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# Unprecedented Complexation of Two Transition Metals to the Concave Surface of a Geodesic Polyarene: $\{[Rh_2(O_2CCF_3)_4]_3(\text{dibenzo}[a,g]\text{corannulene})_2\}$

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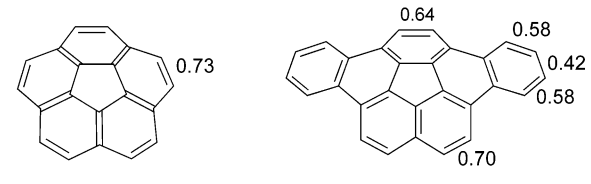
*Summary: X-ray structural characterization of the bowl-shaped dibenzo[a,g]corannulene, $C_{28}H_{14}$, and its first transition-metal complex, $\{[Rh_2(O_2CCF_3)_4]_3(C_{28}H_{14})_2\}$, has been accomplished. The latter exhibits a novel one-dimensional extended structure based on the tridentate $\eta^2{:}\eta^2{:}\eta^2$ rim coordination of dibenzo[a,g]corannulene. The large concave surface area of $C_{28}H_{14}$ allows for the first time two metal units to be endo-coordinated to a geodesic polyarene.*

The bowl-shaped dibenzo[*a*,*g*]corannulene[1] ($C_{28}H_{14}$; Figure 1) was first synthesized more than 10 years ago in the laboratory of Scott by a route that used flash vacuum pyrolysis (FVP) as the source of energy to bend a planar precursor.[2a,b] More recently, we developed a nonpyrolytic route to the same geodesic polyarene based on intramolecular palladium-catalyzed arylation reactions.[2c] No X-ray crystal structure of this fullerene subunit has ever been reported, nor have the reactivity of the hydrocarbon and its donor properties in metal coordination reactions ever been explored. The parent corannulene ($C_{20}H_{10}$; Figure 1) is a poor ligand for transition metals, and numerous attempts were made to bind metal ions to corannulene in solution[3] before Vecchi et al. finally succeeded just this year in preparing and structurally characterizing a corannulene complex having two $\eta^6$-coordinated $\{Cp^*Ru\}^+$ units.[4]

To probe the reactivity of polycyclic aromatic hydrocarbons (PAHs) and to identify their preferred binding sites, we use gas-phase, solvent-free complexation reactions of arenes with the volatile, electrophilic metal complex $[Rh_2(O_2CCF_3)_4]$. This approach has successfully revealed the metal binding behavior of corannulene[5a] and of a $C_{30}H_{12}$ hemibuckminsterfullerene.[5b] Moreover, gas-phase deposition reactions yielded the first metal complexes of these buckybowls to be isolated in crystalline form. Importantly, multiple metal coordination to a PAH can be readily achieved under gas-phase reaction conditions. For example, as many as three metal units were found to bind to corannulene, and four metal centers coordinate to a single hemibuckminsterfullerene ligand in the rhodium-based complexes that have been structurally characterized.[5] We have found the $[Rh_2(O_2CCF_3)_4]$ complex to be an exquisite electrophilic probe in deposition reactions, with the highly acidic rhodium(II) centers coordinating in a $\eta^2$ fashion to the carbon−carbon bonds of polyarenes at the sites having the highest calculated $\pi$-bond orders.[5c]



corannulene, $C_{20}H_{10}$ dibenzo[*a*,*g*]corannulene, $C_{28}H_{14}$

**Figure 1.** Corannulene ($C_{20}H_{10}$) and dibenzo[*a*,*g*]corannulene ($C_{28}H_{14}$) with the Pauling $\pi$-bond orders of the rim CH=CH sites. The Pauling $\pi$-bond orders of all remaining rim sites fall in the range 0.15−0.42.

Herein, we extend our studies on metal binding reactions to a new curved PAH and probe the coordination limits of dibenzo[*a*,*g*]corannulene, $C_{28}H_{14}$. We are interested in learning the effect of buckybowl geometry and curvature on the outcome of coordination reactions. In this regard, a comparison between the metal coordination reactions of corannulene and dibenzo[*a*,*g*]corannulene, two closely related bowl-shaped PAHs, should be very informative. Dibenzo[*a*,*g*]corannulene is expected to have a larger but shallower surface area than the parent corannulene,[6] and the X-ray structure

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(1) The IUPAC name for dibenzo[*a*,*g*]corannulene is acenaphtho-[3,2,1,8-*fghij*]picene.

