

Hexahapto Metal Coordination to Curved Polyaromatic Hydrocarbon Surfaces: The First Transition Metal Corannulene Complex

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Curved networks of trigonal carbon atoms,¹ such as that found in corannulene (**1**, Chart 1),^{1a–e} have attracted increased interest as fragments of buckminsterfullerene (C₆₀, **2**) and related carbon clusters.² Substantial efforts have been directed toward the synthesis of metal-complexed fullerenes, and a number of dihapto transition metal complexes of **2** have been prepared.³ Specifically, Fagan *et al.* reported the reaction of (C₅Me₅)Ru(NCMe)₃⁺O₃SCF₃[−] (**3**) and **2** to give {[C₅Me₅Ru(NCMe)₂]₃-C₆₀}³⁺(O₃SCF₃[−])₃ (**4**), in which each ruthenium is η²-bound to C₆₀.^{3a} This result is striking in that **3** readily forms η⁶-arene complexes with flat polyaromatic hydrocarbons such as corone (**5**),⁴ as well as with highly electron deficient arenes.^{5,6} Indeed, there have been no examples of hexahapto mononuclear metal coordination to **2** or any other curved network of trigonal carbon atoms.⁸ To this point, we report the reaction of **1** with **3** to give the first transition metal complex of corannulene and the first example of η⁶-coordination to a curved polynuclear aromatic hydrocarbon (PAH) surface.^{3b–j}

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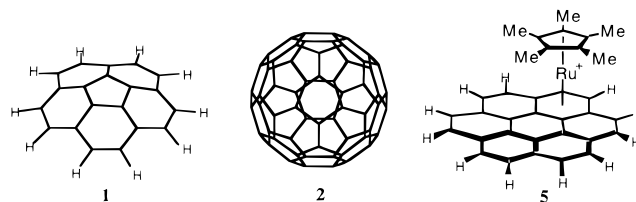
(4) Chávez, I.; Cisternas, A.; Otero, M.; Román, E. Z. *Naturforsch.* **1990**, *45b*, 658.

(5) (a) Dembek, A. A.; Fagan, P. J. *Organometallics* **1995**, *14*, 3741. (b) Dembek, A. A.; Fagan, P. J. *Organometallics* **1996**, *15*, 1319.

(6) An explanation of this preference for η² binding can be seen by considering that the carbon–carbon double bonds of **2** are ideally disposed toward binding in an η²-fashion with the four carbons attached to the double bonds bent back by 31°, approximately the same degree of bending found in many η²-alkene complexes.^{3a} In contrast, the ring substituents of hexahapto arene complexes show only minor deviations from the plane of the ring atoms compared to the deviations seen in **2**.

(7) Shapley has pointed out^{3j} that the gas phase ion CoC₆₀⁺ may have a η⁶-structure: Kan, S. Z.; Byun, Y. G.; Freiser, B. S. *J. Am. Chem. Soc.* **1994**, *116*, 8815.

Chart 1



Although **1** is a structural subunit of **2**, and the smallest bowl-shaped PAH, its surface curvature is substantially less than that of **2**. The carbon substituents on a six-membered ring of **2** are displaced from the mean plane of the ring by 80 pm, whereas for **1** that displacement is ca. 50 pm.⁹ This distinct difference in surface curvature suggested **1** to be an ideal starting point for the study of hexahapto metal coordination to curved networks of trigonal carbon atoms. In addition, **1** also affords the possibility of metal coordination to either the concave (endo) or the convex (exo) surface of the carbon network.

When a room temperature dichloromethane-*d*₂ solution of ruthenium cation **3** (12 mg, 0.03 mmol) and **1** (7.7 mg, 0.03 mmol) is monitored by ¹H NMR spectroscopy, the corannulene resonance at δ 7.84 decreases in intensity and a new set of resonances attributed to (η⁶-corannulene)Ru(C₅Me₅)⁺O₃SCF₃[−] (**6**) grow in at δ 1.65 (s), 6.59 (s), 7.60 (d, *J* = 9.0 Hz), 7.95 (d, *J* = 9.0 Hz), 8.11 (d, *J* = 9.0 Hz), and 8.18 (d, *J* = 9.0 Hz). After approximately 20 h, the ratio of **1**/**6** stabilized at ca. 1:1 and no further change is observed by ¹H NMR spectroscopy (*K*_{eq} = [6][CH₃CN]³/[1][3] = ca. 10² M²). Evaporation of the volatiles and addition of fresh dichloromethane-*d*₂ solvent leads to complete conversion of **1** to **6**, which was spectrally characterized by HRMS and various NMR techniques (Figure 1).^{10,11} Although both electron-rich^{8a,b} and electron-deficient⁵ (η⁶-arene)Ru(C₅Me₅)⁺O₃SCF₃[−] complexes are air-stable, complex **6** decomposes upon exposure to air in both the solid state and in solution.

