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Geodesic Polyarenes

Hemibuckminsterfullerene $C_{30}H_{12}$: X-ray Crystal Structures of the Parent Hydrocarbon and of the Two-Dimensional Organometallic Network $\{[Rh_2(O_2CCF_3)_4]_3\cdot(C_{30}H_{12})\}$**

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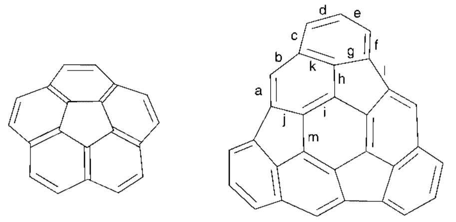
Since the discovery of fullerenes,[1] bowl-shaped polyarenes that map onto the surface of C_{60} have attracted considerable attention.[2] These geodesic fullerene fragments or "buckybowls" represent an exciting new class of aromatic ligands that exhibit unique chemistry.[2f] Substantial efforts have recently been directed toward studies of the reactivity and ligating properties of buckybowls, but very few of their transition metal complexes have been isolated.[3,4] Last year, we finally succeeded in preparing the first crystalline complexes of a geodesic polyarene, using the sublimation–deposition technique in a solvent-free environment with the smallest bowl-shaped polycyclic aromatic hydrocarbon, corannulene (**1**, $C_{20}H_{10}$, Figure 1).[4] The availability of crystallographic data allowed us to determine the preferred sites for metal binding to the curved unsaturated carbon surface of this open geodesic polyarene, and η^2 coordination of as many as three metal atoms to the rim carbon atoms of corannulene



1 **2**

Figure 1. Corannulene (**1**) and hemifullerene (**2**). Pauling π-bond orders: a) 0.74, b) 0.28, c) 0.37, d) 0.63, e) 0.37, f) 0.63, g) 0.37, h) 0.28, i) 0.51, j) 0.28, k) 0.37, l) 0.00, m) 0.23.

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was observed in crystalline complexes with dirhodium(II) tetrakis(trifluoroacetate) [$Rh_2(O_2CCF_3)_4$]. In the present work, we extend this powerful synthetic approach to a new system and use [$Rh_2(O_2CCF_3)_4$] as an electrophilic probe to test the donor properties of the much larger buckybowl hemibuckminsterfullerene **2** ($C_{30}H_{12}$, Figure 1).

Hydrocarbon **2** represents a C_3-symmetrical half of C_{60} fullerene and for this reason has long appealed to chemists as a possible intermediate for the laboratory synthesis of buckminsterfullerene.[5] Furthermore, dehydrogenative dimerization of *endo* metal complexes of **2** might even provide a direct and controlled route for metal encapsulation in fullerenes.

The first synthesis of hemifullerene **2** was completed in 1995;[6] however, no crystal structure has been reported heretofore, owing to the lack of crystals suitable for X-ray analysis. As a consequence, the intriguing question of the preference for metal binding to the concave versus the convex surface of this deep $C_{30}H_{12}$ bowl has been addressed only computationally.[7] Previous attempts to prepare a transition metal complex of **2** by treating it with [$Pt(C_2H_4)(PPh_3)_2$] were thwarted by insertion of platinum into the peripheral C–C bond of one of the five-membered rings.[8] The feasibility of such an unusual aryl–aryl C–C bond breaking has been attributed to the relief of strain at the edge of this curved aromatic hydrocarbon.

Herein we report the first X-ray crystal structures of **2** (two different polymorphs) and the X-ray crystal structure of its coordination complex with [$Rh_2(O_2CCF_3)_4$]. In the latter, four rhodium(II) centers are bound to a single hemifullerene molecule to afford a unique two-dimensional (2D) extended organometallic network.

Hemifullerene **2** was synthesized according to the six-step synthesis we reported in 1997[9] and was crystallized from the vapor phase.[10] Two types of crystals of **2** were deposited at about 240 °C in vacuum, and both were crystallographically characterized.[11] X-ray diffraction studies on the two polymorphs of **2**, one orthorhombic (**2-o**) and the other trigonal (**2-t**), revealed two different molecular packing motifs based on π–π interactions (Figure 2). Ordered assembly of bowls to form interlocking *exo–exo* and *endo–endo* columnar stacks is found in **2-o**. Such stacking differs from the solid-state structures of the simplest curved polycyclic hydrocarbon, corannulene (**1**),[12] and of the largest bowl that has been crystallographically characterized so far, circumtrindene ($C_{36}H_{12}$).[13] Columnar stacking of the $C_{30}H_{12}$ bowls along the threefold axis is found in **2-t**, with insertion of the convex dome of one bowl into the concave cavity of the next (*exo–endo* type), similar to the ordered pattern observed in the crystal structure of circumtrindene.[13] Despite these differences between **2-o** and **2-t**, the estimated volumes per $C_{30}H_{12}$ molecule in the two structures are very similar, 425.4 and 424.1 Å^3, respectively. Several C–C contacts are in the range of typical π–π interactions (3.5–3.7 Å) in the solid-state structures of both **2-o** and **2-t**; the shortest distances are 3.547(4) in **2-o**, and 3.253(4) and 3.323(4) Å in **2-t**.

