Polyarene Coordination

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Corannulene “Hub” Carbon Coordination by $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5]$**

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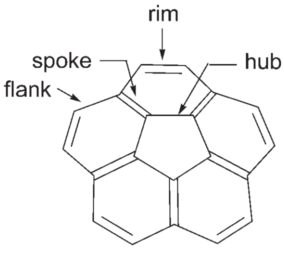
Transition-metal complexes of fullerenes have attracted considerable attention since 1991, when Fagan et al. reported the synthesis and structure of the first complex, $[Pt(PPh_3)_2(\eta^2\text{-}C_{60})]$.[1] A great number of *exo*-bound transition-metal complexes of fullerenes have been synthesized since then.[2] By contrast, bowl-shaped polycyclic aromatic hydrocarbons that constitute fragments of fullerenes[3] could not be coaxed to function as ligands for transition metals until 1997, when Seiders et al. finally isolated and spectroscopically characterized the first cationic metal complex of corannulene, $[(\eta^6\text{-}C_{20}H_{10})Ru(C_5Me_5)]^+$.[4] Corannulene, the smallest open geodesic polyarene that maps onto the ring system of C_{60} (Scheme 1), has served as the primary model for theoretical and experimental coordination studies since then. NMR evidence for η^6 complexation of corannulene by $[Ir(C_5Me_5)]^{2+}$ was reported in 2003,[5] but structural characterization of the first η^6 corannulene complex by X-ray crystallography was not achieved until 2004.[6] Last year, Elliott et al. reported three silver complexes of corannulene, all having extended networks built on η^2 and η^1 binding of Ag^+ centers to the rim CH sites of the hydrocarbon bowl.[7]



Scheme 1. Four types of C–C bonds in corannulene ($C_{20}H_{10}$).

The first crystalline η^2 complexes of corannulene were synthesized and structurally characterized by X-ray crystallography in our laboratory in 2003.[8] Using gas-phase coordination reactions,[9] we prepared two rhodium(II) complexes having different compositions $[\{Rh_2(O_2CCF_3)_4\}_m\cdot(C_{20}H_{10})_n]$ ($m/n = 1{:}1$ and $3{:}2$) in a solvent-free environment. The compounds exhibit extended 1D and 2D structures built on the rim $\mu_2\text{-}\eta^2{:}\eta^2$ and $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ coordination modes, respectively, of corannulene. More recently, we have prepared a discrete bis(corannulene) ruthenium(I) complex, $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(C_{20}H_{10})_2]$, which has terminally η^2-rim-bound $C_{20}H_{10}$ molecules.[10] This work demonstrates that the preference exhibited by corannulene for η^2 coordination on the rim by strongly Lewis acidic rhodium(II) centers[8,9] extends also to isoelectronic ruthenium(I) centers.

As this field has blossomed, we have become increasingly intrigued by the continued absence of any structurally characterized transition-metal complexes of corannulene, or of any other geodesic polyarene, in which a metal center coordinates to one or more of the interior, “fullerene-like” quaternary carbon atoms in preference to the methine atoms on the rim. Taking into consideration some basic principles of chemical bonding, we speculated that fine-tuning the electrophilic properties of metal sites should affect the nature of their coordination to bowl-shaped polyarenes. More specifically, we reasoned that softening the Lewis acidity of the metal complexes used[8–10] should decrease the preference for complexation to corannulene rim carbon atoms, since a weak Lewis acid should not strongly differentiate between the rim

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and hub corannulene sites. Importantly, the coefficients of the highest-occupied molecular orbitals (HOMOs, doubly degenerate, see the Supporting Information) are greatest in corannulene at the five interior carbon atoms. However, the coefficients of the lowest-unoccupied molecular orbitals (LUMOs, doubly degenerate, see the Supporting Information) are greater at the rim (Figure 1). Clearly both HOMOs and LUMOs should be taken into account in metal–arene complexes, since ligand-to-metal donation and metal-to-ligand back-donation equally contribute to bonding in such systems.

