Organometallic chemistry of $\text{C}_6\text{O}_6$ beyond $\eta^2$-C=C co-ordination: Buckminsterfullerenes as pentahapto ($\eta^5$) cyclopentadienyl ligands

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Since the initial discovery and the subsequent development of efficient synthesis of fullerenes\(^1\), studies on the interaction of these molecules with metals have received considerable attention. This is in view of the fact that the metal-containing fullerene derivatives have the potential for the realization of new high surface area catalysts and hybrid materials with exceptional properties. Compared to the well-known chemistry of endohedral fullerenes of the type M@C\(_{\text{6O}}\) (ref. 2), there have been only sporadic reports in the last few years on the chemistry of exohedral organometallic complexes of fullerene\(^3\).\(^4\). The initial work of Pagan and co-workers in early nineties on the exohedral organometallic chemistry of fullerenes revealed that the $\text{C}_{\text{6O}}$ molecule behaves more like an electron-deficient alkene such as tetracyanoethylene rather than relatively electron-rich species such as ethylene or benzene\(^5\). Moreover, the short/long bond alteration found in the six-membered rings of $\text{C}_{\text{6O}}$ suggested that each of the double bonds is somewhat electronically localized, resulting in relatively low ring currents in $\text{C}_{\text{6O}}$. Due to these now obvious reasons, the fullerene co-ordination chemistry has been dominated by only one mode of ligation\(^3\).\(^4\), viz. an $\eta^2$-coordination through the C=C double bonds which are located at the junction of two adjacent six-membered rings (the 6-6 bonds) as shown in $\eta^2$-\(\text{C}_{\text{6O}}\)Pt(PPh\(_3\))\(_2\) (A) (ref. 3).

In an important breakthrough in fullerene organometallic chemistry, Sawamura et al.\(^5\) have recently described the first successful synthesis of pentahapto ($\eta^5$) co-ordination complexes of $\text{C}_{\text{6O}}$ (2-5) with alkali main group, and transition metals by elegantly modifying the $\text{C}_{\text{6O}}$ skeleton in terms of its electronic properties (Scheme 1).

Before going into the details of the recent findings of Sawamura et al.\(^5\), a brief introduction to the $\eta^5$-cyclopentadienyl organometallic complexes is desirable. Since the serendipitous discovery of ferrocene by Kealy and Pauson\(^6\), the organometallic chemistry of transition metals and many lanthanides has been virtually dominated by the use of cyclopentadienyl (Cp) or substituted cyclopentadienyl (Cp') ligands which commonly co-ordinate to the metal in a pentahapto ($\eta^5$) fashion through all the five ring carbon atoms\(^7\).

One of the main and notable reasons for the vast expansion of Cp-organometallic chemistry over the decades has been the ability of these ligands to support a wide range of metals also tolerating their various oxidation states. Moreover, the ability of the appropriately substituted Cp ligands to dictate desired electronic and steric properties on various metals has led to the preparation of a multitude of catalytically useful systems (e.g. the classical olefin polymerization catalyst Cp\(_2\)TiCl\(_2\)/Et\(_2\)AlCl) (ref. 8).

In spite of the parallel advances both in (a) the $\eta^5$-Cp-organometallic chemistry of transition metals and lanthanides and (b) the $\pi$-complex chemistry of fullerenes, until the report of Sawamura et al.\(^5\), there have been no major attempts to combine these two aspects and devise routes to hitherto unknown $\eta^2$-\(\text{C}_{\text{6O}}\) organometallic complexes. The main reasons for the lack of synthetic routes for $\eta^2$-\(\text{C}_{\text{6O}}\) complexes can be easily discerned from the above stated findings of Fagan et al.\(^3\). The fact that the C=C double bonds of $\text{C}_{\text{6O}}$ are localized has so far precluded any possibility of using these molecules as polyhapto ligands.