The nonplanar $C_{30}H_{12}$ molecule is chiral and exists as a pair of enantiomers.[14] Unfortunately, the racemic mixture obtained from the synthesis was inseparable by preparative chiral chromatography, so the crystal structures of **2-o** and **2-t** contain statistical distributions of the two enantiomers in all positions, with an average $^1/_2$ occupancy (Figure 3). This complication adversely affects the quality of structural information extracted from the X-ray experiments and reduces to some extent the reliability of the carbon–carbon distances obtained.

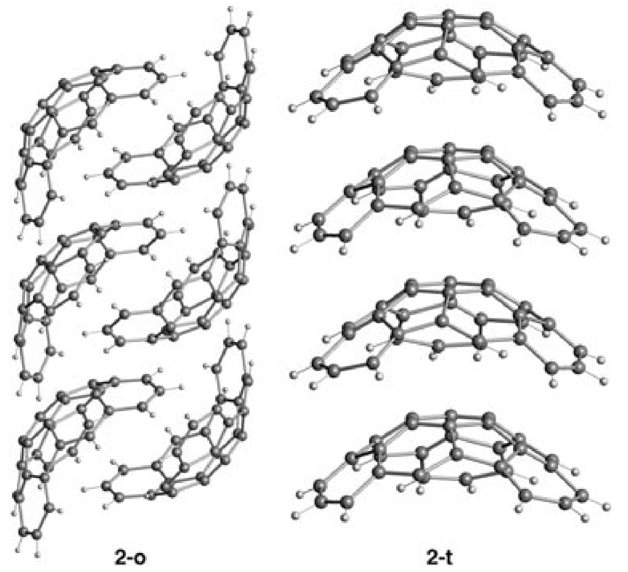

Figure 2. Solid-state packing in the orthorhombic crystals of **2-o** and in the trigonal crystals of **2-t**. Only one enantiomer is shown for clarity.

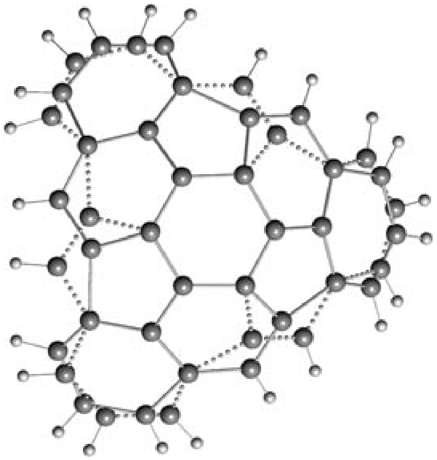

Figure 3. Superposition of the two enantiomers of the $C_{30}H_{12}$ hemifullerene **2**.

The hemifullerene coordination complex was synthesized by the microscale "solventless" ampule technique, which involves the co-deposition of volatile complementary donor and acceptor partners from the gas phase. We first applied this approach to the preparation of complexes of [$Rh_2(O_2CCF_3)_4$][15] with planar polycyclic aromatic hydrocarbons (PAHs)[16] and have successfully used the technique more recently for the synthesis and crystallization of corannulene-based organometallics.[4] With the hemibuckminsterfullerene **2**, only one product, $\{[Rh_2(O_2CCF_3)_4]_3\cdot(C_{30}H_{12})\}$ (**3**), was isolated reproducibly in the form of single crystals from deposition reactions of the dirhodium complex with the hydrocarbon performed at 164 °C.[17] Attempts to change the product composition by varying the reaction temperature or the ratio of reagents in the above system did not result in the formation of other crystalline complexes.

The above deposition reaction afforded **3** in the form of very small dark red crystals. The low yield obtained prevented accurate elemental analysis and may reflect the limited volatility of $C_{30}H_{12}$ compared to $C_{20}H_{10}$. Significant mass transfer of $C_{30}H_{12}$ was achieved at temperatures above 250 °C, but these conditions do not favor the formation of weak π complexes of rhodium(II) with PAHs. Crystals of **3** are stable in air at room temperature but are slightly sensitive to moisture; this behavior is typical for analogous donor–acceptor adducts of $[Rh_2(O_2CCF_3)_4]$ with planar PAHs and with corannulene. When crystals of **3** are dissolved in chloroform, the free hemifullerene is released, as confirmed by ^{1}H NMR spectroscopy.

