Angewandte
Chemie

Buckybowls

Synthesis and Structure of a Dimetallated Buckybowl: Coordination of One $\{Cp^*Ru\}^+$ Unit to Each Side of Corannulene**

Paul A. Vecchi, Celedonio M. Alvarez, Arkady Ellern, Robert J. Angelici, Andrzej Sygula, Renata Sygula, and Peter W. Rabideau*

In transition-metal complexes of buckminsterfullerene (C_{60}),[1] the metal atom is bonded to two carbon atoms (η^2) shared by two six-membered rings. On the other hand, curved-surface fragments of C_{60}, called buckybowls, are difficult to prepare and few transition-metal complexes of them have been reported.[2–4] Improved procedures for the synthesis of corannulene[5,6] ($C_{20}H_{10}$, **1**) have led to the preparation of the η^6 complexes $[Cp^*Ru(\eta^6\text{-}C_{20}H_{10})](O_3SCF_3)$[3] and $[Cp^*Ir(\eta^6\text{-}C_{20}H_{10})](BF_4)_2$,[4] in which Cp* is $\eta^5\text{-}C_5Me_5$. Although these complexes have been well-characterized by their NMR spectra, neither has been isolated as the analytically pure solid. Recently, the gas-phase deposition synthesis of $[\{Rh_2(O_2CCF_3)_4\}_m\cdot(C_{20}H_{10})_n]$ (m:n = 1:1 and 3:2), were reported.[2a] Their structures, as determined by X-ray diffraction studies, contain 1D and 2D networks of $[Rh_2(O_2CCF_3)_4]$ and corannulene units in which the $\{Rh_2\}$ groups are η^2-coordinated to both the convex and concave sides of the corannulene. These are the only crystal structures of transition-metal complexes of corannulene. Herein, we report the first X-ray structural characterization of a corannulene that contains η^6-coordinated metal fragments. Of particular interest are the observations that the two $\{Cp^*Ru\}^+$ fragments are on opposite sides of the corannulene bowl, which is significantly flattened as compared to free corannulene.

The reaction of $[\{Cp^*Ru(\mu_3\text{-}Cl)\}_4]$[7] (0.020 mmol) with $AgBF_4$ (for **2a**) or $AgPF_6$ (**2b**) (0.081 mmol) and **1** (0.040 mmol) in a 2:1 ratio of $\{Cp^*Ru\}^+$ to $C_{20}H_{10}$ in CD_3NO_2 under an Ar atmosphere at room temperature gave the dimetallated complex $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})]X_2$ ($X = BF_4^-$(**2a**), PF_6^-(**2b**)) (Figure 1). Both **2a** and **2b** are stable in CD_3NO_2 and CH_2Cl_2, very soluble in CD_3NO_2, and moderately soluble in CH_2Cl_2 at room temperature. They are insoluble in diethyl ether and hexanes, and the $\{Cp^*Ru\}^+$ units are displaced from the corannulene when the complex is dissolved in acetone. In the solid state, **2a** and **2b** are stable in dry air for weeks. After 1 week, a solution of **2b** in CD_3NO_2 in dry air decomposed ≈50% to $[Cp^*Ru(\eta^6\text{-}C_{20}H_{10})]^+$ with no evidence for free corannulene in the ^1H NMR spectrum. Shaking a CD_3NO_2 solution of **2b** with water results in decomposition with the liberation of free corannulene. While the existence of $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})]^{2+}$ was previously proposed on the basis of unspecified NMR data,[3] it was not further characterized.

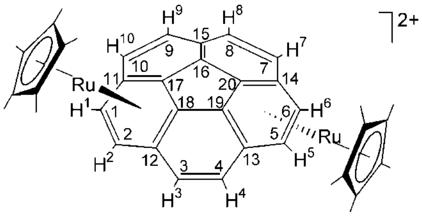

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Figure 1. Atom labeling Scheme for compound **2**.

The ^1H NMR spectrum of **2a** in the corannulene region (Figure 2) has signals in the narrow range ($\delta = 6.87$–6.74 ppm) that are shifted upfield with respect to the signal of free corannulene (e.g., $\delta = 7.85$ ppm for **1** in CD_3NO_2). These protons (H1, H2, H5, H6), which are doublets with J_{HH} values of 6 Hz, are assigned to the six-membered rings that are η^6-

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[*] P. A. Vecchi, Dr. C. M. Alvarez, Prof. Dr. R. J. Angelici
Department of Chemistry
Iowa State University
Ames, IA 50011 (USA)
Fax: (+1) 515-294-0105
E-mail: angelici@iastate.edu
Dr. A. Ellern
Molecular Structure Laboratory
Iowa State University
Ames, IA 50011 (USA)
Prof. Dr. A. Sygula, R. Sygula, Prof. Dr. P. W. Rabideau
Department of Chemistry
Mississippi State University
Mississippi State, MS 39762 (USA)

