Chemistry of η^5-fullerene metal complexes*

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Abstract: Treatment of [60]fullerene with an organocopper reagent converts one of the pentagons of the fullerene into cyclopentadienyl anion through addition of five organic groups on every peripheral carbon atom surrounding the pentagon. Similar treatment of [70]fullerene afforded indenyl anion through regioselective tri-addition of the organic group. These anionic moieties strongly interact with the remainder of the fullerene π-system, and provide unique opportunity for exploration of organometallic chemistry of a new class of metal cyclopentadienides.

INTRODUCTION

Numerous metal complexes of fullerene have been synthesized and characterized in the past ten years. Various attempts to synthesize η^4-diene metal and η^6-arene metal complexes have been unsuccessful [1], and, in all but one case, no other than η^2-complexes could have been synthesized. The difficulty has been ascribed to the radial orientation of the fullerene p-orbitals. The exceptional class of compounds was reported by us in 1996; the cyclopentadienyl and indenyl metal complexes of fullerenes **1**, **3**, **4**, and **6**. Unlike η^2-complexes which are unstable under redox conditions (i.e., obligatory requirement of catalysis), the η^5 complexes are much more robust, as one might expect, by the analogy of a metal olefin complex and a metal cyclopentadienide complex. Given their unique steric, electronic, and photochemical properties, the η^5-fullerene metal complexes are expected to offer exciting new possibilities in organometallic chemistry. This review will summarize the preparation and some fundamental properties of the new cyclopetadienide and indenide ligands embedded in the core of [60] and [70]fullerenes.

QUANTITATIVE PENTA- AND TRI-ADDITION TO FULLERENES

The access to the η^5-fullerene metal complexes **1** was discovered serendipitously; namely, a one-step five-fold addition of a phenylcopper(I) reagent to [60]fullerene. The reaction was first found to take place in 3% yield but eventually improved to give the product in 98% yield, as determined for an analytically pure sample [2]. The reaction is general for various aryl [3] and alkenyl groups as well as for methyl group [4]. Despite our recent knowledge of organocopper mechanisms [5], the mechanism still remains unclear. Nonetheless, we can propose a rationale (Scheme 1), where the reaction goes in a step-wise manner, first putting two R groups in a 1,4-manner, then the third, the fourth, and finally the fifth. The reaction must involve a series of oxidation/reduction steps, as the reaction generates metallic copper as a side product.

There is a series of experimental evidence that supports this pathway. When we treated 1,4-dibenzylated fullerene **2** with a phenylcopper reagent, we found quantitative formation of dibenzyltriphenyl compound **3**, indicating that 1,4-di-adduct lies on the pathway to the penta-adduct. Interestingly, the reaction stops at the tri-addition stage when a phenyl Grignard reagent was used instead of a phenyl
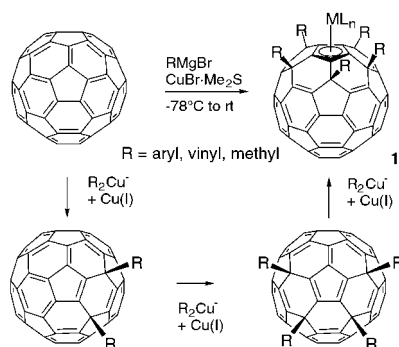
Scheme 1

copper reagent. Thus, the reaction of **2** with PhMgBr cleanly afforded **4**. The result demonstrated not only the feasibility of making a tri-adduct, but also a future possibility of the synthesis of fully unsymmetrically substituted derivatives of tri-addition and penta-addition products [6].
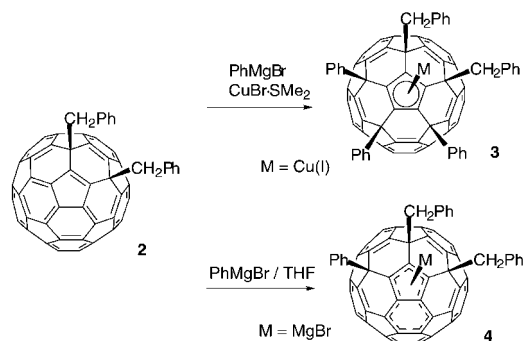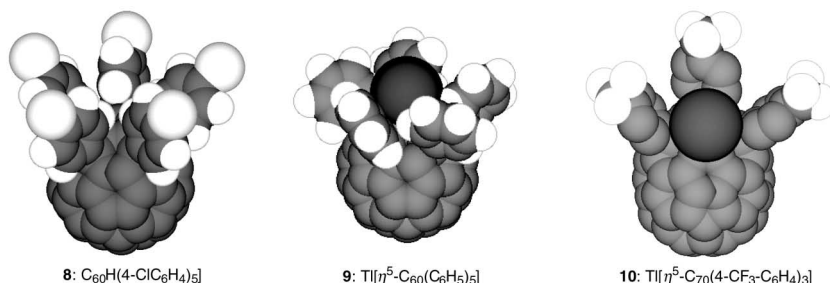

Theoretical calculations on the structure of the model tri-adduct **5** showed that this anion is an indenyl anion rather than an allyl or cyclopentadienyl anion. The bond alternation inherent to [60]fullerene has disappeared, and all bonds associated with the indenide skeleton are almost equal, and the molecular orbital (e.g., HOMO) characteristic of indenyl anion was readily identified. This calculated structural feature received full support from the crystal structure of a related tri-adduct obtained from [70]fullerene [7].

