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Notes

Corannulene: A Preference for *exo*-Metal Binding. X-ray Structural Characterization of $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(\eta^2\text{-}C_{20}H_{10})_2]$

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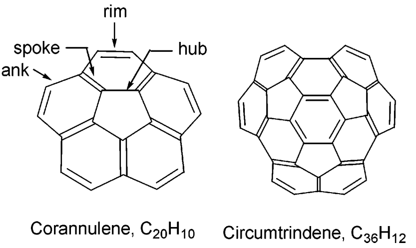
Summary: X-ray crystallographic characterization of the title complex, having only one ruthenium(I) center bound to each bowl, shows exo η^2*-rim coordination of* $C_{20}H_{10}$*.*

Introduction

Nonplanar polyaromatic hydrocarbons composed of five- and six-membered rings that map onto the surfaces of fullerenes have attracted considerable attention in recent years.[1,2] To date, new synthetic methods for their preparation based on flash vacuum pyrolysis[1] or conventional organic techniques[2] have been introduced and developed to yield over two dozen open geodesic polycyclic aromatic hydrocarbons. These synthetic developments have allowed a broad study of this unique class of bowl-shaped polyarenes, in which the outside (convex or *exo*) and the inside (concave or *endo*) unsaturated carbon surfaces exhibit different physical and chemical properties. Substantial efforts have recently been directed toward studying the interactions of metal centers with curved unsaturated carbon surfaces, including the elucidation of the reactivity of open geodesic polyarenes in metal coordination reactions. The question regarding the preferences of such polyarenes for metal binding to the concave π-surface versus the convex surface has been broadly addressed computationally,[3,4] but experimental evidence on the structural details of transition metal coordination to bowl-shaped polyarenes is quite limited.

Corannulene, the smallest bowl-shape polyarene built around a five-membered ring (Scheme 1), with its convex and concave surfaces both accessible, has been the primary model for theoretical and experimental coordination studies. In 1997, Seiders et al. were able to isolate the first cationic metal complex of corannulene, $[(C_5Me_5)Ru(\eta^6\text{-}C_{20}H_{10})]^+$, and to characterize it in solution by spectroscopic methods.[4] DFT calculations at that time clearly indicated a preference for *exo* binding,[4] but no experimental evidence was available to verify the prediction. The NMR confirmation of $[(C_5Me_5)Ir]^{2+}$ complexation by corannulene was reported six years later.[5] Unfortunately, the lack of X-ray-quality crystals again prevented structural determination of facial *endo* versus *exo* metal coordination in these complexes. It was not until 2004 that Vecchi et al. finally succeeded in structurally characterizing the first η^6-corannulene metal complex having one $[(C_5Me_5)Ru]^+$ unit bound to each face of the bowl (Figure 1a).[6] Last year the $[(C_5Me_5)Ru(\eta^6\text{-}C_{20}H_{10})][SbF_6]$ complex having a 1:1 ratio was also reported (Figure 1b).[6b] This was followed by the synthesis of three new

Scheme 1



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† University at Albany.

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silver complexes with corannulene, all having extended networks built on η^2-binding of Ag^+ ions to the rim carbon atoms of corannulene.[7]

Theoretical studies have mostly used alkali metals to examine the potential binding sites of curved π-systems, and additional effects contributed by more complex transition metals are still not well understood. The pioneering calculations by Seiders et al. in 1997 predicted that η^6-complexation of corannulene by $[Ru(C_5Me_5)]^+$ should occur preferentially on the convex face.[4] More recently, Dunbar[3f] found that electronic orbital interaction analysis favors outside (*exo*) binding of transition metal ions to corannulene by amounts ranging from about 5 to 11 kcal mol^{-1}. In contrast, for circumtrindene, a larger $C_{36}H_{12}$ geodesic polyarene (Scheme 1), a preferential binding of Ag^+ cations in the concave (*endo*) pocket of the bowl was predicted by DFT calculations.[3i] A DFT study of the Fe−corannulene system showed that the Fe^+ cation prefers to bind to the convex face of corannulene, whereas the neutral Fe atom prefers slightly the concave to the convex face.[3k] These theoretical predictions are yet to be confirmed experimentally.