In complexes 2-5, the five cyclopentadienyl type carbon atoms are represented by one of the five-membered rings of $\text{C}_{\text{6O}}$. This pentagon is electronically isolated from the remaining 50 sp\(^3\) carbon atoms of $\text{C}_{\text{6O}}$ by the five surrounding sp\(^3\) carbon atoms, each of which bear an exocyclic phenyl substituent. The key step in the synthesis of complexes 2-5 lies in the successful synthesis of the precursor $\text{C}_{\text{6O}}$ molecule $\text{C}_{\text{6O}}\text{Ph}_3\text{H}$ (1), for which the authors have essentially used the strategy employed by Hirsch et al.\(^9\) for the preparation of organodihydrofullerenes. While the
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Figure 1. The top view of the molecular structure of Tl(n^2-C_{60}Ph_3). 2.5 THF showing the C_5 symmetry.

reactions of C_{60} studied by Hirsch et al. with organometallic reagents such as MeLi or PhMgBr yielded the monoaddition products of C_{60}, the remarkable reaction with an excess amount of the organocupper reagent Ph_3CuMgBr (prepared from PhMgBr and CuBr-SMe_2) readily results in the 5-fold addition product C_{60}Ph_3H(1) as a redish amorphous solid in 94% yield. It should be noted that, the fullerene 1 has also been prepared by Kroto and co-workers through aromatic electrophilic substitution of benzene with C_{60}Cl_6 followed by the reduction of the resulting C_{60}Ph_3Cl in the presence of PPh_3 (ref. 10). However, the later procedure involves a multi-step synthesis which results in somewhat lower isolated yields of 1.

The reactions of 1 with monovalent metal alkoxides LiO'Bu, KO'Bu, TiOEt and Cu(O'Bu)(PPh_3) yield the respective n^2-C_{60}Ph_3 complexes 2-5 (ref. 5). A single crystal X-ray diffraction study of the thallium(I) complex 4 reveals that the molecule possesses an aesthetically pleasing C_5 symmetry with the five Ph groups forming a chiral propeller array as shown in Figure 1. In spite of the chemical structural changes around the Cp ring, the C_{60} core in 4 largely retains its original spherical symmetry. Moreover, the average C-C single and double bond lengths in the C_{60} fragment of the molecule are found to be very similar to those found in monofunctionalized C_{60} derivatives. More interestingly, the electronic spectral data of 1 and 4 reveal that the intensity of the absorption of the 50-π-electron C_{60} chromophore (λ_{max} = 240 nm, ε = 1.1 x 10^3 M^-1 cm^-1) is comparable to that of the parent C_{60} suggesting that the electronic properties of the compounds 1-5 are similar to those of C_{60}.

The elegant approach demonstrated by Sawamura et al., has truly opened up the door to the exploration of C_{60} coordination chemistry beyond its previously known limits. Carefully planned research on this type of complexes might prove useful in the discovery of a new class of fullerene-based catalysts and novel materials. Among several intriguing challenges in this direction, the preparation of metalloocene complexes based on C_{60} (such as ferrocene) and other double/triple decker C_{60} complexes (which would require suitable functionalization at the diagonally opposite ends of the sphere) is likely to draw the immediate attention of the synthetic chemists around the world.


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Research snippets (Compiled by A. V. Sankaran)

K-T meteorite relics found

While the enigma about the mass extinction of dinosaurs 65 million years ago (K-T period), whether due to terrestrial or extra-terrestrial agencies is still baffling scientists, that a 10 km wide asteroid or meteorite crashed during that period over Yucatan Peninsula (Mexico), carving the huge Chixulub crater 150 kilometers across, is not being doubted (Figure 1). Though, presumably this meteorite vaporized completely upon impacting, leaving no trace except for their extra-terrestrial signature as iridium enrichment in sediment, search for unburnt relics of the meteorite continued. Recently, two teams of researchers exploring for such bits, came across materials which they