Coordination Modes

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Coordination of Buckybowls: The First Concave-Bound Metal Complex**

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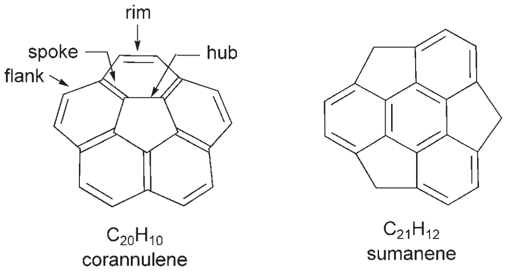
The discovery of fullerenes has opened up a new research area in organometallic and coordination chemistry: the study of metal binding to nonplanar π-carbon surfaces. As a result, a great number of exohedral transition-metal complexes of fullerenes have been synthesized over the last two decades.[1] In contrast, the controlled synthesis of endohedral fullerene complexes by chemical methods is still lacking. Only a limited number of metal centers have been encapsulated in fullerene cages by arc-evaporation of graphite–metal composites at high temperatures. The progress and advances in fullerene chemistry, as well as some unresolved issues, have resulted in special attention being paid to polycyclic aromatic hydrocarbons that have nonplanar π-carbon surfaces. These polyarenes comprise five- and six-membered rings that map onto the surface of C_{60} but which lack the full closure of the fullerene. They are commonly referred to as "open geodesic polyarenes", "buckybowls", or "fullerene fragments". Unlike C_{60}, this new class of polyaromatic hydrocarbons has become available only in the past few years, as a result of successful efforts of synthetic organic chemists.[2] Although there are more than two dozen members of this family known to date, buckybowls are still not commercially available.

The smallest subunit of C_{60} built around a central five-membered ring is corannulene ($C_{20}H_{10}$). It was first prepared in 1966 in very low overall yield by a multistep conventional organic synthesis.[3a] More practical synthetic routes to corannulene were later developed based on flash vacuum pyrolysis[3b] as well as solution-phase approaches.[3c] The simplest fullerene fragment with a central six-membered ring, sumanene ($C_{21}H_{12}$), has been synthesized and structurally characterized only recently.[4]

From a coordination viewpoint, buckybowls are unique ligands that have multisite coordination possibilities, namely convex and concave interior polyaromatic faces, as well as edge and rim carbon atoms capped by hydrogen atoms. They share with fullerenes the convex three-dimensional surface of unsaturated carbon atoms but, in contrast, have a concave π-carbon surface that is open and readily accessible. The study of the relative preference of the convex and concave surfaces for binding metal centers has attracted considerable attention in the last few years because of its fundamental and practical importance.[5] On one hand, the controlled positioning of metal centers inside the bowls is expected to provide a direct route toward the inclusion complexes of fullerenes and nanotubes. On the other hand, the coordination of metal centers to the outside of the bowls should find applications in surface activation and the functionalization of fullerenes and nanotubes. As demonstrated computationally, buckybowls are expected to exhibit system-dependent preferences for metal coordination. However, control of their reactivity in binding reactions presents a challenge, and the few structurally characterized metal complexes of buckybowls are still mainly limited to those of corannulene.



The first η^6-corannulene–metal complex was isolated and spectroscopically characterized 10 years ago,[6] but its structural characterization was not achieved until 2004.[7] The latter study revealed the dramatic impact that transition-metal binding can have on curved polyaromatic surfaces: the coordination of two ruthenium centers to the opposite faces of corannulene was found to completely flatten the bowl-shaped molecule. This effect should be taken into consideration when evaluating the impact of the coordination of metal centers to other nonplanar π surfaces, such as the caps or walls of carbon nanotubes. The family of η^6-corannulene–metal complexes was later expanded to include several new members.[8]

The first crystalline η^2 complexes of corannulene were synthesized and characterized by X-ray crystallography in my laboratory in 2003.[9a] In contrast to the above solution studies,