(2) (a) Bratcher, M. S.; Scott, L. T. In *Abstracts of Papers, 207th National Meeting of the American Chemical Society*; San Diego, CA, March 1994; American Chemical Society: Washington, DC, 1994; ORGN 420. (b) Bratcher, M. S. Ph.D. Dissertation, Boston College, 1996. (c) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430.

(3) (a) Cheng, P.-C.; Preda, D. V.; Scott, L. T. Unpublished results. (b) Seiders, T. J.; Baldridge, K. K.; O'Connor, J. M.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 4781−4782. (c) Alvarez, C. M.; Angelici, R. J.; Sygula, A.; Sygula, R.; Rabideau, P. W. *Organometallics* **2003**, *22*, 624−626.

(4) Vecchi, P. A.; Alvarez, C. M.; Ellern, A.; Angelici, R. J.; Sygula, A.; Sygula, R.; Rabideau, P. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 4497−4500.

(5) (a) Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3375−3379. (b) Petrukhina, M. A.; Andreini, K. W.; Peng, L.; Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5477−5481. (c) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 11655−11663.

(6) (a) Dinadayalane, T. C.; Priyakumar, U. D.; Sastry, G. N. *J. Mol. Struct.* **2001**, *543*, 1−10. (b) Dinadayalane, T. C.; Deepa, S.; Sastry, G. N. *Tetrahedron Lett.* **2003**, *44*, 4527−4529.

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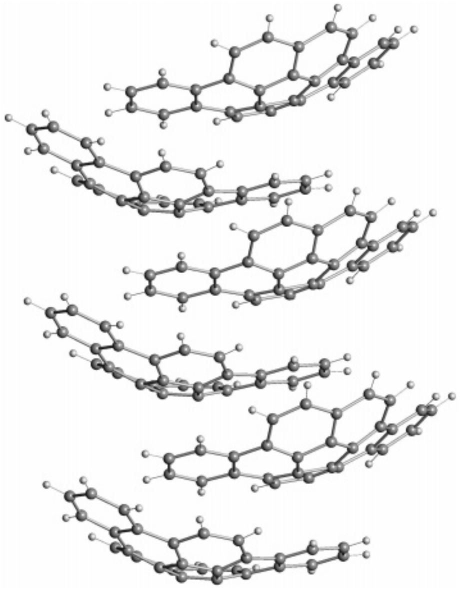

**Figure 2.** Solid-state packing of the $C_{28}H_{14}$ bowls.

reported below confirms this prediction. Moreover, the fusion of two peripheral benzene rings to the corannulene core disrupts the equivalence of the rim CH=CH sites in $C_{28}H_{14}$ (Figure 1). These differences should dictate different coordination modes for corannulene and dibenzo[*a*,*g*]corannulene in the organometallic products formed by their reactions with the linear $[Rh_2(O_2CCF_3)_4]$.

To reveal geometric characteristics of the bowl and to evaluate the effects of metal coordination on the geometry of the ligand, we have conducted a structural characterization of the $C_{28}H_{14}$ hydrocarbon.[7] Crystals of $C_{28}H_{14}$ were obtained by deposition under vacuum at 220 °C. An X-ray diffraction study revealed an ordered assembling of the $C_{28}H_{14}$ bowls into columnar stacks based on close $\pi-\pi$ interactions (Figure 2). Numerous C−C contacts between the bowls fall in the range 3.34−3.60 Å. The solid-state packing of the $C_{28}H_{14}$ molecules differs from that of corannulene[8] but is reminiscent of the stacks formed by the $C_{30}H_{12}$ hemibuckminsterfullerene (trigonal polymorph)[5b] and by circumtrindene ($C_{36}H_{12}$).[9] In the last two structures, however, the bowls were aligned along a crystallographic 3-fold axis, with the convex bottom of one bowl nested precisely within the concave surface of the next. The centers of dibenzo[*a*,*g*]corannulene bowls, by contrast, do not show a similar linear alignment. One may speculate that the type of packing observed in this $C_{28}H_{14}$ structure provides the strongest $\pi-\pi$ interactions for the given geometry of the bowl, because it allows the closest contacts between the peripheral benzene rings of one bowl with the central corannulene cores of the neighboring molecules. This is where the shortest C−C distances of 3.34−3.38 Å were found. As anticipated, the bowl depth[10] of dibenzo[*a*,*g*]corannulene (0.83 Å) is noticeably reduced relative to that of corannulene (0.87 Å).[8]