[**] This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7045-Eng-82 with Iowa State University. Cp* is $\eta^5\text{-}C_5Me_5$.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200454225

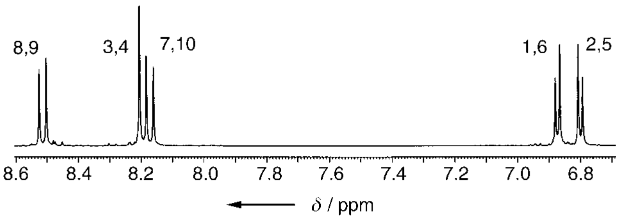


Figure 2. ^{1}H NMR spectrum of the corannulene region of **2A** in CD_3NO_2.

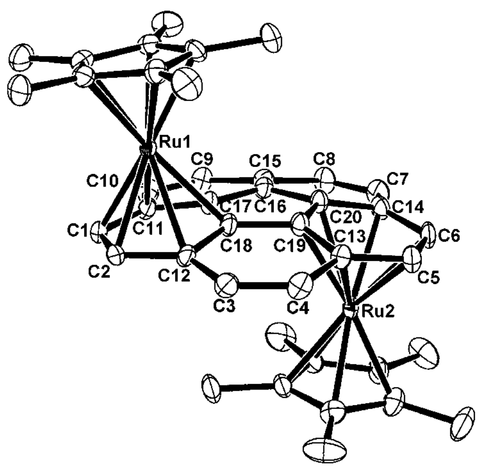
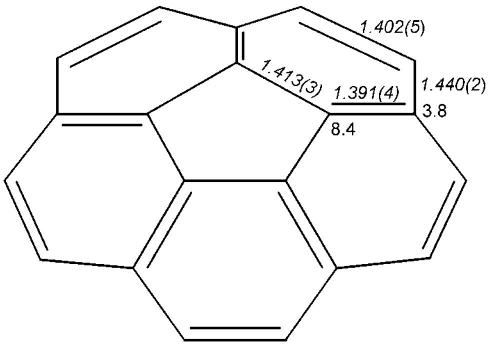


Figure 3. ORTEP drawing of $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})][PF_6]_2$ (**2b**). Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ru1–C1, 2.219(7); Ru1–C2, 2.214(6); Ru1–C12, 2.346(6); Ru1–C18, 2.209(6); Ru1–C17, 2.209(6); Ru1–C11, 2.343(7); Ru2–C5, 2.171(8); Ru2–C6, 2.169(7); Ru2–C14, 2.266(7); Ru2–C20, 2.276(7); Ru2–C19, 2.264(7); Ru2–C13, 2.263(7).

coordinated to the $\{Cp^*Ru\}^+$ units. Such upfield shifts are typical of other $[Cp^*Ru(\eta^6\text{-arene})]^+$ compounds.[7,8] The chemical shifts of the protons on the carbons not bonded to Ru are downfield of free corannulene, as is observed in $[Cp^*Ru(\eta^6\text{-}C_{20}H_{10})]^{+[3]}$ and $[Cp^*Ir(\eta^6\text{-}C_{20}H_{10})]^{2+}$.[4] These six protons appear as two doublets ($J_{HH} = 9$ Hz) and a singlet. Only one methyl signal is observed in the ^{1}H NMR spectrum, and it integrates to 30H. A COSY NMR experiment was carried out on complex **2a** and used in the assignment of the proton chemical shifts. The $^{13}C\{^1H\}$ NMR spectrum of **2a** shows six carbon signals between $\delta = 98.7$ and 81.1 ppm, which were assigned to the carbons bonded directly to the two Ru atoms. These signals are substantially upfield with respect to the uncoordinated carbon atoms ($\delta = 140.2$–126.7 ppm) and free corannulene ($\delta = 136.3$, 132.0 and 128.2 ppm for **1** in CD_3NO_2), a trend that is also observed in other $[Cp^*Ru(\eta^6\text{-arene})]^+$ complexes.[7,8] The NMR data clearly show that the ruthenium atoms are η^6 coordinated to two of the six-membered rings of corannulene.