In contrast to the solution phase experimental complexation studies described above,[4−7] we rely on gas phase reactions to test the reactivity of open geodesic polyarenes and to directly access their crystalline organometallic complexes.[8] For corannulene, two products having different compositions $\{[Rh_2(O_2CCF_3)_4]_m\cdot(C_{20}H_{10})_n\}$ (m:n = 1:1 and 3:2) have been prepared in a solvent-free environment, and both have been structurally characterized.[9] The compounds were found to exhibit extended 1D and 2D structures built on the bridging μ_2-η^2:η^2 and μ_3-η^2:η^2:η^2-modes of corannulene, respectively (Figure 2). This X-ray study revealed the rim preference of corannulene for coordination of electrophilic rhodium(II) centers and demonstrated that metals can readily bind to both the convex and the concave faces of the bowl. The same behavior was later found for larger bowls, dibenzo[*a*,*g*]corannulene and a hemifullerene.[8]

Since all our previously structurally characterized complexes have more than one metal coordinated to a bowl-shaped molecule,[8,9] we have been unable, until now, to determine experimentally the relative preferences of the concave and convex surfaces for metal binding. To address this question, we set out to isolate a discrete complex having a single metal coordinated to the corannulene bowl. For corannulene, the only such complex that has been structurally characterized to date has the $[Ru(C_5Me_5)]^+$ unit η^6-bound to the convex surface of the ligand (Figure 1b). Again, all other reported corannulene-based complexes have multiple metals bound to a single ligand.[6a,7]

Results and Discussion

To achieve our objective, we relied this time on the gas phase co-deposition of corannulene with the diruthenium(I,I) mixed carbonyl carboxylate unit, $[Ru_2(O_2CCF_3)_2(CO)_4]$ (**1**). It is noteworthy that Ru(I) is isoelectronic with the previously used Rh(II). Moreover, we have already shown that **1** uses both of its electrophilic ruthenium(I) centers in its coordination reactions with aromatic substrates.[10] However, the very limited volatility of the diruthenium complex **1**,[10] compared to that of dirhodium tetrakis(trifluoroacetate), $[Rh_2(O_2CCF_3)_4]$,[8,9] allowed us to readily create an excess of hydrocarbon molecules in the gas phase. This resulted in the formation, isolation, and characterization of the first bis-corannulene transition metal complex, namely, $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(C_{20}H_{10})_2]$ (**2**). This new compound was obtained in good yield as a pure single crystalline material, which was characterized spectroscopically and by X-ray crystallography. The isolated crystals are stable in dry air at room temperature but degrade slowly when exposed to moisture. In addition to weak aromatic C−H stretches, the IR spectrum of the product shows bands that are characteristic for carboxylate and carbonyl groups. As expected from group theory considerations, the number of CO and OCO stretches for **2** (C_1) is greater than that for the more symmetrical **1** (C_{2v}) and is consistent with its molecular symmetry (see Supporting Information). The ^1H NMR data indicate that corannulene dissociates from the dimetal complex, even in such noncoordinating solvents as $CHCl_3$ to release free corannulene.

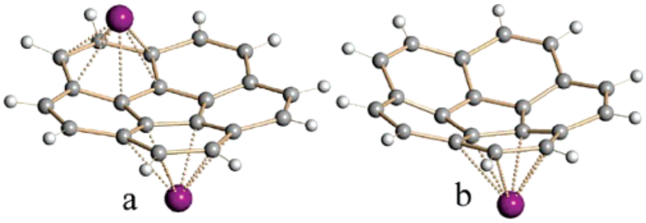

Figure 1. $[Ru(C_5Me_5)]^+$ complexes of corannulene showing (a) μ_2-η^6:η^6-$C_{20}H_{10}$ and (b) η^6-$C_{20}H_{10}$ coordination modes.[6] The C_5Me_5 ligands are omitted for clarity. Ru purple, C gray, H light gray.

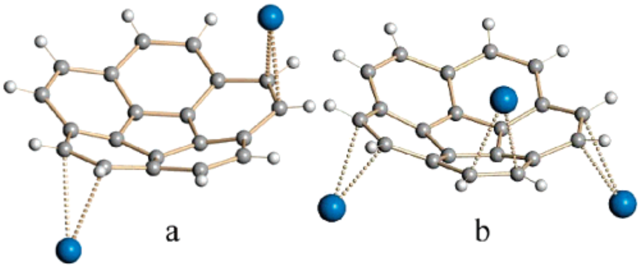

Figure 2. $[Rh_2(O_2CCF_3)_4]$-bound complexes of corannulene showing (a) μ_2-η^2:η^2-$C_{20}H_{10}$ and (b) μ_3-η^2:η^2:η^2-$C_{20}H_{10}$ coordination modes.[9] Only metal centers of the $[Rh_2(O_2CCF_3)_4]$ unit are shown. Rh blue, C gray, H light gray.

