Corannulene Complexes

Transition-Metal Complexes of an Open Geodesic Polyarene**

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Scarcely half a year after the first isolation of solid C_{60},[1] transition-metal complexes of fullerenes began appearing on the rapidly growing list of novel derivatives.[2] At almost the

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same time, a surge of interest in bowl-shaped "fullerene fragments" spawned parallel efforts to prepare transition-metal complexes of open geodesic polyarenes. The intriguing question regarding the preference for metal binding to the concave surface versus the convex surface was first addressed computationally by Faust and Vollhardt,[3] and has been revisited more recently by others.[4, 5] Experimental evidence to support or refute these predictions has, until now, eluded investigators.[6]

Corannulene (Figure 1), the smallest geodesic polyarene ($C_{20}H_{10}$), has previously been found to form a very weak [(η^6-corannulene)Ru(C_5Me_5)] cationic π complex that can be characterized in solution by spectroscopic methods.[4b] Unfortunately, its lability precluded crystallographic analysis that would establish whether the metal binds to the concave surface or the convex surface of the hydrocarbon. In the gas phase, corannulene forms both 1:1 and 2:1 cationic complexes with iron ({(corannulene)Fe^+} and {$(corannulene)_2Fe^+$}, respectively).[7] Ligand attachment studies with the 1:1 complex point to η^4 binding of the corannulene with iron; however, the facial preference of the metal is again undetermined. Attempts to prepare the π complex of the C_3-symmetric "semibuckminsterfullerene" [{η^2-Pt(PPh_3)$_2$}{$C_{30}H_{12}$}] by treatment with [Pt(C_2H_4)(PPh_3)$_2$] did not follow the same course as with C_{60}, but led instead to oxidative addition of a strained aryl–aryl C–C bond to the metal center, yielding an η^2-coordinated σ-bonded {Pt(PPh_3)$_2$} complex.[8] Herein we report the first two X-ray crystal structures of transition metal complexes of a geodesic polyarene, namely, corannulene. These new complexes also represent the first η^2-coordinated π complexes of a hydrocarbon in this class. As many as three metal atoms are seen to form a complex with a single corannulene, and π bonding occurs on both the convex and the concave surface.

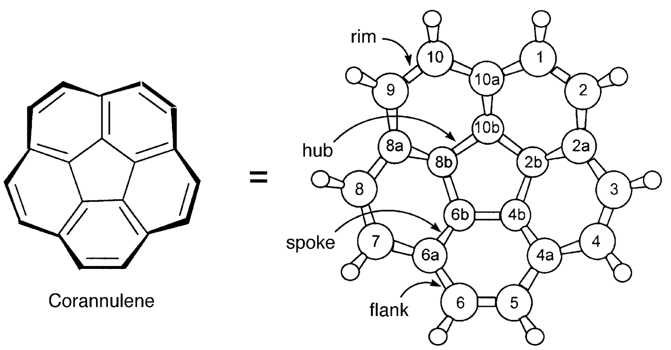

Figure 1. Corannulene structure and atom numbering. There are four types of C–C bonds: rim, hub, spoke, and flank.

To prepare these new complexes, we relied on the recently introduced solvent-free synthesis strategy that has proven so successful for the preparation of other polycyclic aromatic hydrocarbon (PAH) complexes of dirhodium(II) tetrakis(trifluoroacetate), [$Rh_2(O_2CCF_3)_4$].[9] Studies to date with planar PAHs have revealed the interesting trend that η^2 metal coordination is site-selective and is correlated with the π-bond order of the C=C bonds, as determined by simple Hückel calculations. This makes the selected dirhodium complex a very sensitive electrophilic probe to test donor properties of the coordinatively more interesting nonplanar aromatic systems.