Complex **4** has been suggested to undergo exchange of free and bound acetonitrile, concurrent with migration of ruthenium on the C₆₀ surface.^{3a} Addition of acetonitrile to dichloromethane-*d*₂ solutions of isolated **6** leads to arene–nitrile exchange and regeneration of **1** and **3**. Under ambient conditions, exchange occurs faster than the time required to obtain the NMR spectrum. Previously, Mann *et al.* established a second-order rate expression for exchange of arene ligands in (η⁶-arene)Ru(C₅Me₅)⁺ complexes with acetonitrile, but the reactions were much slower.¹² Intermolecular arene exchange between the

(8) An interesting class of hexahapto arene metal complexes with the ring substituents bent out of the plane of the arene is found with cyclophane ligands: (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (b) Ward, M. D.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C. *J. Am. Chem. Soc.* **1989**, *111*, 1719. (c) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2657. (d) de Meijere, A.; Reiser, O.; Stöbbe, M.; Kopf, J.; Adiwidjaja, G.; Sinnwell, V.; Khan, S. I. *Acta Chem. Scand. A* **1988**, *42*, 611. (e) Plitzko, K.-D.; Rapko, B.; Gollas, B.; Wehrle, G.; Weakey, T.; Pierce, D. T.; Geiger, W. E., Jr.; Haddon, R. C.; Boekelheide, V. *J. Am. Chem. Soc.* **1990**, *112*, 6545.

(9) The six-membered rings in buckminsterfullerene are symmetry constrained to a plane, whereas for corannulene the six-membered rings adopt a shallow boat structure with the bow and stern of the boat ca. 10 pm above the boat's base, as defined by the hub and rim carbons of **1**; the fold angle is approximately 10°.

(10) For **6**: ¹H NMR (500 MHz, CD₂Cl₂) δ 1.63 (s, 15H), 6.59 (s, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 9.0 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 2H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 10.17, 83.94, 93.54, 96.40, 101.63, 124.16, 128.83, 129.79, 132.52, 133.97, 136.89, 140.13; UV–vis (CH₂Cl₂) λ_{max} 227 nm (ε = 4.86 × 10³), 245 nm (ε = 4.27 × 10³), 292 (ε = 2.59 × 10³); HRFABMS M⁺ actual 487.0986, calcd 487.100.

(11) Addition of extra equivalents of **3** resulted in the appearance of a new set of corannulene ¹H NMR resonances presumably due to the formation of one isomer of (Cp*⁺Ru)²⁺-corannulene²⁺, but the complex was not isolated.

(12) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.

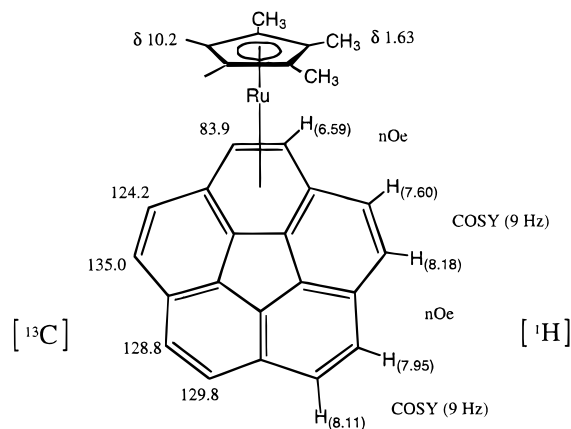


Figure 1. NMR spectral assignments for **6** deduced from COSY, NOE, and HMQC data. Chemical values in ppm relative to TMS. Relative NOE intensities are consistent with computed geometry.

corannulene ligand in **6** and benzene also occurs readily. Thus, addition of an excess of benzene (8.7×10^{-1} M) to CD_2Cl_2 solutions of **6** (8.53×10^{-3} M) at room temperature results in clean conversion to free corannulene and $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{C}_5\text{Me}_5)^+\text{O}_3\text{SCF}_3^-$ over the course of 24 h.