The new coordination complex of hemifullerene **3** exhibits a unique structural motif, as revealed by an X-ray diffraction study.[18] The complex has an infinite 2D layered structure built on weak rhodium–carbon interactions of the two-ended electrophilic dirhodium molecules with the hemifullerene ligands (Figure 4).

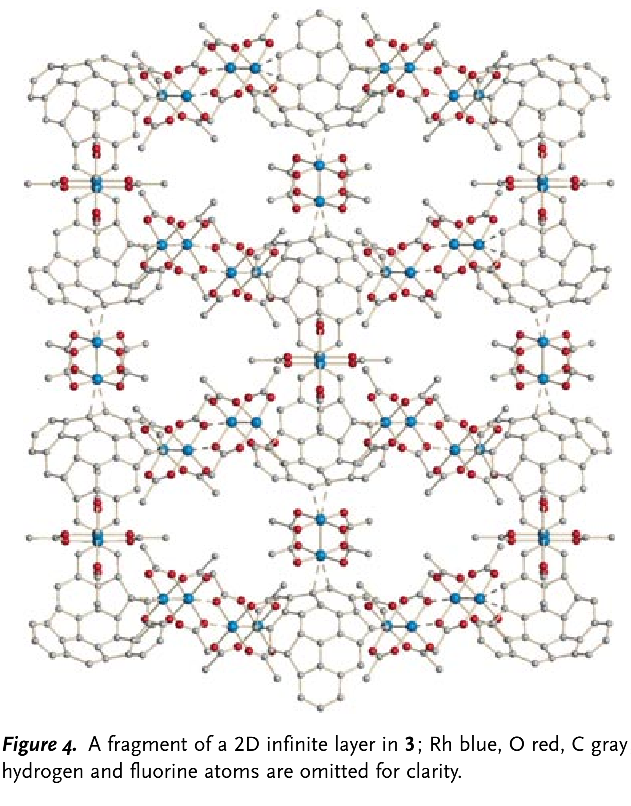

Figure 4. A fragment of a 2D infinite layer in **3**; Rh blue, O red, C gray; hydrogen and fluorine atoms are omitted for clarity.

Four metal centers from three crystallographically independent dirhodium complexes are bound to each $C_{30}H_{12}$ molecule, and this results in a tetradentate coordination mode that is unprecedented for buckybowls. Tetrabridged coordination of a planar PAH with $[Rh_2(O_2CCF_3)_4]$ was seen previously only in the case of chrysene.[16b] Three rhodium centers in **3** approach the hemifullerene ligand from the convex (*exo*) side, and one is bound to the concave (*endo*) side (Figure 5 a). Steric hindrance most probably precludes the coordination of two $[Rh_2(O_2CCF_3)_4]$ units to the concave surface of this deep bowl-shaped molecule and presumably directs positioning of the three $[Rh_2(O_2CCF_3)_4]$ units on the convex surface of the hemifullerene.

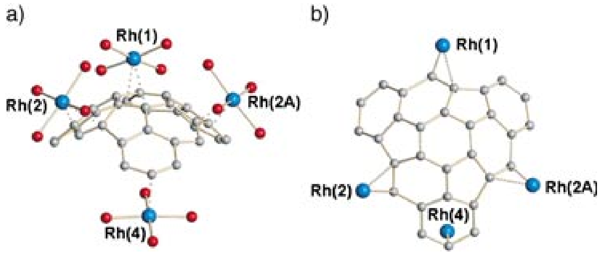

Figure 5. a) Side view of the $C_{30}H_{12}$ hemifullerene in **3** coordinated to four rhodium(II) centers. b) Top view showing the tetradentate $\eta^2{:}\eta^2{:}\eta^2{:}\eta^1$ coordination.