Corannulene was synthesized according to our three-step procedure,[10] and [$Rh_2(O_2CCF_3)_4$] was prepared in a form containing no additional ligands.[11] Synthesis of the complexes was accomplished by sublimation-deposition reactions of the volatile, complementary donor and acceptor partners. Two new products [[$Rh_2(O_2CCF_3)_4$]$_m$·($C_{20}H_{10}$)$_n$] (m:n = 1:1 (**1**) and 3:2 (**2**)) were isolated from two separate reactions performed at 160 °C.[12] The composition of the products was controlled by varying the reagent ratios in the solid state. An excess of ligand in the solid-state mixture (Rh_2:L ≈ 1:2) favored formation of product **1**, which was isolated in the form of green needle-shaped crystals in yields of 15–20 %. On the other hand, an excess of the dimetal complex (Rh_2:L ≈ 3:1) resulted in deposition of dark-green blocks of **2** in yields of 30–35 %. Crystals of both products **1** and **2** were prepared separately under controlled reaction conditions; they have distinctly different colors and shapes. Both products are relatively stable in air at room temperature but are sensitive to moisture; this behavior is typical for analogous donor–acceptor adducts with planar PAHs. When crystals of **1** or **2** are dissolved in acetone, the complexes undergo ligand exchange and release free corannulene, as confirmed by ^{1}H NMR spectroscopy.

X-ray diffraction studies of the crystals of compounds **1** and **2**[13] have revealed two unique structural motifs built on weak η^2 coordination. Compound **1** is a one-dimensional (1D) polymer consisting of alternating dirhodium units and corannulene molecules (Figure 2). Two crystallographically independent rhodium atoms of the dimetal unit each have bonding contacts with two carbon atoms. Rh1 approaches the ligand from the convex (*exo*) side of the corannulene moiety, while Rh2 binds from the concave (*endo*) side. Both rhodium centers interact with the rim C=C bonds of the ligand in an η^2 coordination mode. There is a significant difference between the two Rh–C bond lengths (0.225 Å) for the Rh1

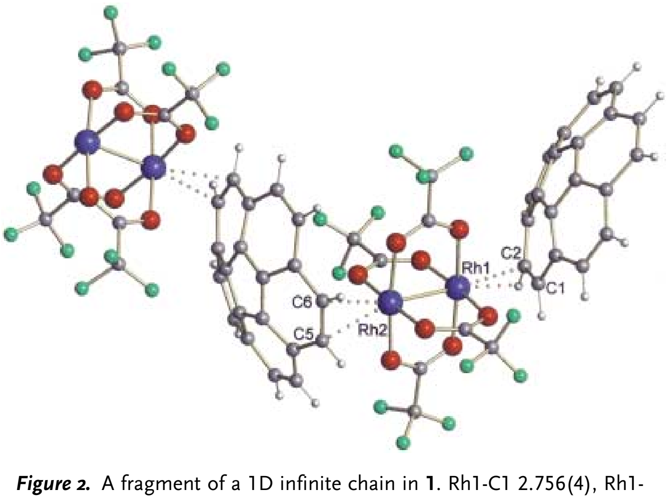

Figure 2. A fragment of a 1D infinite chain in **1**. Rh1-C1 2.756(4), Rh1-C2 2.531(4), Rh2-C5 2.595(4), Rh2-C6 2.564(4) Å.

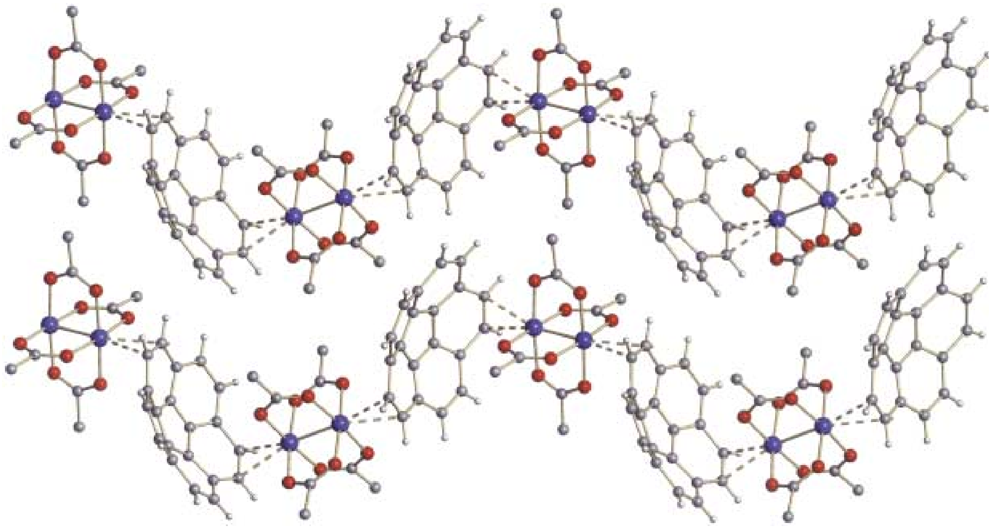

Figure 3. Crystal packing in **1**; Rh blue, O red, C gray, H light gray; fluorine atoms are are omitted for clarity.

atom (*exo* coordination), while there is only a difference of 0.031 Å for the contacts with the Rh2 center (*endo* coordination). The average Rh–C separation is also slightly longer for the rhodium atom that approaches corannulene from the convex side (2.643(4) Å for Rh1; 2.580(4) Å for Rh2). There are no close interactions between the 1D zigzag chains in the crystal structure of **1** (Figure 3).