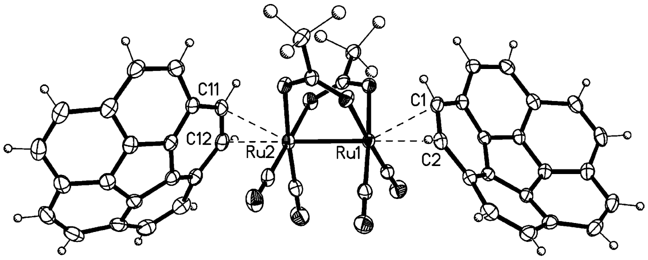

Figure 3. Perspective drawing of a bis-corannulene adduct, $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(\eta^2\text{-}C_{20}H_{10})_2]$ (**2**). Atoms are represented by thermal ellipsoids drawn at the 40% probability level. Fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Axial Ru···C contacts are shown as dashed lines.

The central diruthenium(I,I) unit in the bis-adduct **2** has a separate corannulene molecule attached to each axial position (Figure 3). The two crystallographically independent ruthenium centers of the dimetal unit each have bonding contacts with two carbon atoms: Ru(1)−C of 2.443(3) and 2.548(3) Å, Ru(2)−C of 2.468(3) and 2.574(3) Å. The average metal−carbon distance

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Table 1. Selected Bond Distances (Å) and Angles (deg) in the Structures of $C_{20}H_{10}$ and Complexes 1 and 2[a]

	$C_{20}H_{10}$[11b]	**1**[10]	**2**
Ru−Ru		2.6271(9)	2.6649(3)
Ru−$O_{carboxylate}$		2.153(6)	2.1459(19)
Ru−$C_{carbonyl}$		1.855(9)	1.852(3)
Ru−$C_{corannulene}$			2.508(3)
C≡O		1.135(11)	1.139(3)
C−$C_{rim\ coord}$			1.398(4)
C−$C_{rim\ free}$	1.3800(19)		1.376(4)
C−C_{flank}	1.4438(18)		1.445(4)
C−C_{spoke}	1.3779(16)		1.375(4)
C−C_{hub}	1.4137(17)		1.416(4)
OC−Ru−CO		88.2(4)	88.19(13)
O−Ru−O		84.1(2)	85.70(8)
C−C−$C_{hub-spoke}$	122.91(20)		123.0(3)
C−C−$C_{flank-spoke}$	114.32(24)		114.2(3)
C−C−$C_{flank-rim}$	122.02(17)		122.1(3)
C−C−$C_{flank-flank}$	130.07(36)		130.3(3)

[a] All distances and angles for $C_{20}H_{10}$, **1**, and **2** (except for Ru−Ru) are averaged. All X-ray data are collected at −100 °C.

of 2.508 Å in **2** is noticeably shorter than those distances in the previously reported rhodium(II)−corannulene complexes: 2.612 Å in the 1D chain and 2.584 Å in the 2D layer.[9] As with the isoelectronic rhodium(II),[8,9] both ruthenium(I) centers interact with the rim C═C bonds of the corannulene ligands. In contrast to the previously reported bridging modes of $C_{20}H_{10}$,[9] however, corannulene functions in a terminal mode in **2**. Importantly, there is only one metal center η^2-bound to each corannulene, and it is bound to the bowl on the *exo* face in the solid-state structure.