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the gas-phase co-deposition technique was used,[9] which has proven successful for the crystallization of metal–π complexes and for the multiple metalation of bowls in a solvent-free environment. Several rhodium(II) and ruthenium(I) complexes exhibiting discrete[9c] and extended 1D and 2D structures[9b,d] with terminal η^2, and bridging μ_2-η^2:η^2 and μ_3-η^2:η^2:η^2 coordination to the rim, respectively, have been prepared and structurally characterized. These studies revealed the preference of strong Lewis acidic metal centers to coordinate to the rim of the buckybowls. By deliberately softening the electrophilic properties of the metal we then successfully tuned the binding mode and prepared the first hub-bound corannulene complex. It has a ruthenium(I) center η^1 coordinated to a single interior carbon atom on the convex surface of $C_{20}H_{10}$.[10] Interestingly, this complex remains the only example in which the convex carbon surfaces of $C_{20}H_{10}$ and of C_{60} show a degree of similarity in metal-binding reactions.

Importantly, the above hub complex, along with all other discrete η^2-rim and η^6-corannulene complexes having a single metal atom bound to a bowl, exhibit metal coordination at the convex face (Figure 1 a, b, d, e). A similar trend was seen for the complexation of Ag^+ ions to $C_{20}H_{10}$ in solution.[11] In silver(I)-based extended networks built from the η^2 and η^1 coordination of Ag^+ ions to the rim sites of corannulene, a metal ion was always found at the outside of the bowl (Figure 1 c). This observation clearly demonstrated the general preference of the convex face of corannulene for metal coordination and thus thwarted the idea of using buckybowls to access inclusion metal complexes. In this regard, a new report by Hirao and co-workers[12] on the synthesis and structural characterization of the first *endo*-bound buckybowl complex is a breakthrough. Prior to that work, no selective coordination of metal ions to the concave face had been observed experimentally.

The coordination of a metal ion in an *endo* fashion has been successfully accomplished with sumanene.[4] In contrast to corannulene, this C_{3v}-symmetric C_{60} fragment is more rigid and has a deeper bowl (1.11 Å for $C_{21}H_{12}$ versus 0.875 Å for $C_{20}H_{10}$). Sumanene is expected to show various binding modes, ranging from η^1 to η^6, but its coordination chemistry had previously been limited to a single computational study that predicted an η^2-convex binding of $[Pt(PH_3)_2]$.[13] The Hirao research group took advantage of the solid-state synthesis to place a cyclopentadienyliron unit in the sumanene bowl. The metalation of $C_{21}H_{12}$ was performed by exchanging one cyclopentadienyl (Cp) group of ferrocene with sumanene in the presence of aluminum powder and aluminum chloride under solvent-free conditions. The counterion of the crude product was then replaced by hexafluorophosphate to yield $[CpFe(sumanene)]PF_6$. Elevated temperature (120 °C) and excess ferrocene and aluminum chloride were needed to produce the desired monometalated sumanene complex in high (91 %) yield. It was fully characterized by FAB mass spectrometry, ^1H and ^{13}C NMR spectroscopy, and X-ray crystallography. The latter study unambiguously confirmed the η^6 binding of the cyclopentadienyliron unit to a flank benzene ring of the concave face of sumanene (Figure 2). Again, this *endo* coordination has been achieved for the first time for a bowl-shaped polyaromatic ligand.