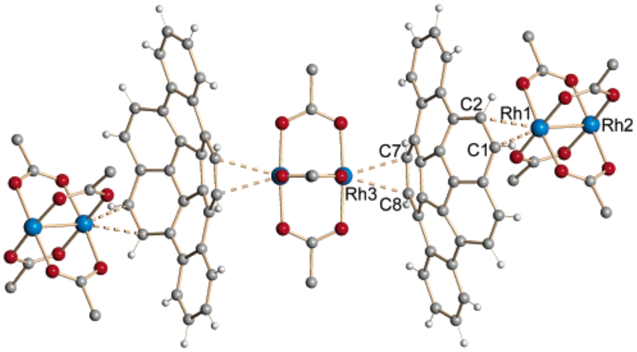

**Figure 3.** Centrosymmetric building unit in the structure of the title complex: Rh, blue; O, red; C, gray; H, light gray. F atoms are omitted for clarity.

Synthesis of the dibenzo[*a*,*g*]corannulene transition-metal complex was accomplished[11] in a solvent-free environment by deposition of the title hydrocarbon with an excess of the dimetal complex $[Rh_2(O_2CCF_3)_4]$. Heating the mixture at 160 °C under vacuum for 7−10 days resulted in the formation of small dark green plates as the only crystalline product. In this manner, the title compound was obtained as a pure single crystalline phase, which was characterized by spectroscopy and by X-ray crystallography. The micro scale on which these gas-phase coordination reactions were performed, combined with the moderate product yields, however, made it difficult to collect enough bulk material for elemental analysis.

The isolated crystals are air stable at room temperature but exhibit a slight sensitivity to moisture. When crystals of the complex are dissolved in dichloromethane or acetone, the free dibenzo[*a*,*g*]corannulene is released, as evidenced by $^1H$ NMR spectroscopy. The IR spectrum of the product shows characteristic aromatic C−H and carboxylate C−O stretches, thereby confirming the presence of both building moieties.

Several different crystals of the product were subjected to X-ray diffraction analysis. All conformed to the same unit crystal cell, thus confirming the homogeneity of the crystalline product obtained. The X-ray diffraction experiment of the metal complex was performed at the

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(7) X-ray crystal data for $C_{28}H_{14}$: $M_r = 350.39$, yellow block, $0.28 \times 0.17 \times 0.11$ mm, orthorhombic *Pbca*, $a = 7.3349(4)$ Å, $b = 17.6370(10)$ Å, $c = 24.6615(14)$ Å, $V = 3190.4(3)$ Å$^3$, $Z = 8$, $T = 90(2)$ K, $\rho_{calcd} = 1.459$ g cm$^{-3}$, $2\theta_{max} = 56.57°$, Bruker SMART APEX CCD diffractometer, Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structure was 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 (minimum/maximum apparent transmissions are 0.9772/0.9909). All carbon atoms were refined anisotropically. All hydrogen atoms of dibenzo[*a*,*g*]corannulene were found in the difference Fourier map and refined independently. Full-matrix refinement on $F^2$ converged at R1 = 0.0426 and wR2 = 0.1104 for 309 parameters and 3359 reflections with $I > 2\sigma(I)$ (R1 = 0.0473, wR2 = 0.1148 for 3779 unique reflections) and a goodness of fit of 1.036.

(8) (a) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr.* **1976**, *B32*, 1147−1153. (b) Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. Submitted for publication.

(9) Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766−5767.

(10) The "bowl depth" is taken as the shortest distance between the mean plane of the 5 interior carbon atoms and the mean plane of the 10 carbon atoms on the corannulene rim.

(11) A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.030 g, 0.045 mmol) and $C_{28}H_{14}$ (0.005 g, 0.014 mmol) was loaded in a small glass ampule under an inert atmosphere. The ampule was sealed under vacuum and placed in a tube furnace having a temperature gradient along the length of the tube. The temperature was set at 160 °C. In 8 days, small dark green plates of the product were deposited in the tube. Yield: 0.016 g, 39%. IR (KBr; cm$^{-1}$): 2854 w, 2928 w, 3052 w, 1667 s, 1462 w, 1426 w, 1235 sh, 1197 s, 1173 s, 866 m, 787 m, 742 s, 676 w, 650 w. $^1H$ NMR (400 MHz, $CD_2Cl_2$; δ): 8.77−8.70 (m, 4H), 8.40 (s, 2H), 8.32 (d, 2H, $J = 8.7$ Hz), 8.03 (d, 2H, $J = 8.7$ Hz), 7.82−7.79 (m, 4H).