A comparison between the geometrical parameters of coordinated corannulene in **2** with those in the uncomplexed $C_{20}H_{10}$ molecule[11] (Table 1) shows that there is little perturbation of the corannulene core upon ruthenium(I) complexation. For example, the distances between the two carbon atoms coordinated to each ruthenium are slightly elongated, being 1.401(4) and 1.394(4) Å for the two metal centers, compared to the average rim bond length of 1.3800(19) Å in uncomplexed $C_{20}H_{10}$. There is also a noticeable reduction in the overall curvature of corannulene in the bis-adduct: the bowl depth of $C_{20}H_{10}$ in **2** is 0.860(1) versus 0.875(2) Å in the free corannulene molecule.[11] At the same time, the Ru−Ru distance of 2.6649(3) Å within the dimetal unit in **2** is elongated compared to that of 2.6271(9) Å in the parent ruthenium(I) carbonyl trifluoroacetate complex **1**.[10]

We anticipated that packing effects in the structure of **2** might affect metal coordination. A thorough analysis of the solid-state packing of the $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{20}H_{10})_2]$ molecules, however, revealed only very weak intermolecular $\pi-\pi$ stacking interactions. The closest contact is found between the six-membered rings of corannulenes belonging to neighboring molecules of **2** that approach each other at a distance of 3.718(3) Å. Such a weak intermolecular contact hardly deserves to be mentioned, and it should not affect the mode of metal coordination to the bowl.

It should be mentioned here that a close analysis of the extended networks formed by Ag^+ cations with corannulene in the presence of several counterions also shows a tendency for η^2-silver coordination to the outside of the bowl. In the three structurally characterized complexes, corannulene was found to be coordinated to two silver ions through proximal or distal rim bonds (Figure 4a and b, respectively), as well as to four silver atoms through four of the five rim bonds (Figure 4c).[7] In all cases silver ions are bound to the corannulene bowl from its convex face.

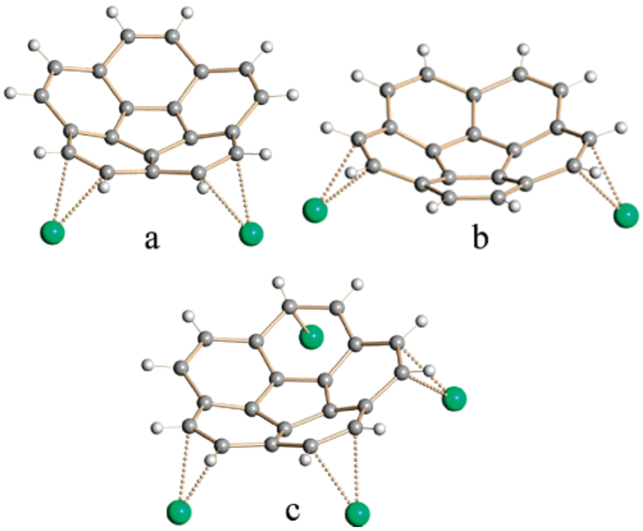

Figure 4. Structurally confirmed examples of silver(+) coordination to corannulene showing (a, b) μ_2-η^2:η^2-$C_{20}H_{10}$ and (c) μ_4-η^2:η^2:η^2:η^1-$C_{20}H_{10}$ modes.[7] All silver ions (shown in green) are *exo*-bound.

Density functional theory (DFT) based theoretical calculations were performed to evaluate the η^2-binding preferences of the $[Ru_2(O_2CCF_3)_2(CO)_4]$ unit to the *exo* and *endo* rim sites of corannulene. The optimized geometries of the diruthenium unit and of two rim-bound corannulene complexes, η^2-outside (*exo*) and η^2-inside (*endo*), are presented in the Supporting Information. The calculated Ru−C bond distances are significantly longer in the *endo*-complex, averaging to 2.539 versus 2.475 Å in the *exo*-complex. The positive charges on the Ru centers dropped upon complexation of corannulene compared to the value of +0.176 in the uncomplexed electrophilic diruthenium unit, but the remaining charge is greater in the *endo*-bound complex being +0.105 versus +0.098 in the *exo*-complex. However, our calculations predicted that both η^2-rim complexes are energetically very close, with only a slight preference of 1.78 kcal mol^{-1} for the η^2-*exo*-bound structure.

In summary, the use of a new diruthenium(I,I) unit having two open centers of Lewis acidity and very limited volatility has resulted in the isolation of the first bis-corannulene metal complex having only one metal coordinated to the bowl. The ruthenium(I) center is η^2-rim-bound, with the metal coordinated to the bowl from the *exo* face. Along with the previously reported $[Ru(C_5Me_5)]^+$− and Ag^+−corannulene complexes,[6,7] this work demonstrates the preference of the convex (*exo*) carbon surface of corannulene for metal coordination. The experimental results were supported by DFT calculations, which predict the η^2-*exo*-rim complex to be slightly favored energetically over the η^2-*endo*-bound structure.

