π-Bowl Complexes

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A Dynamically Inverting π-Bowl Complex**

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The binding of metals to curved carbon π-surfaces has attracted continuous scientific interest since the discovery of metal complexes of buckminsterfullerene C_{60}.[1–3] Molecules that consist of fragments of C_{60}, that is, buckybowls, open geodesic polyarenes, or π bowls, possess curved carbon π-surfaces; examples include corannulene ($C_{20}H_{10}$) and sumanene (**1**, $C_{21}H_{12}$; Figure 1a).[4,5] From a coordination chemistry

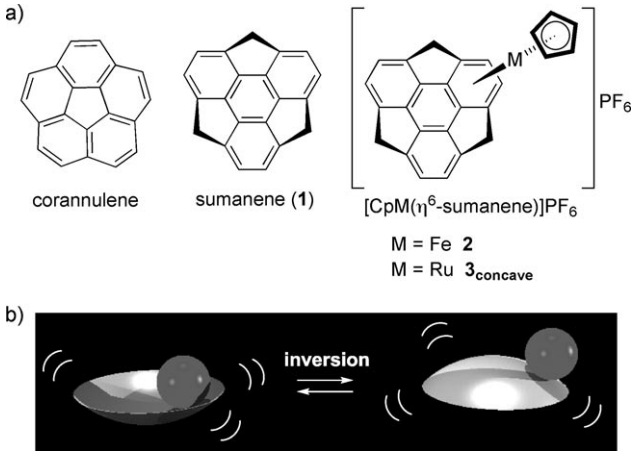

Figure 1. a) Corannulene, sumanene (**1**), and [CpM(η⁶-sumanene)]PF_6. b) The bowl-to-bowl inversion of a π-bowl metal-complex.

viewpoint, π bowls are unique because they can provide not only convex surfaces but also open concave surfaces for metal binding. The preparation and characterization of π-bowl complexes of various transition metals that are in a variety of coordination modes, have been reported for over a decade.[6] Most of those complexes have shown preferential complexation to metals on the convex face. More recently, the first complex to selectively bind on the concave face in both the solution and solid states, [CpFe(η⁶-sumanene)]PF_6 (**2**, Cp = η⁵-C_5H_5), has been reported (Figure 1a), as well as its chiral derivative.[7,8]

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How the preference for metal binding on the concave or convex face arises is an intriguing issue; the selectivity might reflect either kinetic and/or thermodynamic control during the complexation, thermodynamic control during the bowl-to-bowl inversion, or both. Corannulene and sumanene ligands are themselves known to exhibit bowl-to-bowl inversion.[9,10] The ring-to-ring migration of the η⁶-binding fragments $\{Cp^*Ir\}^{2+}$, $\{Cp^*Ru\}^{+}$, or $\{(coe)_2Rh\}^{+}$ ($Cp^* = \eta^5$-C_5Me_5, coe = cyclooctene) on the corannulene scaffold has been reported.[6b,d,m] However, bowl-to-bowl inversion has not yet been elucidated for π-bowl transition metal complexes (Figure 1b).[11] The controllable bowl-to-bowl inversion of transition metal complexes would be of great interest and fundamental importance,[12] providing a novel dynamic molecular system. We focused on the [CpRu(η⁶-sumanene)] complex because it is expected to be more flexible than the {CpFe} analogue owing to its longer carbon–metal bonds. Herein, we describe the dynamic inversion behaviour of [CpRu(η⁶-sumanene)]PF_6 (**3**), which is the first elucidation of bowl-to-bowl inversion in π-bowl transition-metal-complexes.

Ruthenium complex **3** was synthesized in a similar way to iron complex **2** (for experimental details, see the Supporting Information).[7a] Two species were observed in the ^{1}H NMR spectrum of **3** (H_a–H_f for the major species and $H_{a'}$–$H_{f'}$ for the minor species; Figure 2b and 2c). The major and minor species could be assigned to the concave- and convex-sumanene-bound complexes, $\mathbf{3}_{concave}$ and $\mathbf{3}_{convex}$, respectively, as mentioned below.