As in the corannulene complexes reported earlier,[4] only rim carbon atoms of the $C_{30}H_{12}$ hydrocarbon are involved in metal coordination. The three *exo*-coordinated rhodium centers (only two of which are crystallographically independent) each have bonding contacts with two carbon atoms of the hemifullerene (η^2 coordination mode). For these rhodium atoms, Rh(1) and Rh(2), the Rh–C distances average 2.50(2) and 2.46(2) Å, respectively. The coordination of the sole *endo*-bound rhodium atom is best described as η^1 (Figure 5 b), with the shortest Rh(4)–C distance being 2.536(17) Å (the two Rh–C distances to the adjacent carbon atoms are much longer at 2.97(2) Å). These data on Rh–C interactions are equally true for both enantiomers of hemifullerene in the structure of **3.**

In complex **3** only two of the three crystallographically independent dirhodium units have hemifullerene molecules bound to both of their open axial positions; one bridges *endo*/*endo*, and the other *exo*/*exo*. The third dirhodium unit binds to the $C_{30}H_{12}$ molecule only through Rh(2), and two such units are linked together at the other rhodium end to form a dimer of dimers core structure. This $[Rh_2(O_2CCF_3)_4]_2$ bridge is built on axial interactions of the Rh(1) centers with the carboxylic oxygen atoms of the neighboring dimetal unit at a distance of 2.347(8) Å. Analogous rhodium carboxylates with tetranuclear cores are known from both solution and gas-phase reactions.[19] The characteristics of the dimetal core in all of the dirhodium units in **3** are very similar to one another and are typical for donor–acceptor adducts with weakly bound π-donor ligands.

The observed coordination of the electrophilic rhodium(II) centers exclusively at the rim C=C bonds of the $C_{30}H_{12}$ bowl in complex **3**, which has four metal atoms coordinated to one ligand, may seem surprising at first. On the other hand, complexation of planar PAHs as well as corannulene by

$[Rh_2(O_2CCF_3)_4]$ units has invariably been seen at the rim, where η^2 bonding occurs at the C=C sites with the highest Pauling π-bond order. In this connection, a simple analysis of the 35 canonical resonance structures of hemifullerene **2** (Figure 1) indicates a significantly higher Pauling π-bond order on the rim than for any of the interior C=C bonds.[20] It is noteworthy that the *exo*-bound rhodium centers are coordinated to the rim carbon–carbon bonds of hemifullerene **2** that have the highest calculated π-bond orders.[21]

In conclusion, the X-ray structural study on the new hemifullerene-based organometallic complex $\{[Rh_2(O_2CCF_3)_4]_3\cdot(C_{30}H_{12})\}$ (**3**) reaffirms preference of buckybowls for metal η^2 binding at the rim. A tetradentate η^2:η^2:η^2:η^1-bridging coordination of the hemifullerene in **3** directs the formation of a unique 2D organometallic network built on rhodium(II)–carbon π interactions. The average Rh–C distances are shorter in **3** than in the corannulene-based organometallic compounds and thus indicate stronger π bonding in the title hemifullerene coordination complex.

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[10] Crystals of **2** were prepared by sublimation–deposition procedures. Solid microcrystalline powder of **2** (0.020 g, 0.054 mmol) was loaded into a small glass ampule, which was sealed under vacuum. The ampule was placed in an electric furnace having a small temperature gradient along the length of the tube. The temperature was set at 240 °C. Over 4 d, two types of crystals had grown in the tube. Small orange blocks (**2-o**) were found at the coldest end of the ampule where the temperature was set at ca. 230 °C. Yield for **2-o**: ca. 25 %. Yellow-orange needles (**2-t**) were collected from the middle part of the ampule. Yield for **2-t**: ca. 35 %. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): $\delta = 7.37$ (dd, 3H), 7.61 (d, 3H), 7.65 (d, 3H), 7.83 ppm (s, 3H).