Compound **2** has an infinite 2D layered network consisting of giant hexagonal cells built of six dimetal units and six corannulene molecules (Figure 4). Each corannulene molecule is coordinated to three dimetal units; two from the convex side and one from the concave side (Figure 5). As in **1**, only rim carbon atoms of the ligand are involved in coordination to the rhodium atoms. All three linear dirhodium units use both axial positions for coordination, with each rhodium center binding two carbon atoms of a corannulene (η^2 coordination mode). For the three crystallographically independent rhodium atoms in the asymmetric unit (Rh1, Rh2, and Rh3), the Rh–C bond lengths are averaged to

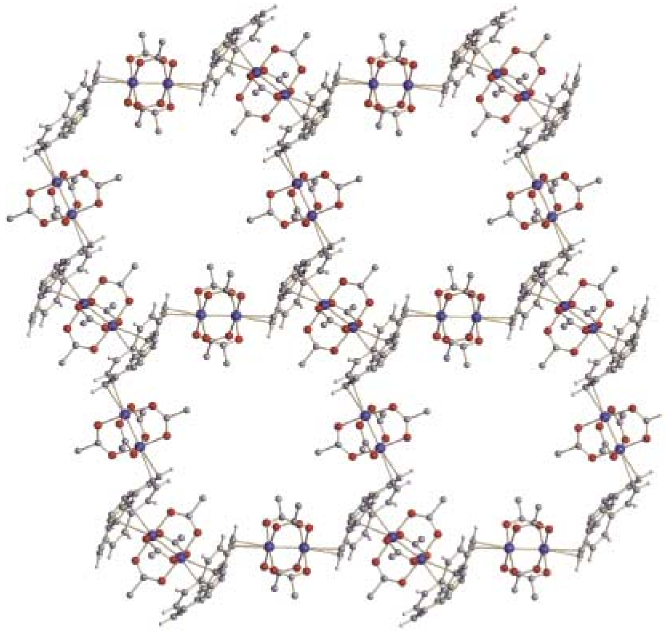

Figure 4. A fragment of a 2D infinite layer in **2**; Rh blue, O red, C gray, H light gray; fluorine atoms are omitted for clarity.

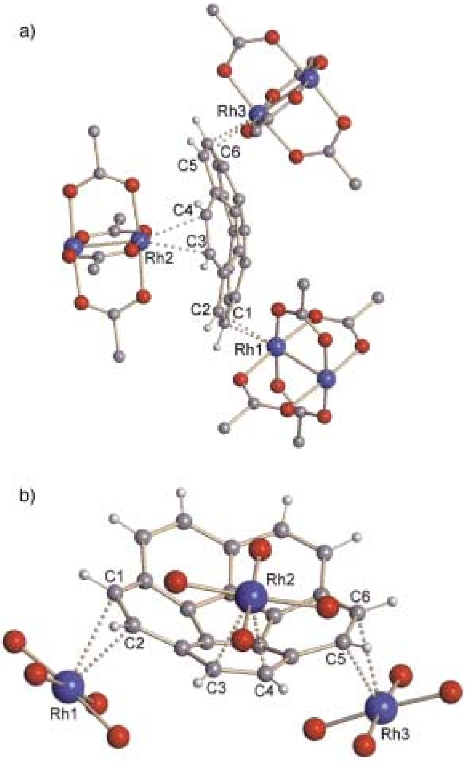

Figure 5. a) A side view of a corannulene molecule in **2** coordinated to three dimetal units. Rh1-C1 2.775(3), Rh1-C2 2.496(3), Rh2-C3 2.565(3), Rh2-C4 2.575(4), Rh3-C5 2.477(3), and Rh3-C6 2.618(3) Å; b) a front view of corannulene showing the six coordinating carbon atoms.