The reaction course was found to change when [70]fullerene is used for the copper reaction. We expected that a phenylcopper would react with [70]fullerene to give a penta-addition product **7** by sacrificing the most strained part—the top. However, reaction afforded a tri-addition product **6** to give an indenyl metal complex [8]. One can reason that the phenylcopper addition to a C–C double bond took place in such a manner that each addition reaction generates an sp^3 center at the more strained sp^2 atom, and to generate a more planar and better conjugated anion.
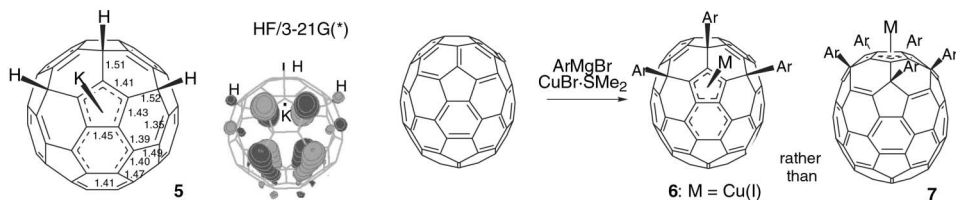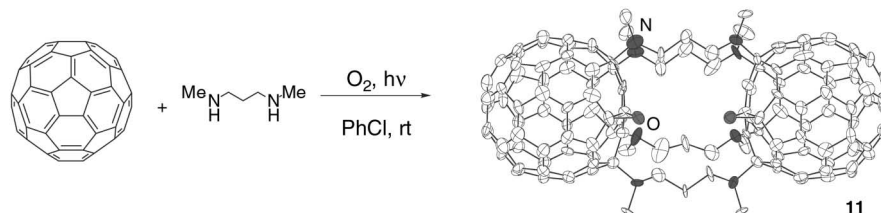
FULLERENE CYCLOPENTADIENES AND CYCLOPENTADIENIDES

The structures of the tri- and penta-addition products were determined unambiguously through X-ray analysis of the cyclopentadiene compound and the metal complexes. The aryl groups in the cyclopentadiene are freely rotating, but, in crystals, are arranged in a near C_{5v} symmetric manner (**8**). Those in metal cyclopentadienide (**9**), on the other hand, suffer steric interactions with the center metal and are arranged in a near C_5 manner. The metal atom is located deep in the cavity created by the five phenyl groups. The cavity in the indenyl complex derived from [70]fullerene (**10**) is half-open toward the indenide skeleton, where the metal (Tl) is located right above the pentagon.

8: $C_{60}H(4\text{-}ClC_6H_4)_5$ **9**: $Tl[\eta^5\text{-}C_{60}(C_6H_5)_5]$ **10**: $Tl[\eta^5\text{-}C_{70}(4\text{-}CF_3\text{-}C_6H_4)_3]$

These structures in turn suggest utilization of the cavity for its own sake. One future direction will be a dimeric penta-adduct, where a cavity can be formed between the two fullerene cores. An example below (**11**) illustrates the synthesis of such a dimer tethered by four 1,3-diaminopropane chains. Between the two fullerene endcaps, a small cavity is formed, whose size is large enough to potentially include a molecule of methane [9].

FULLERENE CYCLOPENTADIENIDE IN AQUEOUS SOLUTION AND ON SOLID SURFACE

Interestingly, the pentaaryl- and pentamethylfullerene anions $R_5C_{60}^-$ **1** show remarkable stability and solubility in water. Being composed solely of carbon atoms and hydrogen atoms, these compounds represent a rare example of hydrocarbon anions with well-defined water solubility. The unique feature of this water-soluble fullerene is that the solubility arises from the charge in the fullerene core rather than that in the pendant side chains as in the previously known water-soluble organofullerenes. The atomic microscopic image of the solution on mica surface (Fig. 1) showed flat, round-shaped objects corre-
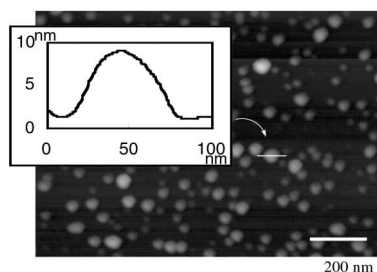

Fig. 1 Atomic force microscope image (AC mode) of aqueous $Ph_5C_{60}K$ aggregate on mica.

sponding to the aggregates of the cyclopentadienide. A typical object measures 70 nm in diameter and 10 nm in height (roughly corresponding to a radius of 17 nm for a spherical object). This estimate is in good accord with the results of the light-scattering experiment [10].

Some efforts are going on to prepare epitaxial films of the fullerene metal complexes on solid surface. A solution spray technique has been developed and will prove useful for the purpose [11].

CONCLUSION

The cyclopentadienide moiety in the penta-adduct **1** appears to be electronically isolated from the bottom 50 sp^2 carbon atom with the surrounding 5 sp^3 carbon atoms. Experimentally, however, these two parts show a strong sign of mutual electronic interaction [12]. In such a sense, one can draw an analogy between the η^5-fullerene metal complexes **12** and metal porphyrin **13**: Porphyrin acts as an electron-rich donor ligand to the center metal, while fullerene may act as an electron-deficient acceptor ligand. Together with companion phosphinofullerene metal complexes $[R_2(C_{60}H)P\bullet M]$, [13] the new η^5-fullerene metal complexes will serve as unique organometallics to be used as catalyst and materials of unique steric, electronic, and photonic properties.
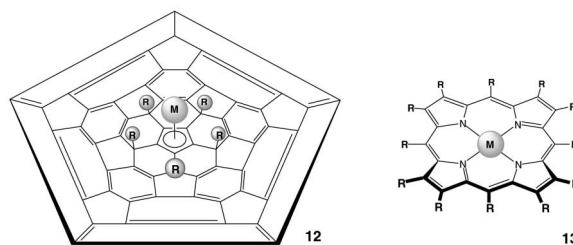
ACKNOWLEDGMENTS

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