The chemical shifts for the major species ($\mathbf{3}_{concave}$) were comparable to the concave-bound $\{CpFe\}^+$ complex **2** (the higher-field shift of Cp protons H_f and the lower-field shift of *endo*-benzylic protons H_{dendo} due to the complexation).[7a] Irradiation of the Cp protons caused positive nuclear Overhauser effects (nOes) at the *endo*-benzylic protons H_{dendo} and aromatic protons (0.7% for each H_{dendo}, 0.4% for each H_a, < 0.3% for each H_b and each H_c; see the Supporting Information, Figures S1a and S1b); no nOes were observed for the corresponding *exo*-protons H_{dexo}.[13] These results suggest that the ruthenium atom is located on the concave face of the sumanene skeleton of the major species; therefore, the main species was determined to be the concave-bound complex $\mathbf{3}_{concave}$. Furthermore, a negative nOe was observed at $\delta = 5.34$ ppm (singlet, $H_{f'}$; Supporting Information, Figure S1), which indicates that there is chemical exchange between the Cp protons H_f and $H_{f'}$ on the NMR timescale. The $\mathbf{3}_{convex}$ $H_{f'}$ protons were observed downfield of the corresponding $\mathbf{3}_{concave}$ H_f protons (at $\delta = 5.35$ ppm and $\delta = 3.82$ ppm, respectively). The downfield shift observed in the conformational change from concave-bound complex $\mathbf{3}_{concave}$ to the convex-bound $\mathbf{3}_{convex}$ is presumably because of the deshielding effect of the ring current. 2D EXSY (exchange spectroscopy) of **3** clearly showed negative cross-peaks for the