In principle, two types of intramolecular fluxional processes are possible for **6**: migration of the metal on the corannulene surface and bowl-to-bowl inversion (exo/endo interconversion). The barrier for bowl-to-bowl inversion in alkyl substituted corannulenes has been measured at ~ 10 kcal/mol.^{2d,13,1h} Although arene migration in RuCp^* systems is notoriously slow, one might assume that the air sensitive character of **6** and its anomalous propensity toward exchanging the corannulene fragment for nitriles betray faster intramolecular chemical dynamics. To address the dynamic behavior of **6**, we carried out variable-temperature ^1H NMR spectroscopic studies between -90 °C (CD_2Cl_2) and 140 °C ($\text{C}_2\text{D}_2\text{Cl}_4$). The ^1H NMR resonances for **6** remained unchanged across the entire temperature range, with onset of a slow irreversible decomposition occurring at 150 °C. Contrary to the scenario described above based on reactivity, the high-temperature results rule out intramolecular arene exchange in **6** on the NMR time scale ($\Delta G^\ddagger > 20$ kcal/mol). The low-temperature studies are consistent with either a rapid exo/endo interconversion on the NMR time scale or a slow exo/endo interconversion for which the population of the minor isomer is too low for detection by 500 MHz NMR spectroscopy.

Fagan et al. have pointed out that the p-orbitals of **2** are tilted away from the normal of the six-membered rings which may weaken overlap of the HOMO and LUMO with ruthenium-centered unfilled and filled d-orbitals.^{3a,12} Assuming no unusual rehybridization effects, the p-orbitals in corannulene tilt out on the convex face but in on the concave face. On the basis of Haddon's POAV analysis, the degrees of p-orbital tilting in **2** and **1** are 11.6° and 8.7° , respectively.¹⁴ The spectroscopic data for **6** do not distinguish between endo- and exo-coordination

(13) Scott, L. T.; Hashemi, M. M.; Bratcher, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 1920.

(14) In this context, we define tilt angle as POAV-90, see: (a) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243. (b) Haddon, R. C. *Science* **1993**, *261*, 1545. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.

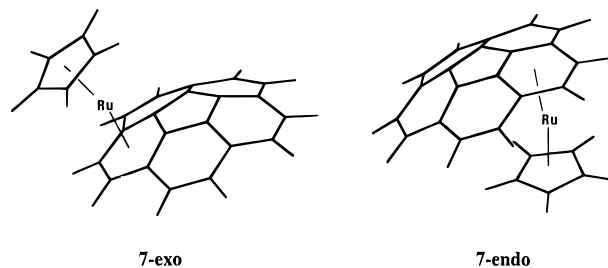


Figure 2. *Ab initio* (RHF/6-31G(d) plus Ru core potentials) structures of exo- and endo-**7** (H's unlabeled).

of ruthenium. We therefore carried out *ab initio* computations on the cyclopentadienyl analogue of **6** at the RHF/6-31G(d) level of theory with split valence effective core potentials for Ru.¹⁵

The computational results on $(\eta^6\text{-corannulene})\text{Ru}(\text{C}_5\text{H}_5)^+$ (**7**) predict the exo-**7** isomer to be ca. 6 kcal/mol more stable than the endo-**7** isomer (Figure 2); this energy difference at a T_c comparable to that measured for free **1** would lead to only one form being observed. The closest nonbonding interaction between the C_5H_5 ligand and the corannulene ring in endo-**7** is 3.5 Å. Assuming normal bond lengths, the methyls of endo-**6** would come into van der Waals contact with the umbrella of the corannulene fragment. The Ru-to-arene centroid distance is predicted to be slightly extended in the complexes of **7** as compared to simple benzene analogues. The cyclopentadienyl and arene rings remain essentially parallel, and the plane-to-plane angles for endo-**7** and exo-**7** is 2.9° and 0.5° , respectively. The bond lengths of the ring of corannulene bound to Ru show the normal Dewar-Chatte slight elongation, but nothing significant can be said about changes in bond alternation throughout the corannulene network.

The results found here impact upon the general question of how metals bind to curved surfaces. The outlook is promising that this phenomenon will be further elucidated experimentally and computationally through organometallic studies of more highly curved polynuclear aromatic hydrocarbon surfaces.

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Supporting Information Available: Spectra (^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, COSY, and HMQC 2-D NMR, HRMS) (6 pages). See any current masthead page for ordering and Internet access instructions.

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(15) The molecular structure of **1**, exo-**7**, and endo-**7** have been determined at the restricted Hartree-Fock (RHF) SCF level of theory with the analytically determined gradients and the search algorithms contained within GAMESS,¹⁶ using the 6-31G(d)¹⁷ split valence basis set for all second row atoms and the Stevens, Basch, Krauss split valence effective core potentials¹⁸ for Ru. The nature of each stationary point was uniquely characterized by calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies.

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