

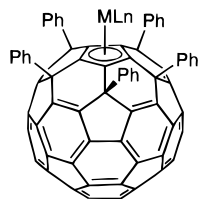
The First Pentahaptofullerene Metal Complexes

Masaya Sawamura,* Hitoshi Iikura, and Eiichi Nakamura*

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

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Cyclopentadienyl metal complexes have played important roles in chemistry owing to their unique structures and functional activities. Here we report the synthesis and characterization of an entirely new class of cyclopentadienyl (Cp) metal complexes (η^5 -C₆₀Ph₅)MLn (MLn = Li, K, Tl, and Cu·PEt₃, 5–8). In these



- 5: MLn = Li
6: MLn = K
7: MLn = Tl
8: MLn = Cu·PEt₃

molecules, the five Cp carbons represent one pentagon of C₆₀, isolated from the remaining 50 sp² carbon atoms by five surrounding sp³ carbon atoms each bearing a phenyl group. The X-ray crystal structure analysis of the thallium complex Tl(η^5 -C₆₀Ph₅)·2.5THF revealed its unique and esthetically pleasing C₅ symmetrical molecular structure with the phenyl groups forming a chiral propeller array. The thallium atom is deeply buried in the cavity created by the phenyl groups, bonding to the five Cp carbons (η^5 -coordination) with an averaged Tl–C distance of 2.87 Å.

The key finding that we made in this research was a remarkable 5-fold addition of an organocopper reagent to C₆₀, which stands in contrast to the monoaddition reaction of Grignard or organolithium reagents.¹ The reaction of C₆₀ with an excess amount of organocopper reagent prepared from PhMgBr (16 equiv) and CuBr·SMe₂ (16 equiv) followed by quenching with aqueous NH₄Cl gave, in 94% isolated yield, the pentaphenyl adduct C₆₀Ph₅H (**1**, reddish amorphous solid),^{2,3} which contains a cyclopentadiene moiety within the spherical surface of C₆₀ core (Scheme 1). Monitoring (HPLC) of the reaction throughout the reaction period indicated direct conversion of C₆₀ to **1** without formation of detectable amounts of mono- to tetra-adducts, and quenching of the reaction with D₂O afforded C₆₀Ph₅D with 96% deuterium incorporation. While the detailed mechanism remains unclear, we speculate that the five phenyl groups were introduced through sequential additions of the cuprate Ph₂Cu[−], as shown in Scheme 1. Thus, the first addition of one molecule of Ph₂Cu[−] gives the 1,4-bisadduct **2**,⁴ which is more reactive than C₆₀ and accepts readily a second equivalent of the copper reagent, and finally a third equivalent introduces the fifth phenyl group to generate the [Cu(η^5 -C₆₀-Ph₅)(Ph)][−] (**4**) by 1,2-addition to the fulvene moiety in **3**.

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

(2) This sample has 99% purity by HPLC analysis. Satisfactory analytical data was obtained as 1·0.5toluene. See Supporting Information for experimental details.

(3) Multistep synthesis of C₆₀Ph₅H via electrophilic aromatic substitution of benzene with C₆₀Cl₆ has been reported, see: 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.

(4) For examples of 1,4-addition to C₆₀, see: (a) Nagashima, H.; Terasaki, H.; Kimura, E.; Nakajima, K.; Itoh, K. *J. Org. Chem.* **1994**, 59, 1246. (b) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023. (c) Miki, S.; Kitao, M.; Fukunishi, K. *Tetrahedron Lett.* **1996**, 37, 2049. (d) Wang, G.-W.; Murata, Y.; Komatsu, K.; Wan, T. S. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2059.