Orange crystals of $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})][PF_6]_2$ (**2b**) suitable for an X-ray structure investigation were grown by inverse diffusion of a saturated methylene chloride solution of the complex surrounded by hexanes at −20 °C over a period of one week.[9] The crystals, which contained four molecules of CH_2Cl_2 per unit cell, quickly deteriorated when removed from the methylene chloride solution. The structure reveals that the $\{Cp^*Ru\}^+$ units bind to both the convex and concave sides of the $C_{20}H_{10}$ bowl (Figure 3). Coordination of the two $\{Cp^*Ru\}^+$ cations to the corannulene causes significant structural changes in the shape of the bowl. Differences in bond lengths are observed in the six-membered rings to which the $\{Cp^*Ru\}^+$ groups are coordinated; in these rings, the HC=CH rim bonds are elongated to an average of 1.454(11) Å from 1.402(5) Å in corannulene itself.[10] This elongation releases some strain in the corannulene subunit of **2b** causing a notable flattening of the bowl as compared to **1**. The diminished curvature of the coordinated bowl is clearly demonstrated by a π-orbital axis vector (POAV) analysis.[11] (Figure 4). The pyramidalization angles of the five central carbon atoms and those that are attached to them are on average 4.2° and 1.3°, respectively, in **2b**, whereas the analogous values for corannulene and its derivatives are 8.4° and 3.8°, respectively.[11,12] Thus, the curvature of the corannulene bowl in **2b** is reduced to approximately half of the curvature of corannulene. A closer view of the POAV values shows that they are smaller for the carbon atoms bonded to the convex $\{Cp^*Ru\}^+$ unit (0.8, 3.5, 3.7, 0.5°) than for those bonded to the concave $\{Cp^*Ru\}^+$ unit (2.1, 4.3, 4.4, 1.2°), which indicates that the convex $\{Cp^*Ru\}^+$ causes a greater flattening of the six-membered ring than the concave $\{Cp^*Ru\}^+$. This flattening of the bowl might be expected to



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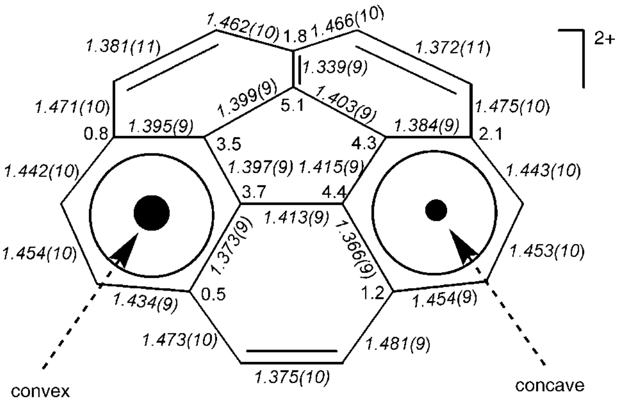

2b

Figure 4. POAV pyramidalization angles and C–C bond lengths (Å; values shown in italics) as found in corannulene (**1**) and $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})](PF_6)_2\cdot 4\,CH_2Cl_2$ (**2b**). Only the carbon atoms of the corannulene are shown for clarity.

reduce the barrier to inversion of the $C_{20}H_{10}$ bowl, which is known to have a barrier of 10–11 kcal mol^{-1} in corannulenes functionalized by organic groups on the rim carbon atoms.[13] A previous investigation of corannulene derivatives showed that a flattening of the bowl leads to a decrease in the bowl inversion barrier.[13] The methyl carbon atoms of the two Cp* ligands give a singlet in the room temperature ^{13}C NMR spectrum of **2b** in CD_2Cl_2 indicating rapid inversion of the bowl. Due to the insolubility of **2b** in CD_2Cl_2 at low temperatures, separate resonances for the convex and concave {Cp*Ru}$^+$ groups have not been observed.

Besides the different effects that the concave and convex {Cp*Ru}$^+$ units have on the flattening of the bowl, they also appear to interact with the six-ring carbon atoms differently. The Ru2−C distances for the concave {Cp*Ru}$^+$ unit are significantly shorter to the rim carbon atoms (C5, C6) (2.173(5) Å) than to the other four carbon atoms (C14, C20, C19, C13) (2.267(4) Å). However, the Ru1−C distances for the convex {Cp*Ru}$^+$ group are significantly longer to the atoms C11 and C12 (2.345(5) Å) than to the other four carbon atoms (C1, C2, C18, C17; 2.213(3) Å). Although these results await a theoretical interpretation, it is obvious that the binding of {Cp*Ru}$^+$ is different to the two sides of the bowl. It should be noted that a study of [Cp*Ru(η^6-fluoradene)]$^+$,[8] in which fluoradene ($C_{19}H_{12}$) is another type of curved surface hydrocarbon, showed that {Cp*Ru}$^+$ binds more strongly to the concave side than to the convex side.

In conclusion, complex **2b** is the first structurally characterized compound in which a buckybowl is η^6-coordinated. The {Cp*Ru}$^+$ moieties bind to non-adjacent arene rings on opposite sides of corannulene, and ^{13}C NMR spectroscopic evidence shows that the bowl undergoes rapid inversion at room temperature. Coordination of the {Cp*Ru}$^+$ fragments significantly reduces the overall curvature of the buckybowl; the convex {Cp*Ru}$^+$ group causes a greater flattening than the concave {Cp*Ru}$^+$ unit. These substantial structural effects of the {Cp*Ru}$^+$ units, which contrast with the absence of significant structural changes upon η^2-coordination to $[Rh_2(O_2CCF_3)_4]$,[2a] appear to be caused by the preference of {Cp*Ru}$^+$ for η^6-coordination to a planar arene ring.