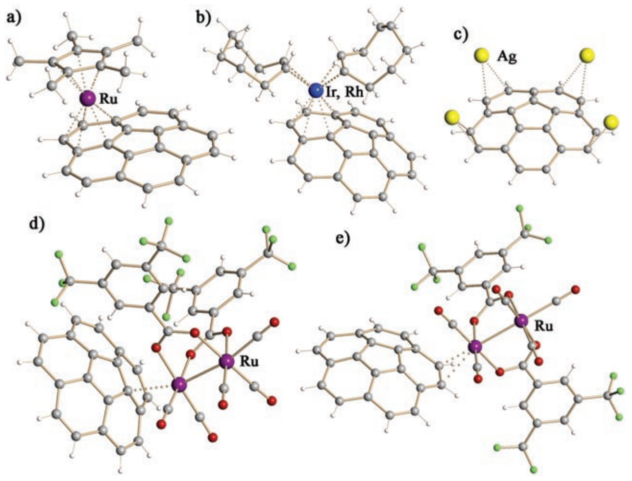

Figure 1. Metal coordination to the convex face in: a) $[Cp^*Ru(\eta^6\text{-}C_{20}H_{10})]^+$,[7] $[(coe)_2M(\eta^6\text{-}C_{20}H_{10})]^+$ (M = Rh, Ir),[8a] c) $[Ag_4(\eta^2{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_{20}H_{10})]^{4+}$,[11] d) $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5(\eta^1\text{-}C_{20}H_{10})]$,[10] and e) $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5(\eta^2\text{-}C_{20}H_{10})]$.[10] $Cp^* = C_5Me_5$, coe = cyclooctene.

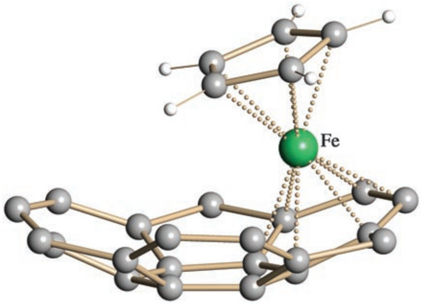

Figure 2. Metal coordination to the concave face in $[CpFe(\eta^6\text{-}C_{21}H_{12})]^+$.[12]

The importance of this original result goes beyond simple expansion of the number of experimentally characterized complexes of buckybowls, or the report of the first example of a 3d-transition-metal complex of a bowl and the discovery of a new coordination mode. First, it confirms that bowl-shaped polyarenes indeed serve as excellent multisite models to reveal trends and evaluate preferences in the binding of metal centers to curved π-carbon surfaces. Second, it proves, that despite all prior examples of the preferential coordination of metal centers to the convex surfaces of buckybowls, their inside concave carbon face can also be reactive toward coordination. This confirmation is expected to have wide-ranging implications. While the study by Hirao and co-workers may serve as the first step toward the elusive inclusion complexes of buckybowls, it should greatly stimulate further search in this direction. As the next stage, buckybowls with a greater curvature and larger surface area than corannulene and sumanene should be targeted.

Currently, very little is known regarding the coordination limits and ligating properties of large open geodesic polyarenes. So far only one metalated product of dibenzo[*a*,*g*]corannulene ($C_{28}H_{14}$) and two metal complexes of hemibuckminsterfullerene ($C_{30}H_{12}$)—the C_3-symmetric half of C_{60}—have been reported, all showing reactivity at the periphery of the bowls.[9b,d,14] All other complexation studies have used corannulene as a model bowl. In this regard, the preparation and structural characterization of the largest subunits of C_{60}—pentaindenocorannulene ($C_{50}H_{20}$) and tetraindenocorannulene ($C_{44}H_{18}$)—reported in 2007 are very promising.[15] Their extended π surfaces should provide very deep all-carbon cavities in which metal centers can be deeply buried to form unique metal-inclusion reagents. The latter should find applications in such fields as molecular electronics and magnetic resonance imaging, catalysis, reagent storage, and transport.

One additional important outcome of the innovative study by Hirao and co-workers should be emphasized. Since large polyarenes are expected to show low volatility and low solubility, these intrinsic properties may limit the use of solution- and gas-phase methods for metalation reactions. However, the first successful application of the solid-state technique to place a metal ion in a bowl can serve as a useful and promising guide for synthetic chemists working in this area. For larger bowls, novel preparative methods based on solid-state reactions should be sought and developed to achieve controlled metal binding to specific sites on nonplanar polyaromatic surfaces.

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