5MgBr (0.98M, 1.86 ml, 1.82 mmol, 30 equiv.) at 28 °C and stirring was continued for 20 minutes at this temperature. To the resulting yellow suspension was added a degassed solution of C_{70} (49.6 mg, 59.0 µmol) in 1,2-$Cl_2C_6H_4$ (25.0 ml) and stirring was continued for 24 hours at 28 °C. The reaction mixture was quenched with a 5% HCl aqueous solution. The crude mixture was washed with water and brine continuously, dried over anhydrous $MgSO_4$, filtered, evaporated to a small volume and precipitated by adding CH_3OH.The precipitated dark brown solid was washed thoroughly with CH_3OH, ether and water, then dried under reduced pressure to obtain $C_{70}(C_6H_5)_3H$ (61.2 mg, 95% yield, 96% purity).

*2,5,10-Tris(biphenyl-4-yl)-2,5,6,10-tetrahydro[70]fullerene (**1e**).* To a suspension of $CuBr\cdot S(CH_3)_2$ (374 mg, 1.82 mmol, 30 equiv.) in THF (23.0 ml) was added a THF solution of 4-$(C_6H_5)C_6H_4MgBr$ (1.04M, 1.72 ml, 1.82 mmol, 30 equiv.) at 24 °C and stirring was continued for 20 min at this temperature. To the resulting yellow suspension was added a degassed solution of C_{70} (50.2mg, 59.7 µmol) in 1,2-$Cl_2C_6H_4$ (25.0 ml) and this was stirred for 14 hours at 24 °C. The reaction mixture was quenched with a 15% HCl aqueous solution. The crude mixture was dried over anhydrous $MgSO_4$, filtered through a pad of SiO_2, evaporated to a small volume and precipitated by adding CH_3OH.The dark brown solid was washed thoroughly with CH_3OH, ether and water, then dried under reduced pressure to obtain $C_{70}[4\text{-}(C_6H_5)C_6H_4]_3H$ (76.7 mg, 99% yield, 98% purity). ^{1}H NMR (CS_2, 400 MHz) δ 8.21 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.98

(d, J = 8.0 Hz, 2H), 7.51–7.95 (m, 21H), 4.82 (s, 1H); ^{13}C NMR spectra could not be obtained because of low solubility in common organic solvents; APCI-MS m/z 1299 [(M − H)$^-$].

2,5,10-Trimethyl-2,5,6,10-tetrahydro[70]fullerene (***1f***). To a suspension of CuBr·S(CH$_3$)$_2$ (245 mg, 1.19 mmol, 20 equiv.) and 1,3-dimethyl-2-imidazolidinone (128 µl, 1.19 mmol, 20 equiv.) in THF (24.0 ml) was added a THF solution of MeMgBr (1.0 M, 1.19 ml, 1.19 mmol, 20 equiv.) at 28 °C and stirring was continued for 15 minutes at this temperature. To the resulting yellow suspension was added a degassed solution of C$_{70}$ (49.8 mg, 59.2 µmol) in 1,2-Cl$_2$C$_6$H$_4$ (25.0 ml) and this was stirred for 24 hours at 28 °C. The reaction mixture was quenched with a 10% HCl aqueous solution. The crude mixture was washed with water and brine, dried over anhydrous MgSO$_4$, filtered, evaporated to a small volume and precipitated by adding CH$_3$OH.The precipitated dark brown solid was washed thoroughly with CH$_3$OH, ether and hexane, then dried under reduced pressure to obtain C$_{70}$(CH$_3$)$_3$H (51.0 mg, 90% yield, 91% purity). ^{1}H NMR (400 MHz, CDCl$_3$–CS$_2$) δ 3.90 (s, 1H), 2.52, (s, 3H), 2.27 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (CS$_2$, 100 MHz) δ 33.91, 29.12, 26.12 (Other signals are too weak to be identified.); FAB-MS m/z 887 (M$^+$).

Preparation of K and Tl complexes. *K[η^5-C$_{70}$(4-CF$_3$C$_6$H$_4$)$_3$]* (***2a***). To a 0.50 ml KOC(CH$_3$)$_3$ solution (18 mM, 9.0 µmol) in THF-d_8 was added C$_{70}$(4-CF$_3$C$_6$H$_4$)$_3$H (11 mg, 9.0 µmol) at 25 °C. The resulting dark red solution was used for ^{1}H and ^{13}C NMR measurements. ^{1}H NMR (400 MHz, THF-d_8) δ 8.07–8,05 (m, 6 H), 7.57–7.54 (m, 6H); ^{13}C NMR (100 MHz, THF-d_8) δ 166.18, 160.50, 153.30, 151.99, 151.04, 150.32, 149.79, 149.77, 149.17, 148.88, 148.82, 148.48, 148.44, 148.26, 147.14, 146.90, 146.81, 146.37, 146.19,146.07, 145.72, 145.61, 145.43, 144.71, 142.53, 142.28, 137.87, 136.81, 134.54, 134.46, 133.24, 132.92, 132.60, 129.36–129.23 (m), 128.93, 125.80–125.77 (m), 125.6 (q, J = 271.19 Hz), 121.07, 61.06, 59.11.