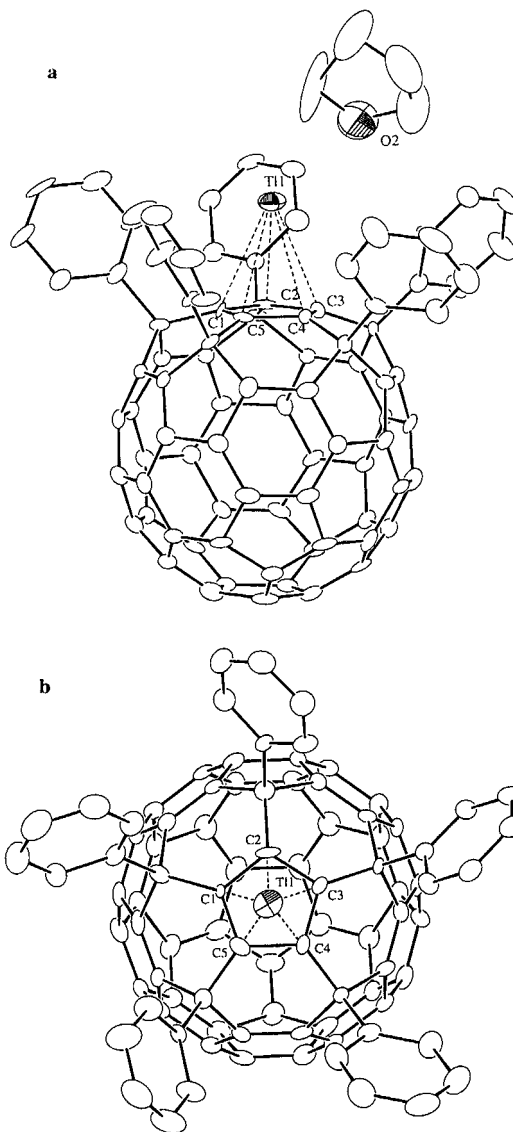
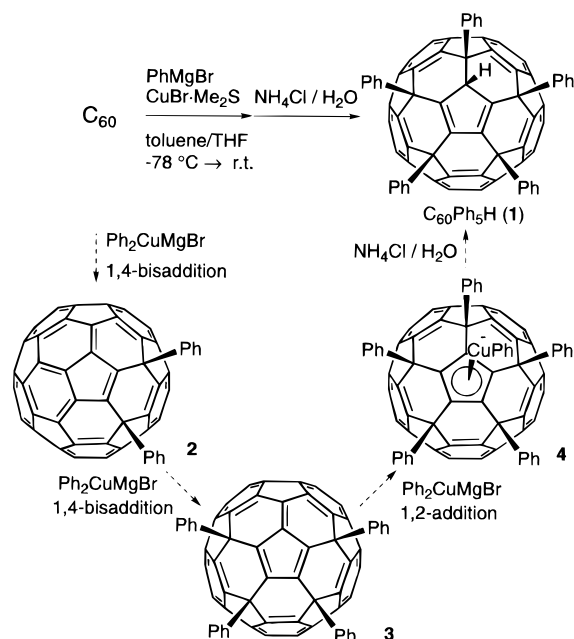


Figure 1. Molecular structure of Tl(η^5 -C₆₀Ph₅)·2.5THF (**7**·2.5THF) determined by X-ray crystal structure analysis. Selected bond lengths (Å): Tl–Cp(centroid), 2.60; Tl–C(1), 2.87(1); Tl–C(2), 2.88(1); Tl–C(3), 2.90(1); Tl–C(4), 2.83(1); Tl–C(5), 2.85(1); Tl–O 3.16(2); C(1)–C(2), 1.41(2); C(2)–C(3), 1.41(2); C(3)–C(4), 1.40(2); C(4)–C(5), 1.45(2); C(5)–C(1), 1.34(2). (a) Front view with weakly coordinated THF. Lattice-bound THF molecules and all hydrogen atoms are omitted for clarity. (b) Top view. All THF molecules and hydrogen atoms are omitted for clarity.

Treatment of a THF-*d*₈ solution of the cyclopentadiene derivative **1** with an alkali metal alkoxide such as LiO^tBu and KO^tBu at room temperature caused color change of the solution from red to dark red, which accompanied conversion of the C_s symmetric C₆₀Ph₅H (**1**) to a new species possessing C_{5v} symmetry, as observed by the ¹H and ¹³C NMR spectra. The distinctive molecular symmetry and disappearance of the singlet peak due to the CpH proton (δ 5.31 for **1**, CDCl₃) led us to assign the new species as Li(η^5 -C₆₀Ph₅) (**5**) and K(η^5 -C₆₀Ph₅) (**6**), respectively. Similarly a thallium(I) complex Tl(η^5 -C₆₀-Ph₅) (**7**) was also prepared by the reaction with TlOEt in THF-*d*₈. The reaction of **1** with Cu(O^tBu)(PEt₃)⁵ in THF-*d*₈ at −70 °C gave a phosphine-coordinated transition metal complex Cu(η^5 -C₆₀Ph₅)(PEt₃) (**8**). These complexes (**5**–**8**) were found to be air and moisture sensitive but thermally stable in solution at room temperature.