[11] X-ray crystal data for **2-o**: $C_{30}H_{12}$, $M_r = 372.40$, orange block, $0.07 \times 0.07 \times 0.11$ mm, orthorhombic, space group *Pbca*, $a = 11.6064(8)$, $b = 13.0322(9)$, $c = 22.4925(15)$ Å, $V = 3402.1(4)$ Å^3, $Z = 8$, $T = 90(2)$ K, $\rho_{calcd} = 1.454$ g cm^{-3}, $2\theta_{max} = 56.5°$. **2-t**: $C_{30}H_{12}$, $M_r = 372.40$, yellow-orange needle, $0.03 \times 0.04 \times 0.26$ mm, trigonal, space group *R*3*m*, $a = 18.612(2)$, $c = 4.2196(5)$ Å, $V = 1265.9(3)$ Å^3, $Z = 3$, $T = 90(2)$ K, $\rho_{calcd} = 1.466$ g cm^{-3}, $2\theta_{max} = 50.0°$. Bruker SMART APEX CCD diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. The structures were solved by direct methods and refined with the Bruker SHELXTL (Version 6.1) Software Package. For **2-t**, data were corrected for absorption effects by using the empirical methods SADABS. For **2-o** and **2-t**, only C atoms having full occupancies were refined anisotropically. All H atoms of the hemifullerene were included at idealized positions for structure-factor calculations. For **2-o**, full-matrix refinement on F^2 converged at $R1 = 0.0679$ and $wR2 = 0.1638$ for 250 parameters and 2135 reflections with $I > 2\sigma(I)$ ($R1 = 0.1341$, $wR2 = 0.1884$ for 4121 unique reflections) and a GOF of 0.956. For **2-t**, full-matrix refinement on F^2 converged at $R1 = 0.0333$ and $wR2 = 0.0687$ for 77 parameters and 462 reflections with $I > 2\sigma(I)$ ($R1 = 0.0423$, $wR2 = 0.0718$ for 542 unique reflections) and a GOF of 1.072. CCDC-238109 and CCDC-238110 (**2-o** and **2-t**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[14] The Cahn–Ingold–Prelog (CIP) rules for designating chirality do not cover cases such as this. A simple convention is therefore proposed here to designate the chirality of open geodesic polyarenes, whether they be inherently chiral (e.g., **2**) or owe their chirality to some symmetry-lowering substitution. Step 1: View the molecule from the concave face, i.e., looking "into" the bowl. Step 2: Identify the rim atom that ranks highest in priority according to the CIP rules. Step 3: Compare the two rim atoms attached to this point of origin, and subsequent atoms attached thereto, if necessary, until two rim atoms that lie the same number of positions away on the clockwise and counterclockwise paths are found that differ in CIP priority. Step 4: If the direction of travel to the atom of higher CIP priority is clockwise, the chiral bowl is designated as *P*; a bowl requiring counterclockwise travel is designated as *M*. By this convention, the $C_{30}H_{12}$ bowl (**2**) pictured in Figure 1 would be designated as *M*, assuming that the concave surface is facing the reader.

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[17] Synthesis of **3**: A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.020 g, 0.030 mmol) and **2** (0.005 g, 0.013 mmol) was sealed under vacuum in a small glass ampule. The ampule was placed in an electric furnace at 164 °C. Over 3 d, tiny, dark red crystals of **3** grew in the hot zone of the tube. Yield: ca. 10 %. IR (KBr): $\tilde{\nu} =$ 3035(w), 2966(w), 1663(sh), 1665(sh), 1646(s), 1563(w), 1544(w), 1510(w), 1463(w), 1252(sh), 1199(s), 1168(sh), 1991(sh), 876(w), 868(w), 780(w), 745(m), 673(m), 615(w), 531 cm^{-1} (w). ^1H NMR (300 MHz, $CDCl_3$, 22 °C): $\delta = 7.37$ (dd, 3H), 7.61 (d, 3H), 7.65(d, 3H), 7.83 ppm (s, 3H).

[18] X-ray crystal data for **3**: $Rh_6C_{54}O_{24}F_{36}H_{12}$, $M_r = 2346.10$, dark red block, $0.03 \times 0.03 \times 0.04$ mm, monoclinic, space group $C2/m$, $a = 22.732(2)$, $b = 27.799(3)$, $c = 12.2244(11)$ Å, $\beta = 95.455(2)°$, $V = 7690.1(12)$ Å^3, $Z = 4$, $T = 213(2)$ K, $\rho_{calcd} = 2.026\ g\,cm^{-3}$, $2\theta_{max} = 45.04°$. Only rhodium and oxygen atoms were refined anisotropically. All H atoms of the hemifullerene were included at idealized positions for structure-factor calculations. 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. Full-matrix refinement on F^2 converged at $R1 = 0.0613$ and $wR2 = 0.1092$ for 412 parameters, 30 restraints, and 2375 reflections with $I > 2\sigma(I)$ ($R1 = 0.1461$, $wR2 = 0.1292$ for 5169 unique reflections) and a GOF of 0.821. CCDC-238111 contains the supplementary crystallographic data for **3**; see ref. [11] for ordering information.

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[21] Higher level molecular orbital calculations (B3LYP/6-31G*) predict bond lengths [Å] that correlate approximately with those derived from simple considerations of Pauling bond orders (see Figure 1): a) 1.3917, b) 1.4571, c) 1.4237, d) 1.3908, e) 1.4228, f) 1.3851, g) 1.4342, h) 1.4063, i) 1.3787, j) 1.4424, k) 1.4124, l) 1.5138, m) 1.4278. It is interesting to note that metal complexation is observed at the rim bond with the highest Pauling order (a), in preference even to bonds that are calculated to have shorter lengths (d, f, and i).