K[η^5-C$_{70}$(C$_6$H$_5$)$_3$] (***2b***). ^{1}H NMR (400 MHz, THF-d_8) δ 7.88–7.82 (m, 5H), 7.24–7.08 (m, 10H). ^{13}C NMR spectra could not be obtained because of low solubility in common organic solvents.

K[η^5-C$_{70}$(4-ClC$_6$H$_4$)$_3$] (***2c***). ^{1}H NMR (400 MHz, THF-d_8) δ 7.92–7.81 (m, 6 H), 7.27–7.24 (m, 6H); ^{13}C NMR (100 MHz, THF-d_8) δ 166.82, 160.75, 153.48, 152.11, 151.19, 149.90, 149.80, 149.29, 148.90, 148.86, 148.64, 148.47, 147.32, 147.02, 146.95, 146.82, 146.77, 146.42, 146.28, 146.18, 145.79, 145.60, 145.58, 145.26, 144.65, 142.84, 142.52, 142.48, 138.07, 136.78, 134.93, 134.50, 133.35, 133.02, 132.97, 132.76, 132.65, 130.41, 130.09, 129.50, 128.98, 121.44, 60.09, 58.79.

K(η^5-C$_{70}$(CH$_3$)$_3$) (***2f***). ^{1}H NMR (400 MHz, THF-d_8) δ 2.86, (s, 3H), 1.97, (s, 6H); ^{13}C NMR (100 MHz, THF-d_8) δ 168.84, 162.04, 153.62, 151.90, 151.20, 149.77, 149.09, 148.75, 148.63, 148.34, 148.29, 147.46, 147.28, 146.49, 146.36, 146.26, 146.17, 145.98, 145.84, 145.70, 145.47, 145.32, 143.80, 142.36, 142.27, 138.54, 135.84, 135.02, 133.86, 133.35, 133.09, 132.32, 130.17, 124.27, 52.96, 52.67, 33.07, 31.77.

Tl[η^5-C$_{70}$(4-CF$_3$C$_6$H$_4$)$_3$] (***3a***). To a THF solution (10 ml) of C$_{70}$(4-CF$_3$C$_6$H$_4$)$_3$H (46 mg, 35 µmol) was added 10 µL solution of TlOC$_2$H$_5$ (25 µL, 0.35 mmol) in THF (75 µL) *via* syringe at 25 °C without stirring under protection from light. After 2 hours, the resulting dark red suspension was freed of the solvent *in vacuo* at 25 °C to give the Tl complex quantitatively. Recrystallization by solvent diffusion technique with 1,2-Cl$_2$C$_6$H$_4$–hexane under darkness gave dark red crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, THF-d_8) δ 8.09–8.07 (m, 6H),7.59–7.53 (m, 6H); ^{13}C NMR spectra could not be obtained because of low solubility in common organic solvents.

Table 2 Crystal data and data collection parameters of **3a**

Complex	**3a**·(1,2-Cl$_2$C$_6$H$_4$)$_2$
Formula	C$_{103}$H$_{20}$Cl$_4$F$_9$Tl
Formula weight	1774.47
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a, Å	18.419(5)
b, Å	17.565(5)
c, Å	20.638(5)
α, deg	90
β, deg	109.861(5)
γ, deg	90
V, Å^3	6280(3)
Z	4
D_{calcd}, g cm^{-3}	1.877
F(000)	3472
T, K	293(2)
Crystal size, mm	0.32 × 0.22 × 0.10
$2\theta_{\text{min}}$, $2\theta_{\text{max}}$, deg.	5.0, 51.8
No. of refl. measured (Total)	5791
No. of refl. measured ($I > 2.0\sigma(I)$)	2323
No. of variables	785
$R1$, $wR2$ (all data)	0.223, 0.319
R, Rw ($I > 2.0\sigma(I)$)	0.097, 0.240
GOF on F^2	1.01
Δ, eÅ^{-3}	1.32, −0.63

Crystallographic data collections and structure determination of ***3a***. A crystal of **3a** suitable for the X-ray diffraction study was mounted on a MacScience DIP2030 Imaging Plate diffractometer for data collection using MoKα (graphite monochromated, λ = 0.71069) radiation. Crystal data [CCDC 180836. See http://www.rsc.org/suppdata/jm/b2/b202130g/ for crystallographic data in .cif format.] and data statistics are summarized in Table 2. The camera distance was 120 mm. All data was corrected for Lorentz and polarization effects. The structure of the complex **3a** was solved by the direct method (SHELXS-97)[15] and expanded using Fourier techniques (DIRDIF-94).[16]The non-hydrogen atoms except for several carbon atoms of **3a** were refined anisotropically by the full-matrix least squares method. Hydrogen atoms were placed at calculated positions (C–H = 0.95 Å) and kept fixed. Measured non-equivalent reflections were used for the structure determination. In the subsequent refinement, the function $\sum\omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma(\omega F_o^4)]^{1/2}$.The quality of the crystals of **3a** was not good presumably due to the presence of solvent molecule.

Acknowledgement

This work was supported by Grant-in-Aid for Scientific Research (Specially Promoted Research) from the Ministry of Education, Science, Culture and Sports. Generous allotment of computational time from the Institute for Molecular Science, Okazaki, Japan, and the Intelligent Modeling Laboratory, The University of Tokyo, is gratefully acknowledged. M. T. thanks JSPS for a predoctral fellowship.

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