(5) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, 94, 658.

Scheme 1



Crystals suitable for X-ray structure analysis were obtained for the thallium(I) complex **7** as Tl(η^5 -C₆₀Ph₅)·2.5THF (dark red plates) by slow solvent-diffusion techniques with THF/hexane. The molecular structure and selected bond lengths are shown in Figure 1.⁶ The thallium atom is deeply buried in a cavity created by the five phenyl groups and is equally bonded to the five Cp carbons (C1–C5) (η^5 -coordination) with an average bond length of 2.87 Å (2.83–2.90 Å). This length is longer by 3% than the value reported for the Tl[η^5 -C₅(CH₂-Ph)₅].⁷ The distance between the thallium atom and the centroid of the η^5 -coordinating cyclopentadienyl moiety is 2.60 Å. One of the THF molecules may have a weak interaction with the thallium atom (Tl–O, 3.16 Å) while other THF molecules have no short contacts to the complex. The thallium complex adopts approximately C₅ symmetric conformation with the phenyl groups arranged in a chiral propeller array. Although the ¹H and ¹³C NMR spectra of **7** in THF-*d*₈ indicated free rotation of

the phenyl groups at room temperature in solution, the solid phase structure implies that the enantiomer separation may become possible by a suitable modification of the aromatic substituents for inhibition of the ring rotation. The structural constraints of the fullerene core caused significant deformation of local structure around the Cp ring, as observed for the five sp³ carbon atoms connected to the Cp moiety, which are tilted away from the plane of the Cp ring against the thallium atom with the average angle of as much as 22°. In spite of the large structural change around the Cp ring, the C₆₀ core largely retains the measure of its original spherical form (e.g., as to the distance between the Cp pentagon and the bottom pentagon and the diameter along the “equator”). The average lengths of the C–C double bonds (1.38 Å) and the single bonds (1.44 Å) in the C₅₀ moiety are similar to those of monofunctionalized C₆₀ derivatives.

The UV-vis spectra (CH₂Cl₂) of both the cyclopentadiene derivative **1** and the thallium complex **7** show that the 50 π -electron C₅₀ moiety beneath the Cp group is a chromophore of intensity ($\epsilon = 1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 240 nm) comparable to that of the parent C₆₀. The absorption extends to fairly long wavelengths (670 nm for **1**, 720 nm for **7**). These properties suggest that these fullerene derivatives have electronic properties similar to those of the parent C₆₀.

We presented the first example of η^5 -fullerene metal complexes. In other reported exohedral fullerene-transition metal complexes, the fullerenes act as an olefinic ligand carrying a low-valent, electron-rich metal center in an η^2 -fashion.^{8–10} Now [60]fullerene has become a cyclopentadienyl ligand, which can potentially accept a wide range of metal atoms and tolerate various metal oxidation states. Efforts will be continued to explore the applicability of the new class of cyclopentadienyl metal complexes.

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Supporting Information Available: Experimental details for the preparation of **1**, the ¹H and ¹³C NMR spectra for **5**–**8**, analytical data for **1** and **7**, UV-vis spectra for **1** and **7**, and details of the structure determination of **7**·2.5THF (18 pages). See any current masthead page for ordering and Internet access instructions.

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(6) Crystal data for Tl(η^5 -C₆₀Ph₅)·2.5THF (**7**·2.5THF): Monoclinic, P2₁/n, *a* = 27.509(4) Å, *b* = 17.498(8) Å, *c* = 14.275(3) Å, β = 104.57(1)°, *V* = 6650(5) Å³, *Z* = 4. Data were collected at 25 °C on Rigaku AFC5R diffractometer using graphite-monochromated Mo K α radiation to a maximum 2 θ = 55.2°, giving 11 663 unique reflections; the structure was solved by direct method (SAPI 91), yielding *R* = 0.079, *R*_w = 0.110 for 4443 independent reflections with *I* > 3 σ (*I*).

(7) Schumann, H.; Janiak, C.; Khan, M. A.; Zuckerman, J. J. *J. Organomet. Chem.* **1988**, 354, 7.

(8) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, 25, 134.

(9) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, 114, 7807.

(10) Yamago, S.; Yanagawa, M.; Mukai, H.; Nakamura, E. *Tetrahedron* **1996**, 52, 5091.