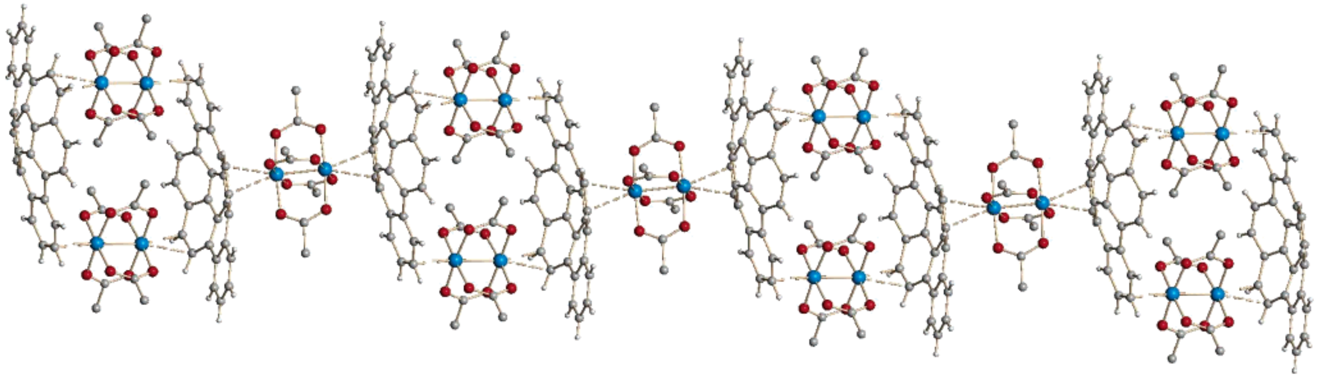

**Figure 4.** Fragment of the 1D chain in $\{[Rh_2(O_2CCF_3)_4]_3(C_{28}H_{14})_2\}_\infty$.

same temperature (−183 °C)[12] as that of the ligand for evaluation of the metal binding effect on the geometry of the bowl. The composition of the complex, $\{[Rh_2(O_2CCF_3)_4]_3(C_{28}H_{14})_2\}$, was revealed from the X-ray structural analysis. Interestingly, the product composition is the same as that found in the 2D corannulene-based network reported earlier ($[Rh_2]$:L = 3:2);[5a] however, the dibenzo[*a*,*g*]corannulene complex assembles the pieces in a different structural motif.

There are two crystallographically independent dimetal units, with one unit being centrosymmetric (Figure 3). The Rh(3) atom of the latter approaches the bowl from the exo face and has two bonding Rh−C interactions at 2.555(4) and 2.598(4) Å with the rim carbon atoms of the central corannulene part. The Rh(1) atom coordinates with two other rim carbon atoms of the corannulene core at distances of 2.583(4) and 2.599(4) Å, but it approaches the bowl from the endo face. The metal at the other end of this noncentrosymmetric unit, Rh(2), is endo-bound to one of the fused benzene rings of the neighboring $C_{28}H_{14}$ bowl. The two Rh(2)−C distances are 2.673(4) and 2.722(4) Å. This coordination results in the formation of a complex one-dimensional hybrid chain, $\{[Rh_2(O_2CCF_3)_4]_3(C_{28}H_{14})_2\}_\infty$ (Figure 4).

There are three metal centers coordinated to each dibenzo[*a*,*g*]corannulene bowl in the new organometallic rhodium complex (Figure 5). The average Rh(2)−C distance to the peripheral benzene ring of the bowl is slightly longer than the Rh(1)−C and Rh(3)−C distances to the central corannulene core, and this difference presumably reflects stronger $\eta^2$ coordination to the CH=CH sites with the largest Pauling π−bond orders (Figure 1). Steric crowding on the concave face of the dibenzo[*a*,*g*]corannulene may be responsible for $\eta^2$ coordination of Rh(2) to the most remote CH=CH site on the peripheral benzene ring, rather than to one of the adjacent sites, both of which have larger Pauling π-bond orders (compare Figures 1 and 5).