Experimental Section

General Remarks. Commercially available reagents were used as received to synthesize $[Ru_2(O_2CCF_3)_2(CO)_4]$ using the published procedure.[10] The IR spectrum was measured on a Nicolet Magna 550 FTIR spectrometer using a KBr pellet. The NMR spectra were collected on a Varian Gemini spectrometer at 300 MHz for ^1H and 282 MHz for ^{19}F at 22 °C. Elemental analysis was performed by Canadian Microanalytical Service, Delta, British Columbia.

Synthesis of $[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}(C_{20}H_{10})_2]$ (2). A mixture of corannulene, $C_{20}H_{10}$ (0.002 g, 0.008 mmol), and $[Ru_2(O_2CCF_3)_2(CO)_4]$

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(0.005 g, 0.010 mmol) was loaded into a small glass ampule under an inert atmosphere. The ampule was sealed under vacuum and placed in a tube furnace at 110 °C. Small block-shaped orange crystals started to appear in the cold part of the ampule in 1 day. To increase the yield, the ampule was kept in the oven for 12 days. Yield: 70%. Anal. Calcd for $C_{48}H_{20}F_6O_8Ru_2$: C, 55.38; H, 1.92. Found: C, 55.43; H, 1.69. IR (KBr, cm^{-1}): 3040(w), 2974(w), 2928(w), 2855(w), 2080(sh), 2047(s), 2031(sh), 2012(s), 1976(s), 1650(s), 1633(sh), 1459(m), 1431(w), 1346(w), 1313(w), 1263(sh), 1211(s), 1200(sh), 1159(sh), 1152(s), 1120(sh), 864(s), 848(w), 833(m), 825(sh), 791(w), 736(m), 670(m), 662(m), 566(m), 556(sh), 516(w). ^{1}H NMR ($CDCl_3$, 22 °C): δ 7.80 ($C-H_{arom}$ of free corannulene). ^{19}F NMR ($CDCl_3$, 22 °C): δ -74.72 (same as the ^{19}F NMR of **1** in $CDCl_3$).

X-ray Crystal Structure Determination of 2. The X-ray diffraction experiment was carried out on a Bruker SMART APEX CCD diffractometer equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operating at 1800 W power. The orange block of **2** (0.11 × 0.07 × 0.07 mm) was found to be triclinic, $P\bar{1}$, a = 8.2756(5) Å, b = 15.8362(9) Å, c = 16.2107(10) Å, α = 110.210(1)°, β = 92.539(1)°, γ = 103.155(1)°, V = 1923.7(2) Å^3, Z = 2, D_c = 1.797 g·cm^{-3}, μ = 0.875 mm^{-1}. A total of 16 881 reflections were collected at 173(2) K in the range 1.56° ≤ θ ≤ 28.33°. The frames were integrated with the Bruker SAINT software package[12] using a narrow-frame integration algorithm. The data were corrected for absorption effects using the empirical method SADABS[13] (minimum/maximum apparent transmissions are 0.9099/0.9413). The structure was solved by direct methods and refined using the Bruker SHELXTL (Version 6.10) software package.[14] All non-hydrogen atoms were refined anisotropically, except the disordered fluorine atoms of the two CF_3 groups, for which disorder was modeled over three rotational orientations. Hydrogen atoms of corannulene were found in the difference Fourier map and refined independently. Full-matrix least-squares refinement on F^2 converged at R_1 = 0.0322 and wR_2 = 0.0792 for 675 parameters and 7567 reflections with $I > 2\sigma(I)$ (R_1 = 0.0378, wR_2 = 0.0822 for 8657 unique reflections) and a goodness of fit 1.006. Final difference map is between +0.713 and −0.500 e/Å^3.

DFT Calculations. Molecular geometry optimizations were performed at the DFT level of theory using the hybrid exchange−correlation functional PBE0 as implemented in the PC GAMESS 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, while the 6-31G(d) basis sets were employed for all other atoms. Single-point calculations along with the NBO analyses were performed using the above ECP and the same basis set for Ru atoms and the 6-311G(d,p) basis sets for all other atoms (for calculation details see Supporting Information).

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Supporting Information Available: An X-ray crystallographic file, in a CIF format; computation details and tabular materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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