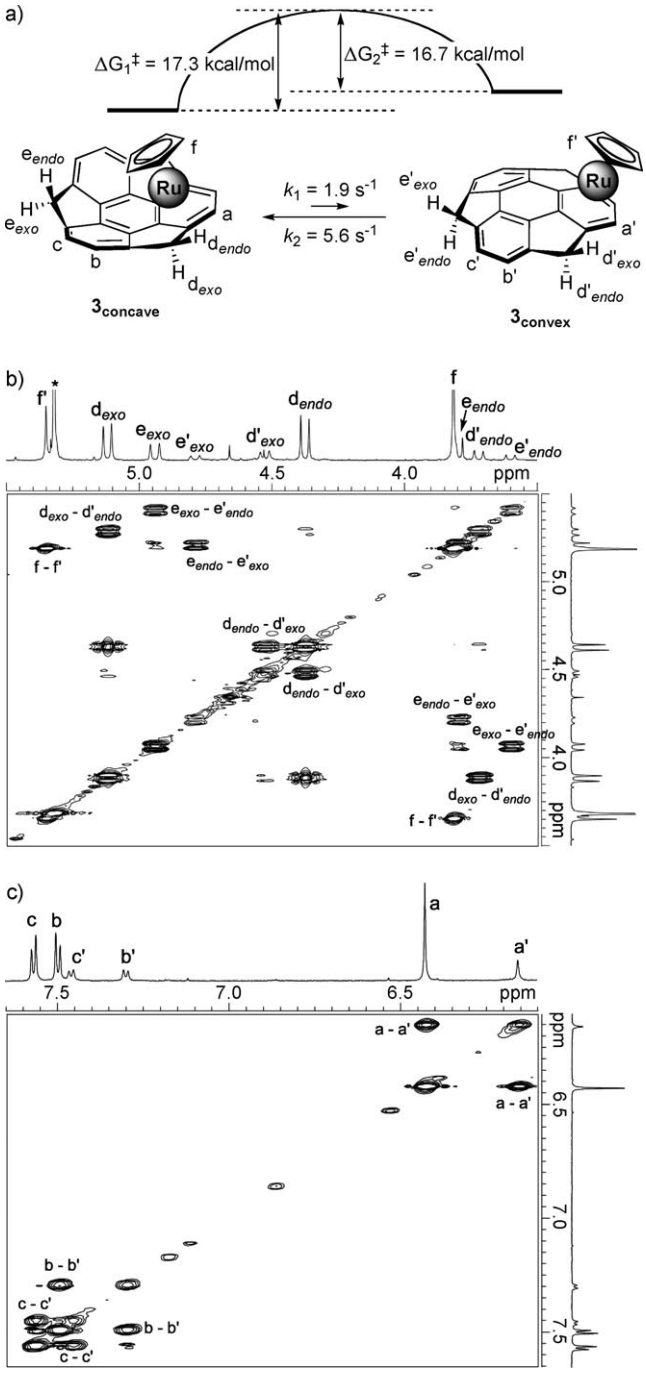

Figure 2. a) Bowl-to-bowl inversion of $\mathbf{3}_{concave}$ and $\mathbf{3}_{convex}$ including activation free energies $\Delta G^{\ddagger}_1$ and $\Delta G^{\ddagger}_2$ [kcal mol^{-1}], and kinetic constants k_1 and k_2 [s^{-1}]. b,c) Selected regions of the 2D EXSY spectrum of **3**, and assignment of the proton signals: b) $\delta = 3.5$–5.5 ppm (* = residual solvent peak); c) $\delta = 6.1$–7.65 ppm (600 MHz; 303 K; $[\mathbf{3}]_{total} = 5$ mmol L^{-1}; [D$_2$]dichloromethane; mixing time 0.3 s).

chemical exchange between $H_{a\text{-}f}$ and $H_{a'\text{-}f'}$ in one-to-one correspondence, as exemplified by a–a′ (Figures 2b and 2c). The $\mathbf{3}_{concave}$ *endo*-benzylic protons $H_{d\,endo}$ and $H_{e\,endo}$ show correlations with the $\mathbf{3}_{convex}$ *exo*-benzylic peaks $H_{d'\,exo}$ and $H_{e'\,exo}$ (at $\delta = 4.53$ and 4.79 ppm, respectively), which are in a typical region for *exo*-benzylic protons. Conversely, the $\mathbf{3}_{concave}$ *exo*-benzylic protons $H_{d\,exo}$ and $H_{e\,exo}$ show correlations with the $\mathbf{3}_{convex}$ *endo*-benzylic peaks $H_{d'\,endo}$ and $H_{e'\,endo}$ (at $\delta = 3.72$ and 3.60 ppm, respectively), which are in a typical region for the *endo*-benzylic protons. The $H_{d'\,endo}$ peak ($\mathbf{3}_{convex}$) appears $\Delta\delta =$ 0.65 ppm upfield of the $H_{d\,endo}$ proton ($\mathbf{3}_{concave}$). This can be explained by the conformational change to the convex-bound complex ($\mathbf{3}_{convex}$) causing a lowering of the deshielding effect from the ruthenium(II) center. To further investigate the structure of the minor species, an nOe experiment was carried out at low temperature (−50 °C). Judging from the activation free energy, as described below, the isomerization was estimated to be much slower than the NMR timescale at this temperature. Irradiation of the $\mathbf{3}_{convex}$ Cp protons ($H_{f'}$) resulted in nOes for *exo*-benzylic proton $H_{d'\,exo}$ and aromatic proton $H_{a'}$ (Supporting Information, Figure S1c), and no nOes for the corresponding *endo*-proton $H_{d'\,endo}$. These results show that the minor species observed by ^{1}H NMR spectroscopy is the convex-bound complex $\mathbf{3}_{convex}$. Therefore, π-bowl-complexes $\mathbf{3}_{concave}$ and $\mathbf{3}_{convex}$ isomerize through a bowl-to-bowl inversion pathway.

The cross-peak for the chemical exchange was quantified to estimate the kinetic constant k and activation free energy $\Delta G^{\ddagger}$ for the bowl-to-bowl inversion (Figure 2a). The k_1 and k_2 values were calculated to be 1.9 and 5.6 s^{-1}, respectively (303 K, [D$_2$]dichloromethane). The values of $\Delta G^{\ddagger}_1$ and $\Delta G^{\ddagger}_2$ were calculated from their corresponding kinetic constants to be 17.3 and 16.7 kcal mol^{-1}, respectively; these values are approximately 3 kcal mol^{-1} smaller than that of the sumanene ligand alone.[10] Slight flattening around the coordinating benzene ring of $\mathbf{3}_{concave}$, as discussed below, could lower the value of $\Delta G^{\ddagger}$. One possible pathway for isomerization between the concave-bound and convex-bound bowls might be the dissociation and recombination of the sumanene ligand. To examine the effect of the sumanene ligand, a 2D EXSY NMR spectroscopy experiment was carried out in the presence of free sumanene. However, neither cross-peaks between coordinated and free sumanenes nor an increase in the value of the kinetic constant for bowl-to-bowl isomerization were observed. Thus, the dissociation and recombination mechanism is not a likely pathway for this isomerization.[14]

