Synthesis of Pentamethyl-monohydro[60]fullerene $C_{60}Me_5H$ and Its Use as Cyclopentadienyl-Type Ligand Precursor

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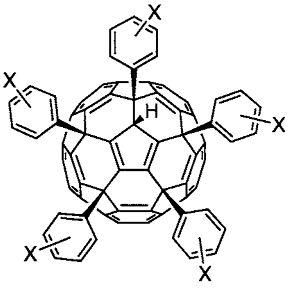
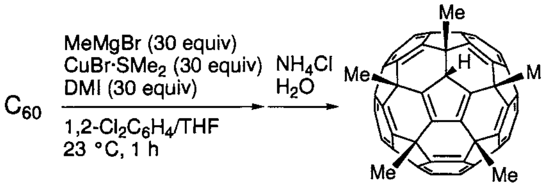
Pentamethyl-monohydro[60]fullerene $C_{60}Me_5H$ has been synthesized through five-fold addition of methylcopper reagent to C_{60}. The anion $C_{60}Me_5^-$ generated by deprotonation of $C_{60}Me_5H$ forms organometallic complexes with K^+ and Tl^+ ions with stronger metal-carbon interaction than that in the corresponding pentaphenylated ligand $C_{60}Ph_5^-$.

We previously reported the synthesis of a series of 1,4,11,15,30-pentaaryl-2-hydro[60]fullerenes ($C_{60}Ar_5H$, **1**) through quantitative five-fold addition of an organocopper reagent ($ArMgBr/CuBr{\cdot}SMe_2$ (1:1)) to C_{60}.[1,2] The fullerene derivatives **1** possess a cyclopentadiene (CpH) moiety embedded in the C_{60} cage; namely, each carbon atom of the cyclopentadiene moiety is connected with an sp^3 carbon atom that in turn is bound to the remaining fullerene core and the aryl substituent originated from the organocopper reagent. The cyclopentadiene $C_{60}Ph_5H$ (**1a**) can be deprotonated to generate the corresponding cyclopentadienyl anion $C_{60}Ph_5^-$, which forms a variety of η^5-organometallic complexes. The η^5-bonding has been proven by X-ray crystallographic analysis for one of these complexes, $Tl(\eta^5\text{-}C_{60}Ph_5){\cdot}2.5THF$. It was noted however that the five aryl groups in **1** exercise rather excessive steric (and likely electronic) effects both upon the metal complexation process and upon the complexes themselves. Obviously, this problem should be circumvented through introduction of a smaller substituent such as a methyl group. We report here the synthesis of a new cyclopentadiene-type fullerene ($C_{60}Me_5H$) that carries methyl groups instead of aryl groups, and that the anion of this new compound, $C_{60}Me_5^-$, serves as a better ligand for K^+ and Tl^+ ions than $C_{60}Ph_5^-$.



$C_{60}Ar_5H$ (**1**)
$C_{60}Ph_5H$ (**1a**, X = H)

Synthesis of the target molecule 1,4,11,15,30-pentamethyl-2-hydro[60]fullerene (**2**) could be achieved in a manner similar to that employed for **1**, while the slightly higher susceptability of the synthetic procedure to oxidation initially caused some difficulty in optimization of the conditions. Quantitative pentamethylation of C_{60} could be achieved by employing 1,3-dimethyl-2-imidazolidinone (DMI) as an additive. The pentamethylation of C_{60} (0.5 g) with 30 equiv each of MeMgBr, $CuBr{\cdot}SMe_2$ and DMI in 1,2-dichlorobenzene/THF at 23 °C completed within 1 h, and after aqueous work up **2** was obtained as an orange amorphous solid in 92% isolated yield [>95% purity by HPLC (350 nm) and ^1H NMR] (Scheme 1).[3] We used a larger amount (30 equiv) of the organocopper reagent in this experiment than in the synthesis of **1a** (15 equiv), because decomposition of the reagent to form ethane is faster than the biphenyl formation in the later. DMI appears to play a role of a stabilizer of the organocopper reagent. In the absence of DMI, the copper reagent was consumed rapidly before complete conversion of C_{60}, resulting in the recovery of a considerable amount of C_{60}. The cyclopentadiene **2** thus obtained was an air-stable solid. In an organic solvent, however, it is gradually converted to several oxidation products [$\tau_{1/2}$ (1 mM in toluene) = 2 h]. The ^1H NMR ($CDCl_3$, 23 °C) spectrum of **2** showed only four sharp singlets at 2.30 (Me x 2), 2.32 (Me x 2), 2.42 (Me) and 4.46 (Cp-H) ppm in a ratio of 6:6:3:1, indicating *Cs* symmetry of **2**.[3]

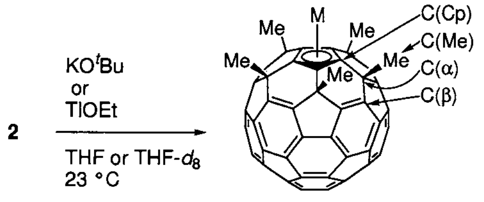


$C_{60}Me_5H$ (**2**)

Scheme 1.