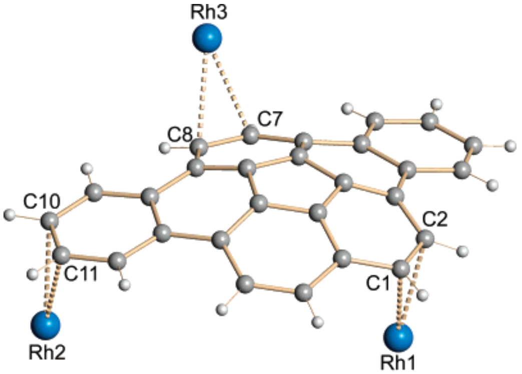

**Figure 5.** Tridentate $\eta^2$:$\eta^2$:$\eta^2$ coordination of dibenzo[*a*,*g*]-corannulene in its metal complex. Selected bond distances (Å): Rh(1)−C(1), 2.583(4); Rh(1)−C(2), 2.599(4); Rh(2)−C(10), 2.673(4); Rh(2)−C(11), 2.722(4); Rh(3)−C(7), 2.555(4); Rh(3)−C(8), 2.598(4).

Coordination is seen at the rim carbon atoms of dibenzo[*a*,*g*]corannulene only, and this is consistent with the binding preferences of the same electrophilic dirhodium complex to corannulene and the hemibuckminsterfullerene reported earlier.[5] On the other hand, this rim $\eta^2$ binding contrasts with the $\eta^6$ coordination of $\{Cp^*Ru\}^+$ units to corannulene in the crystallographically characterized dimetalated corannulene complex.[4] The latter coordination was found to cause significant structural changes in the ligand, such as reduction of the overall curvature of corannulene. A comparison of the geometrical parameters for dibenzo[*a*,*g*]corannulene in the free and coordinated forms (see the Supporting Information) shows no significant differences in the C−C distances in the structure of $C_{28}H_{14}$. However, the result of binding of three rhodium(II) centers to one bowl is clearly seen in the change of the bowl depth[10] from 0.83 to 0.77 Å.

In summary, the large concave surface area of dibenzo[*a*,*g*]corannulene in the new $\{[Rh_2(O_2CCF_3)_4]_3(\eta^2{:}\eta^2{:}\eta^2\text{-}C_{28}H_{14})_2\}$ complex allows coordination of two dirhodium units at endo sites on the bowl, which results in an unusual one-dimensional structural motif that was not seen in the corannulene complex of the same composition. In contrast, the corannulene complex $\{[Rh_2(O_2CCF_3)_4]_3(\eta^2{:}\eta^2{:}\eta^2\text{-}C_{20}H_{10})_2\}$ had a two-dimensional layered structure[5a] with two dimetal units exo-bound and only one unit endo-coordinated to $C_{20}H_{10}$. This comparison clearly demonstrates the role of the

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(12) X-ray crystal data for $C_{80}H_{28}F_{36}O_{24}Rh_6$: $M_r$ = 2674.48, dark green plate, 0.09 × 0.06 × 0.01 mm, triclinic $P\bar{1}$, $a$ = 9.3502(6) Å, $b$ = 15.1627(11) Å, $c$ = 16.7332(10) Å, $\alpha$ = 110.1980(10)°, $\beta$ = 96.4660(10)°, $\gamma$ = 107.7990(10)°, $V$ = 2055.7(2) Å$^3$, $Z$ = 1, $T$ = 90(2) K, $\rho_{calcd}$ = 2.160 g cm$^{-3}$, $2\theta_{max}$ = 56.31°, Bruker SMART APEX CCD diffractometer, Mo Kα radiation ($\lambda$ = 0.710 73 Å). Data were corrected for absorption effects using the empirical methods SADABS (minimum/maximum apparent transmissions are 0.8890/0.9867). All non-hydrogen atoms were refined anisotropically, except the disordered fluorine atoms. All hydrogen atoms of dibenzo[*a*,*g*]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. Full-matrix refinement on $F^2$ converged at R1 = 0.0434 and wR2 = 0.0801 for 709 parameters and 6927 reflections with $I > 2\sigma(I)$ (R1 = 0.0678, wR2 = 0.0874 for 9200 unique reflections) and a goodness of fit of 1.039.

geometry and curvature of a bowl in coordination reactions with the same linear metal complex.

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**Supporting Information Available:** Crystallographic data for $C_{28}H_{14}$ and its metal complex as CIF files and a figure giving comparative structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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