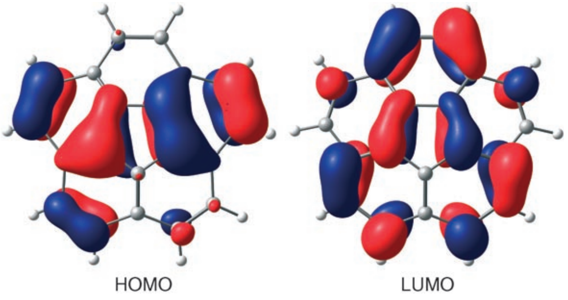

Figure 1. HOMO and LUMO of corannulene (PBE0/6-31G(d)//6-311G(d,p)). One of the two doubly degenerate orbitals is shown in each case.

Pursuing this line of thought, we turned our attention to the gas-phase reactions of corannulene with a single-end Lewis acidic site, the diruthenium(I,I) mixed carbonyl 3,5-bis(trifluoromethyl)benzoate, $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5]$.[11] According to our DFT charge-distribution analysis, this complex should behave as a much softer Lewis acid than the dimetal trifluoroacetate complexes used previously,[8–10] and our experimental results seem to confirm this conclusion. We report herein a new transition-metal complex in which one corannulene is η^1-coordinated to ruthenium at an interior "hub" carbon atom while another is η^2-rim-bound.

The gas-phase codeposition of corannulene with $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5]$ was performed at 165 °C. This reaction resulted in the formation of the new corannulene-based product $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5\cdot(C_{20}H_{10})]\cdot(^1/_4\,C_{20}H_{10})$, which was isolated in moderate yield. The crystals are air-stable at room temperature but show a slight sensitivity to moisture. They were characterized by elemental analysis, IR, UV/Vis, and NMR spectroscopy, and by X-ray crystallography (Supporting Information).

X-ray structural characterization reveals that one corannulene molecule functions as a guest, occupying a cavity in the crystal lattice (Figure 2), whereas the others function as ligands coordinated to diruthenium units. In contrast to the coordinated corannulene, the clathrated bowl is severely disordered and may even be undergoing bowl-to-bowl inversion in the crystal.

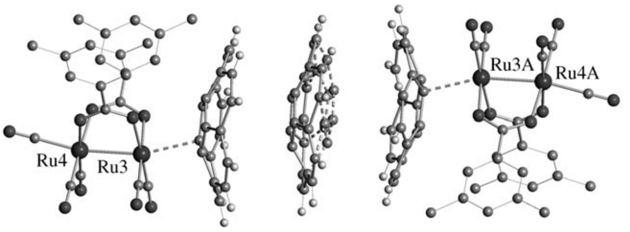

Figure 2. A fragment of the structure showing two types of corannulene. The fluorine and hydrogen atoms of the benzoate ligands are omitted.

There are two crystallographically independent diruthenium(I,I) units with bound corannulene molecules in the same crystal. A comparison of these complexes reveals two different coordination modes of the $C_{20}H_{10}$ bowl. One has an η^2-rim-bound corannulene, with Ru1–C1 and Ru1–C2 bond lengths of 2.517(3) and 2.573(3) Å (Figure 3).

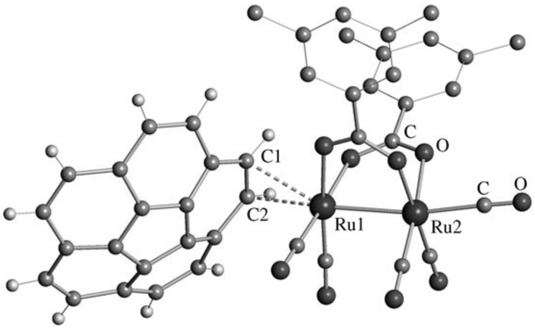

Figure 3. A rim-coordinated corannulene unit.

In the other complex, the open ruthenium end of the dimetal unit is η^1-bound to a single interior "hub" carbon atom on the convex surface of corannulene, with a Ru3–C12B bond length of 2.611(3) Å (Figure 4). The much longer Ru3–C12A separation (2.965(4) Å) leads us to classify the metal–ligand interaction in this complex as η^1 binding to a single interior "hub" carbon atom, rather than as η^2 binding to a "spoke" double bond. The C12A-C12B-Ru3 bond angle (90.26°) is very close to the angle one would expect for pure η^1 binding.