Experimental Section

Synthesis and characterization of $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})](X)_2$ ($X = BF_4^-$ **2a**, PF_6^- **2b**): $AgBF_4$ or $AgPF_6$ (0.081 mmol) was added to a solution of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (0.022 g, 0.020 mmol) and corannulene (**1**; 0.010 g, 0.040 mmol) in 1 mL of CD_3NO_2. The solution was stirred at room temperature for 1 h, and the AgCl precipitate was removed by filtration. The resulting dark-orange solution was evaporated to dryness under vacuum to give an oily residue of **2a** or **2b**. These reactions are nearly quantitative by NMR spectroscopy. The residue was washed with diethyl ether (2 × 3 mL) and dried under vacuum. After **2a** or **2b** had been dissolved in 1–2 mL of CH_2Cl_2, the resulting solution was added to ≈5 mL of hexanes by cannula to give orange powders (0.034 g, 85 % yield, for **2b**). ^{1}H NMR (400.13 MHz, CD_3NO_2, RT, **2a**): $\delta = 8.51$ (d, ^3J(H,H) = 9 Hz, 2H, H8,9), 8.20 (s, 2H, H3,4), 8.17 (d, ^3J(H,H) = 9 Hz, 2H, H7,10), 6.87 (d, ^3J(H,H) = 6 Hz, 2H, H1,6), 6.80 (d, ^3J(H,H) = 6 Hz, 2H, H2,5), 1.27 ppm (s, Cp*, 30H). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3NO_2, RT, **2a**): $\delta = 135.1$ (C8,9), 132.2 (C3,4), 128.8 (C7,10), 98.7 (C-Ru), 98.5 (C-Ru), 96.9 (C-Ru), 96.8 (C_5Me_5), 95.6 (C-Ru), 86.9 (C2,5), 85.8 (C1,6), 9.0 (C_5Me_5), 135.6, 132.7 ppm (C15, C16). MS *m/z* 362 ($[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})]^{2+}$), electrospray in CD_3NO_2. Anal. Calcd for $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})](PF_6)_2\cdot 1\,CH_2Cl_2$: C, 44.86; H, 3.86. Found: C, 45.32; H, 3.99. The presence of CH_2Cl_2 in the sample was confirmed by an ^{1}H NMR spectrum of the compound in CD_3NO_2.

Full details of the synthesis and complete characterization of compounds **2a** and **2b**, including ^{1}H, ^{13}C{1H}, COSY NMR and mass spectra (**2a**), elemental analysis (**2b**), and thermal ellipsoid drawings and numbering Scheme for **2b** are given in the Supporting Information.

Received: March 9, 2004 [Z54225]

Keywords: aromaticity · corannulenes · ruthenium · structure elucidation

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[9] X-ray crystal data for $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{20}H_{10})][PF_6]_2\cdot 4\,CH_2Cl_2$ (**2b**): Orange single crystals were obtained by slow cooling a saturated CH_2Cl_2 solution of **2b** at room temperature to −77 °C. The crystals decomposed within seconds if contacted with air, and were therefore covered with premixed epoxy glue under the layer of solvent. The sample was immediately mounted under a stream of cold nitrogen and centered in the X-ray beam using a video camera for data collection. $C_{40}H_{40}F_{12}P_2Ru_2\cdot 4\,CH_2Cl_2$, $M = 1352.50$, triclinic, space group $P\bar{1}$, $a = 11.351(4)$ Å, $b = 12.414(4)$ Å, $c = 19.508(7)$ Å, $\alpha = 89.068(6)^\circ$, $\beta = 74.322(6)^\circ$, $\gamma = 82.114(6)^\circ$, $V = 2620.9(16)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.714$ g cm^{-3}; crystal dimensions 0.30 × 0.20 × 0.20 mm. A total of 23448 reflections (11787 unique, $R_{int} = 0.0398$) were collected using a full-sphere ω-scan routine ($2\theta_{max} = 56.64^\circ$) with Bruker SMART APEX CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at $T = 193(2)$ K. Data were corrected for absorption effects by empirical methods using SADABS software (min/max. transmission 0.67). The structure was solved by direct methods and refined using the SHELXTL (version 5.1) software package in full-matrix anisotropic approx-

imation for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and refined using the "riding model". The refinement converged to $R1 = 0.0760$, $wR2 = 0.2048$ for $I > 2\sigma(I)$, and $R1 = 0.1076$, $wR2 = 0.2357$ for all data, and a goodness-of-fit of 1.048. All significant electron density residuals were found approximately 1 Å from Ru atoms. CCDC-236736 contains 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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