As in the case of $C_{60}Ph_5H$, the cyclopentadiene $C_{60}Me_5H$ could be deprotonated readily with a metal alkoxide such as KO^tBu and TlOEt and converted to the corresponding cyclopentadienide $C_{60}Me_5M$ (**3**: M = K, **4**: M = Tl), where we found the difference in strength of ligand–metal interaction between $C_{60}Me_5$ and $C_{60}Ph_5$. Upon addition of 1.1 equiv of KO^tBu/THF at 23 °C, an orange suspension of **2** in THF-d_8 became a dark red solution. The ^1H and ^{13}C NMR spectra indicated complete conversion of **2** into C_{5v} symmetric $K(\eta^5\text{-}C_{60}Me_5)$ (**3**) (Scheme 2).[4] When excess 18-crown-6 was added to the solution in order to form "naked anion" $C_{60}Me_5^-$, downfield shift of the ^{13}C NMR signals was observed for the carbon atoms around the Cp moiety (Table 1, entry 1).[5] On the other hand, the addition of 18-crown-6 to a THF-d_8 solution of $C_{60}Ph_5H/KO^tBu$ caused much smaller change in the ^{13}C NMR spectrum (Table 1, entry 2). These observations suggest that ligand-metal interaction is stronger in $K(\eta^5\text{-}C_{60}Me_5)$ (**3**) than in $K(\eta^5\text{-}C_{60}Ph_5)$.

More significant difference between $C_{60}Me_5$ and $C_{60}Ph_5$ was observed for their Tl(I) complexes. Upon addition of TlOEt (1.1 eq), an orange suspension of **2** in THF-d_8 immediately became a dark red suspension. The ^1H NMR indicated



K(η^5-$C_{60}Me_5$) (**3**)
Tl(η^5-$C_{60}Me_5$) (**4**)

Scheme 2.

complete conversion of **2** into Tl(η^5-$C_{60}Me_5$) (**4**) (Scheme 2).[6] In sharp contrast to the case of Tl(η^5-$C_{60}Ph_5$), the ^{13}C NMR spectrum of **4** showed several Tl–C couplings [C(Cp), $^1J_{C\text{-}Tl}$ = 28.1 Hz; C(Me), $^3J_{C\text{-}Tl}$ = 3.3 Hz; C(α), $^2J_{C\text{-}Tl}$ = 10.0 Hz; C(β), $^3J_{C\text{-}Tl}$ = 4.1 Hz)].[7] The presence of the Tl–C coupling in **4** and not in Tl(η^5-$C_{60}Ph_5$) clearly indicates that the Tl-Cp bonding in **4** is stronger than the latter, and the Tl-Cp bonding in **4** possesses a considerable covalent character, although the ^{13}C NMR chemical shift change upon coordination to the Tl^+ ion is comparable between $C_{60}Me_5^-$ and $C_{60}Ph_5^-$ (Table 1, entries 2, 3).

Table 1. The ^{13}C NMR spectrum changes of $C_{60}R_5$ (R = Me, Ph) upon coordination to a metal fragment

		Δδ (ppm, $C_{60}R_5M$ – $C_{60}R_5^-$, THF-d_8)			
Entry	Complex	C(β)[a]	C(Cp)[a]	C(α)[a]	C(Me)[a]
1	$C_{60}Me_5K$ (**3**)	–1.28	–0.39	–0.30	–0.01
2	$C_{60}Ph_5K$	+0.23	+0.11	+0.01	N.A.[b]
3	$C_{60}Me_5Tl$ (**4**)	–5.19	+1.63	–1.63	+0.68
4	$C_{60}Ph_5Tl$	–4.51	+3.59	–1.12	N.A.[b]

[a] The notations are shown in the chemical structure of **3** and **4**. [b] Not applicable.

Notably, the nature of the metal ion attached to the Cp moiety causes significant effects on the ^{13}C NMR shift values of the C(β) carbon atoms, though these sp^2 carbon atoms are neither directly conjugated to the Cp moiety nor susceptible to through-space effects that will affect the NMR chemical shift (e.g., steric compression). Even more notable is that the effect of metal ion in the chemical shift is larger on the sp^2 C(β) than on the sp^3 C(α) which is directly attached to the Cp moiety. These observations provide a strong case for the endohedral homoconjugation in **4** (through-space π conjugation) that has previously shown for the $C_{60}Ph_5^-$ anion through *ab initio* molecular orbital calculations and electrochemical measurements.[1c]

In conclusion, pentamethyl-monohydro[60]fullerene $C_{60}Me_5H$ (**2**) has been synthesized from C_{60} in a single step and in a quantitative yield. In contrast to $C_{60}Ph_5H$ (**1a**) previously reported, the steric hindrance expected upon complexation with a metal cation is much reduced, and the $C_{60}Me_5^-$ ligand showed higher affinity to a metal ion such as K^+ and Tl^+ ions. Metalation of $C_{60}Me_5H$ (**2**) with other metal complexes and further transformations of the potassium (**3**) and thallium complexes (**4**) will be reported in a due course.