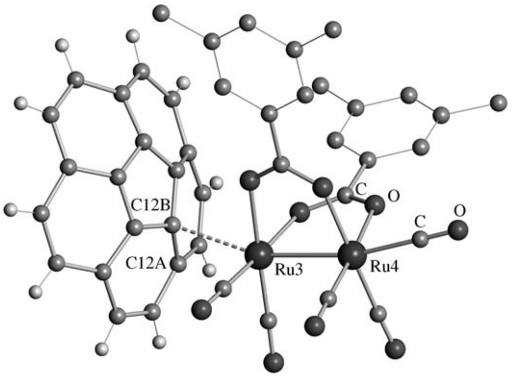

Figure 4. A hub-coordinated corannulene unit.

It is noteworthy that the Ru–C bond lengths of 2.547 (rim-complex average) and 2.611 Å (hub-carbon complex) are appreciably longer than the average bond length observed in the recently isolated bis(corannulene) adduct $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(C_{20}H_{10})_2]$ (2.508 Å).[10] Interestingly, metal centers in all three ruthenium(I)–corannulene complexes bind the bowl from the *exo* face.

A comparison between the geometrical parameters of the coordinated corannulenes in these two complexes with those in the uncomplexed $C_{20}H_{10}$ molecule[12] (Supporting Information) shows that there is little perturbation of the corannulene core upon complexation with ruthenium(I) in the η^2 complex (Figure 3); however, one noticeable perturbation can be seen in the η^1 complex (Figure 4). The carbon atom bound to ruthenium in the η^1 complex is significantly more pyramidalized than the other four hub carbon atoms of the complexed ligand. The p-orbital axis vector (POAV) analysis of Haddon[13] provides an excellent method for quantifying this degree of pyramidalization. As reference points, we note that a planar trigonal carbon atom (such as that in benzene) has a POAV angle of 0.0°, whereas the highly pyramidalized carbon atoms of C_{60} have POAV angles of 11.6°. The four uncomplexed hub carbon atoms of the ligand in the η^1 complex (Figure 4) have POAV angles of $8.3° \pm 0.2°$, a value which is indistinguishable from that in unbound corannulene (POAV angle also 8.3°). The hub carbon atom that is η^1-bound, on the other hand, has a POAV angle of 10.6°. This increase in pyramidalization by nearly 30% constitutes compelling experimental evidence for a bonding interaction between the metal center and the hub carbon atom.

To compare the binding energies of the η^2-rim and the η^1-hub corannulene $[Ru_2\{O_2C(3,5\text{-}CF_3)_2C_6H_3\}_2(CO)_5\cdot(C_{20}H_{10})]$ complexes, we performed density functional theory (DFT) calculations (Supporting Information).[14] Our calculations predict a small preference of 2.5 kcal mol^{-1} for the rim-bound structure over the hub complex. The absolute binding energies for the rim (11.5 kcal mol^{-1}) and hub (9.0 kcal mol^{-1}) isomers, however, fall significantly below the value for the $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(C_{20}H_{10})]$ complex (20.3 kcal mol^{-1}).[10] Consistently, the latter shows the shortest Ru–C bonding interactions in this ruthenium(I)–corannulene series. Importantly, a molecular-orbital analysis of the two optimized gas-phase structures confirms both the η^2 binding in the rim isomer and the η^1 hapticity in the hub complex.

In summary, the use of a very soft, single-end diruthenium(I,I) Lewis acid has resulted in the isolation of a unique ruthenium(I)–corannulene complex with two crystallographically independent units cocrystallized in one crystal. One unit is an η^2-rim-bound complex, while the other represents the first example of metal coordination exclusively to the interior region on the convex surface of a geodesic polyarene. The formation of a hub-coordinated complex in this work demonstrates for the first time a degree of similarity between the convex carbon surfaces of corannulene and of fullerenes in metal-binding reactions.

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[14] Molecular-geometry optimizations were performed at the DFT level by using the hybrid exchange-correlation functional PBE0 as implemented in the PCGAMESS version of the GAMESS-US program package. The Hay and Wadt effective core potential (ECP) and the LANL2DZ basis set were used for Ru atoms, the 3-21G(d) basis sets were used for the benzene rings and the CF_3 groups of the carboxylate ligands, and the 6-31G(d) basis sets were employed for all other atoms.