2.636(3), 2.570(3), and 2.548(3) Å, respectively, with the differences between the two Rh–C bonds for each rhodium atom being 0.279, 0.010, and 0.141 Å, respectively. Again, a significant difference is observed for two Rh–C separations with metal atoms that approach the curved surface of corannulene from the convex side (Rh1 and Rh3).

It is informative to compare the structural characteristics of corannulene in complexes **1** and **2** with those of the "free" $C_{20}H_{10}$ polyarene molecule obtained at −70 °C.[14] This comparison (Table 1) reveals that the metal–π interaction is very weak and does not perturb the structure of the corannulene molecule significantly. Only a slight elongation of the rim C=C bond occurs upon coordination (0.009 Å in **1** and 0.018 Å in **2**), while other geometric characteristics of corannulene in the complexed and uncomplexed forms remain very similar. For example, the sum of the bond angles at the carbon atoms of the complexed rim C=C bonds in corannulene are essentially identical to those of the uncomplexed rim C=C bonds; they all fall in the range 359–360°. Thus, there is no detectable pyramidalization of carbon atoms upon complexation. The characteristics of the dimetal core in both complexes are quite typical for donor–acceptor adducts with weakly bound π-donor ligands.

Table 1: Geometric characteristics of corannulene in the free and coordinated forms

C–C Type	Corannulene (−70 °C)[14a]	**1**	**2**	C=C π-bond order[14b]
hub	1.413(2)	1.413(6)	1.415(4)	0.27
spoke	1.391(4)	1.375(6)	1.371(4)	0.46
flank	1.440(2)	1.447(6)	1.445(5)	0.27
rim (free)	1.402(5)	1.387(6)	1.379(5)	0.73
rim (coordinated)	–	1.396(6)	1.397(4)	–

The observed coordination of electrophilic Rh^{II} centers exclusively at the rim C=C bonds of corannulene in both **1** and **2** is surprising in light of the high kinetic preference shown by other electrophilic species for attack at the radial C=C bonds of corannulene (for example, dihalocarbenes (:CX_2); X = Cl, Br, and I)[15,16] and at the hub carbon atoms (for example, CCl_3, $CHCl_2$, and *i*Pr cations).[16,17] On the other hand, complexation of planar PAHs by $[Rh_2(O_2CCF_3)_4]$ is invariably seen at the rim where η^2-type bonding occurs at the C=C sites with the highest π-bond order.[9] In this connection, a simple analysis of the eleven canonical resonance structures of corannulene indicates a significantly higher Pauling π-bond order for the rim than for the radial C=C bonds (Table 1).[14b]

It is noteworthy that every corannulene unit in both the 1D (**1**) and the 2D (**2**) organometallic networks has one $[Rh_2(O_2CCF_3)_4]$ unit complexed to the concave surface. Baldridge and co-workers calculated that the $[Ru(C_5Me_5)]$ cation should show a preference of about 6 kcal mol^{-1} for complexation to the convex surface of corannulene, whereas Frash et al. calculated a 3 kcal mol^{-1} preference for complexation of Li^+ ions to the convex surface.[4] With $[Rh_2(O_2CCF_3)_4]$, on the other hand, DFT calculations predict a slight preference for complexation to the concave surface of corannulene (approximately 2 kcal mol^{-1}).[18] This result conforms to the view that the electrostatic potential of geodesic polyarenes is more negative on the concave surface than on the convex surface[19] and that $[Rh_2(O_2CCF_3)_4]$ is an exquisite probe for sites of high electron density. Steric hindrance precludes the coordination of two $[Rh_2(O_2CCF_3)_4]$ units to the concave surface of corannulene and presumably directs the two $[Rh_2(O_2CCF_3)_4]$ units on the convex surface in **2** to distal, rather than adjacent rings. It is not obvious, however, why the *endo* $[Rh_2(O_2CCF_3)_4]$ unit in **2** then complexes to the ring between these two, rather than to one of the less congested rings.

With this designed synthesis of corannulene-based organometallic networks we have demonstrated the potential of the gas-phase deposition technique for the coordination of curved surface geodesic polyarenes. This approach readily afforded transition-metal complexes of corannulene in crystalline forms suitable for structural characterization for the first time. Other geodesic polyarenes are currently being examined under similar experimental conditions.