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References and Notes

1 a) M. Sawamura, H. Iikura, and E. Nakamura, *J. Am. Chem. Soc.*, **118**, 12850 (1996). b) M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, and E. Nakamura, *J. Organometal. Chem.*, in press. c) H. Iikura, S. Mori, M. Sawamura, and E. Nakamura, *J. Org. Chem.*, **62**, 7912 (1997). d) M. Sawamura, H. Iikura, A. Hirai, and E. Nakamura, *J. Am. Chem. Soc.*, **120**, 8285 (1998).

2 For an example of fivefold addition, see: Y. Murata, M. Shiro, and K. Komatsu, *J. Am. Chem. Soc.*, **119**, 8117 (1997).

3 Procedure for the preparation of $C_{60}Me_5H$ (**2**): A white suspension of CuBr·SMe_2 (4.28 g, 20.8 mmol) in 30 mL of THF was successively treated at 23 °C with a solution of MeMgBr (1.0 M, 20.8 mL, 20.8 mmol) in THF and with DMI (2.25 mL, 20.8 mmol). To the resulting yellow suspension, a solution of C_{60} (500 mg, 0.694 mmol) in 50 mL of 1,2-dichlorobenzene was added in one portion. After stirring at 23 °C for 1 h, the reaction was quenched by the addition of 0.5 mL of sat. aq. NH_4Cl (color changed from dark green to dark red). The mixture was diluted by 250 mL of toluene and filtered through a pad of silica gel, which was pre-washed with MeOH. A red-colored eluent was concentrated to a volume of ca. 20 mL, and then 200 mL of ether was added to precipitate an orange-brown amorphous solid. The solid was extensively washed with EtOH and ether, and dried *in vacuo* to afford 507 mg of $C_{60}Me_5H$. (92%, >95% purity by HPLC): ^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 6H), 2.32 (s, 6H), 2.42 (s, 3H), 4.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.91 (2C, Me), 27.26 (2C, Me), 32.86 (1C, Me), 50.98 (1C), 51.12 (2C), 53.13 (2C), 59.22 (1C), 142.89 (2C), 143.52 (2C), 143.74 (2C), 143.81 (2C), 144.04 (2C), 144.08 (2C), 144.28 (2C), 144.64 (2C), 144.82 (2C), 145.27 (2C), 145.37 (2C), 146.39 (1C), 146.55 (2C), 146.66 (2C), 147.49 (2C), 147.53 (2C), 147.69 (2C), 147.76 (1C), 147.93 (2C), 148.00 (2C), 148.26 (2C), 148.32 (2C), 148.38 (2C), 149.57 (2C), 153.70 (2C), 153.74 (2C), 154.02 (2C), 157.17 (2C); IR (neat) ν/cm^{-1} 2957 (m), 2918 (m), 2856 (m), 1575 (w), 1548 (w), 1521 (w), 1444 (s), 1417 (w), 1370 (w), 1343 (w), 1324 (w), 1285 (w), 1262 (w), 1235 (w), 1200 (w), 1170 (w), 1146 (w), 1127 (w), 1092 (w), 1054 (w), 1034 (w), 1011 (w), 953 (w), 830 (w), 807 (w), 745 (w), 683 (s); MS *m/z* (LC–APCI, toluene:*i*-PrOH = 7:3) 796 (M^+).

4 **3**: ^1H NMR (400 MHz, THF-d_8) δ 2.42 (s, 15H); ^{13}C NMR (100 MHz, THF-d_8) δ 31.80 (5C, C(Me)), 54.35 (5C, C(α)), 129.70 (5C, C(Cp)), 143.15 (10C), 146.26 (5C), 147.27 (10C), 148.21 (10C), 148.88 (5C), 160.72 (10C, C(β)). The ^{13}C NMR signals of (Cp), C(Me), C(α) and C(β) were unambiguously by HMQC/HMBC 2D NMR.

5 When the THF-d_8 solution of **3** was titrated with 1 equiv each of 18-crown-6, the Δδ values became constant at the point of **3**:18-crown-6 = 1:3.

6 **4**: ^1H NMR (400 MHz, THF-d_8) δ 2.41 (s, 15H); ^{13}C NMR (100MHz, THF-d_8) δ 32.49 (d, J = 3.3 Hz, 5C, C(Me)), 53.02 (d, J = 10.0 Hz, 5C, C(α)), 131.72 (d, J = 28.1 Hz, 5C, C(Cp)), 143.97 (s, 10C), 146.58 (s, 10C), 147.03 (s, 5C), 148.04 (s, 10C), 149.02 (s, 5C), 156.81 (d, J = 4.1 Hz, 10C, C(β)). The ^{13}C NMR signals of (Cp), C(Me), C(α) and C(β) were assigned on the basis of the comparison with those of **3**.

7 These values (THF-d_8) are reasonable but smaller than those for Tl(η^5-C_5Me_5) and Tl[η^5-$C_5(CH_2Ph)_5$] in benzene-d_6. See: H. Schumann, C. Janiak, and H. Khani, *J. Organometal. Chem.* **330**, 347 (1987).