The equilibrium position of the bowl-to-bowl inversion was investigated in various solvents. The ratio of $\mathbf{3}_{concave}/\mathbf{3}_{convex}$ in [D$_2$]dichloromethane at 298 K was 75:25 (Table 1). The percentage of $\mathbf{3}_{concave}$ increased with the polarity of solvent. In highly polar [D$_3$]acetonitrile or [D$_3$]nitromethane solvent, equilibrium values of up to 90 % $\mathbf{3}_{concave}$ were observed ($\Delta G_1 =$ 1.30 kcal mol^{-1}; Table 1). The temperature dependence of the equilibrium position was also studied to determine the values of ΔH_1 and ΔS_1. The temperature was varied within the range 253–313 K,[15] a small increase in the relative amount of $\mathbf{3}_{convex}$ (approx. 3 %) was observed with increasing temperature for each solvent tested. Linear van′t Hoff plots (Figure 3; Supporting Information, Figure S2) gave a positive value for ΔH_1 and a negative value for ΔS_1 (Table 1). This result suggests that bowl-to-bowl inversion from $\mathbf{3}_{concave}$ to $\mathbf{3}_{convex}$ is enthalpically unfavorable. Furthermore, the isomerization may be entropically unfavorable, although the conformation of $\mathbf{3}_{convex}$ looks more divergent. Solvation is assumed to contribute to the bowl-to-bowl inversion.

Table 1: Ratios of $\mathbf{3}_{concave}$ and $\mathbf{3}_{convex}$ (%),[a] free energy ΔG_1, enthalpy ΔH_1,[a] and entropy ΔS_1; $[\mathbf{3}]_{total} = 5$ mmol L^{-1}.

$\mathbf{3}_{concave}$ ⟵ ΔG_1, ΔH_1, and ΔS_1 ⟶ $\mathbf{3}_{convex}$

Solvent	Ratio [%][a]		ΔG_1[a] [kcal mol^{-1}]	ΔH_1[b] [kcal mol^{-1}]	ΔS_1[b] [cal mol^{-1} K^{-1}]
	$\mathbf{3}_{concave}$	$\mathbf{3}_{convex}$			
CD_2Cl_2	75	25	0.64	0.31	−1.14
[D$_6$]Acetone	84	16	0.98	0.63	−1.21
CD_3CN	90	10	1.30	1.08	−0.79
CD_3NO_2	90	10	1.30	1.11	−0.67

[a] 298 K; 600 MHz. [b] Determined from the van't Hoff plots.

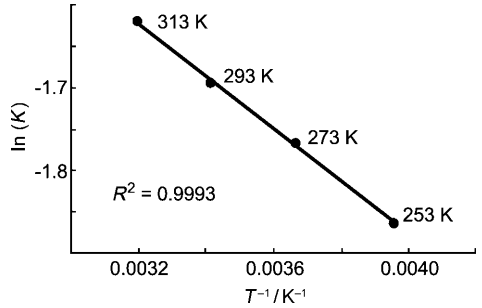

Figure 3. Van't Hoff plot in [D$_6$]acetone (600 MHz; $[\mathbf{3}]_{total} = 5$ mmol L^{-1}).