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[12] Synthesis of **1** and **2**: Mixtures of [$Rh_2(O_2CCF_3)_4$] with corannulene were sealed under vacuum in two separate small glass ampoules. The ratio of the dirhodium complex (0.020 g, 0.030 mmol) to the ligand (0.014 g, 0.056 mmol) was ca. 1:2 in the synthesis of **1**. This ratio in the synthesis of **2** was ca. 2.7:1 (dirhodium complex (0.035 g, 0.053 mmol); corannulene (0.005 g, 0.020 mmol)). The ampoules were placed in electric furnaces that had a small temperature gradient along the length of the tube. The temperature was set at 160 °C in both cases. In three days, crystals of **1** and **2** were deposited in the middle or coldest parts of the ampoules where the temperature was a few degrees below 160 °C. **1**: Yield ca. 15–20 %; IR (KBr): 3067(w), 3041(w), 1664(s), 1464(w), 1441(w), 1402(w), 1349(w), 1314(w), 1225(s), 1194(s), 1170(s), 863(m), 856(m), 785(m), 740(s), 677(m), 663(m) cm^{-1}. **2**: Yield ca. 30–35 %; IR (KBr): 3061(w), 3041(w), 1664(s), 1463(w), 1439(w), 1401(w), 1318(w), 1230(s), 1196(s), 1165(s), 866(s), 788(m), 742(s), 671(m) cm^{-1}. ^1H NMR (200 MHz, [D_6]acetone, 22 °C): $\delta = 7.94$ ppm (s).

[13] X-ray crystal data for **1**: $Rh_2C_{28}F_{12}O_8H_{10}$, $M_r = 908.18$, green needle, $0.25 \times 0.07 \times 0.05$ mm, monoclinic, space group $C2/c$, $a = 34.767(2)$, $b = 8.9125(6)$, $c = 18.9825(12)$ Å, $\beta = 104.0530(10)°$, $V = 5705.9(6)$ Å^3, $Z = 8$, $T = 173(2)$ K, $\rho_{calcd} = 2.114$ g cm^{-3}, $2\theta_{max} = 56.38°$. For **2**: $Rh_6C_{64}F_{36}O_{24}H_{20}$, $M_r = 2474.26$, dark-green block, $0.14 \times 0.09 \times 0.08$ mm, triclinic, space group $P\bar{1}$, $a = 11.2082(7)$, $b = 12.8271(8)$, $c = 13.3417(8)$ Å, $\alpha = 94.7400(10)$, $\beta = 96.5280(10)$, $\gamma = 92.9660(10)°$, $V = 1895.5(2)$ Å^3, $Z = 1$, $T = 173(2)$ K, $\rho_{calcd} = 2.168$ g cm^{-3}, $2\theta_{max} = 56.54°$. Bruker SMART APEX CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.1) Software Package. Data were corrected for absorption effects using the empirical methods SADABS (min./max. apparent transmission are 0.7390/0.9384 and 0.8237/0.8934 for **1** and **2**, respectively. All non-hydrogen atoms were refined anisotropically except the disordered fluorine atoms. All H-atoms of corannulene were found in the difference Fourier map and refined independently. The fluorine atoms of some CF_3 groups were disordered over two or three different rotational orientations. This disorder was modeled individually in each case. For **1**, full-matrix refinement on F^2 converged at $R1 = 0.0433$ and $wR2 = 0.1114$ for 494 parameters and 5799 reflections with $I > 2\sigma(I)$ ($R1 = 0.0489$, $wR2 = 0.1164$ for 6572 unique reflections) and a goodness-of-fit of 1.055. For **2**, full-matrix refinement on F^2 converged at $R1 = 0.0285$ and $wR2 = 0.0705$ for 644 parameters and 7607 reflections with $I > 2\sigma(I)$ ($R1 = 0.0330$, $wR2 = 0.0734$ for 8556 unique reflections) and a goodness-of-fit of 1.046. CCDC-201188 and -201189 contain the supplementary crystallographic data for structures **1** and **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retreiving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax (+44)1223–336–033; or deposit@ccdc.cam.ac.uk).

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[18] Our calculations were performed at the B3LYP/3-21G* level of theory, with an [(ethylene)$Rh_2(O_2CCF_3)_4$] unit as the electrophile, using the Spartan suite of programs (Wavefunction Inc., Irvine, CA). Higher level basis sets (e.g., 6-31G*) do not have orbitals for rhodium in Spartan. Note that these calculations probe the intrinsic interaction of only a single corannulene molecule with a single dirhodium unit in the gas phase; no attempt was made to assess the influence of the extended network in the crystal.

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