Single crystals suitable for X-ray diffraction analysis were obtained from a dichloromethane/diethyl ether solution. The ORTEP of [CpRu(η^6-sumanene)]PF$_6$ ($\mathbf{3}_{concave}$) clearly shows the concave coordination (Figure 4).[16] Bowl depth is defined as the perpendicular distance from the plane of the hub benzene ring (C21–C26) to the rim carbon atoms. The bowl depths of the coordinated side are 0.98 and 1.00 Å (C6 and C20, respectively), and those of the non-coordinated side are 1.14 Å (C10 and C16, respectively) and 1.07 and 1.10 Å (C11 and C15, respectively); those values are similar to those observed for complex **2**. The Ru–C bond lengths between the ruthenium center and the six-membered ring (C6, C7, C19, and C20) are in the range 2.15–2.22 Å, and the distances to the hub carbon atoms (C21 and C26) are a little longer (approx. 2.28 Å; Supporting Information, Figure S3). These values are approximately 0.1 Å longer than the metal–carbon bond lengths in the iron analogue **2**,[7a] which might also be related to the above mentioned bowl-to-bowl inversion. Columnar stacking was observed in the packing structure (Supporting Information, Figure S4), partial π–π orbital overlap is suggested between the cyclopentadienyl and hub benzene rings. As expected, when the crystal of $\mathbf{3}_{concave}$ was re-dissolved in solvent, both isomers of **3** were observed by ^{1}H NMR spectroscopy.

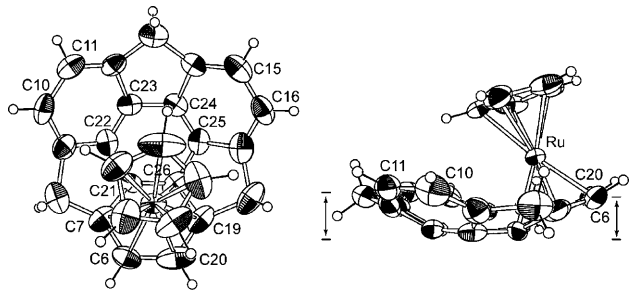

Figure 4. ORTEP of the cation of $\mathbf{3}_{concave}$ (thermal ellipsoids set at the 40% probability level). A top view (left) and a side view with bowl depth indicated (right). The hexafluorophosphate anion is omitted for clarity. Bowl depths [Å]: C16 1.14, C10 1.14, C6 1.00, C15 1.10, C11 1.07, C20 0.98.

In conclusion, the dynamic bowl-to-bowl inversion behavior in the solution of [CpRu(η^6-sumanene)]PF$_6$ (**3**) has been presented. It should be noted that this is the first elucidation of the bowl-to-bowl inversion of π-bowl transition metal complexes. The preference for inversion between the concave and convex isomers is thought to depend on the solvent and temperature and is under thermodynamic control. Further study to elucidate the isomerization mechanism, including theoretical calculation, is currently underway.

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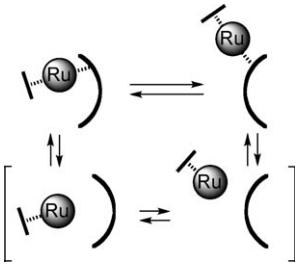
[11] The very rapid bowl-to-bowl inversion of $[(Cp^*Ru)_2(\mu_2\text{-}(\eta^6{:}\eta^6\text{-}C_{20}H_6)][PF_6]_2$ and $[(Cp^*Ru)_2(\mu_2\text{-}(\eta^6{:}\eta^6\text{-}C_{20}H_6Me_4)][PF_6]_2$ has been previously suggested; see Ref. [6j].

[12] The dynamic behavior of organometallic compounds has been recognized as fluxionality, and has attracted interest since the 1960s; see F. A. Cotton, *Acc. Chem. Res.* **1968**, *1*, 257 – 265.

[13] Performed in $[D_3]$acetonitrile; all signals were resolved in the ^{1}H NMR spectrum (see the Supporting Information).

[14] The dissociation–recombination inversion pathway:



[15] Performed in $[D_2]$dichloromethane or $[D_3]$nitromethane; the temperature was varied within the range 253–303 K and 273–313 K, respectively.

[16] Crystal data for $\mathbf{3}_{\mathbf{concave}}$: monoclinic, space group $P2_1/c$ (no. 14), $a = 10.4881(9)$, $b = 7.3013(6)$, $c = 27.050(2)$ Å, $\beta = 91.024(2)°$, $V = 2071.1(3)$ Å^3, $Z = 4$; $R1 = 0.0989$, $wR2 = 0.3015$. CCDC 736060 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

