Ring selectivity and migratory aptitude of Cp*Ru+ complexation to acecorannulene†

T. Jon Seiders,[a] Kim K. Baldridge,[abc] Joseph M. O'Connor[a] and Jay S. Siegel*[ac]

[a] Department of Chemistry, University of California, San Diego, La Jolla, CA 92093-0358, USA
[b] San Diego Supercomputer Center, P.O. Box 85608, San Diego, CA 92186-9784, USA
[c] Organisch-chemisches Institut, Universität Zürich, Zürich, CH-8057, Switzerland

Synthesis and spectral characterization of acecorannulene CpRu+ complexes, in combination with *ab initio* quantum chemical computations, leads to the hypothesis that η^6-metal binding prefers the *exo* face in the region of least curvature.

Metal complexation chemistry of fullerenes and fullerene fragments[1] differs substantially from that of simple arene or planar polynuclear aromatic hydrocarbons. The propensity of metals to form dihapto complexes of C_{60} and C_{70} has been well documented.[2] Presumably complexes of greater hapticity have not been isolated because of the divergence of the p-orbitals on the fullerene, and thus poor orbital overlap between metal and carbon. Specifically, Fagan's report of the reaction of $RuCp^*(CH_3CN)_3^+OTf^-$ with C_{60} and C_{70} to give η^2 complexes with two molecules of acetonitrile still bound to ruthenium stands as an example of the instability of fullerene complexes with a hapticity greater than 2.[3] Indeed, computations corroborate the findings of diminished stability of η^6 complexes with C_{60}.[4] Acecorannulene (**1**),[5] with a variable curvature and a non-inverting bowl-structure provides an excellent bridge between the organometallic chemistry of fullerenes and flat aromatic compounds. Herein we report on the preparation and structure of η^6-ruthenium complexes of acecorannulene (**2**).

Acecorannulene (**1**) exhibits a significantly deeper bowl (1.1 Å) than corannulene[6] (**3**) (0.87 Å). Unlike **3** and C_{60}, the curvature and pyramidalization is not uniformly spread throughout **1**. As seen in the π-orbital axis vector (POAV) angles[7] in the crystal structure of **1**,[8] the carbons near the five-membered ring annelation are significantly more pyramidalized than the carbons further away. One can ascribe an average POAV angle for each of the 3 independent aromatic six-membered rings (A, B, and C) of 8.1°, 5.3° and 5.0°, respectively (Fig. 1). Consistent with the increase in bowl depth, the bowl inversion barrier of **1** has been measure to be 27.7 kcal mol⁻¹, a value significantly higher than corannulene (~ 11.5 kcal mol⁻¹).[5,9] This increase in activation energy locks the corannulene nucleus into one bowl-shaped conformation and allows for the diastereofacial differentiation of a metal to complex the *endo* or *exo* face.

To test the ring and facial selectivity of η^6 complexes of **1**, a solution of **1** and $RuCp^*(CH_3CN)_3OTf$ (**4**)[10] in methylene chloride-d_2 is monitored at room temperature by ¹H NMR spectroscopy.† Initially, only one complex (**2b**) and free **1** are observed but, after 2 hours a 6 : 2 : 1 ratio of unbound **1** to two isomeric complexes (**2b : 2c**) equilibrates. Evaporation of the volatiles and addition of fresh methylene chloride-d_2 converts all of **1** to **2b** and **2c**, maintaining a
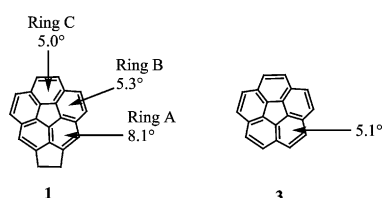
2 : 1 ratio of isomeric complexes (Fig. 2); **2b** and **2c** are air sensitive complexes in solution as well as in the solid state. These two complexes are the only ones formed from the six possible isomeric possible η^6 ruthenium complexes (A, B, and C rings and *endo* or *exo* faces of each ring).[11] Similar phenomena have been observed with η^6 iridium complexes of **1** and methylated derivatives of **1**.[1c]

By analyzing the number of signals, the multiplicity and relative size of the ¹H NMR signals, the major isomer **2b** was determined to be the η^6 complex of ring B and the minor isomer **2c** the η^6 complex of ring C (conclusively determined by the symmetry of any C_s complex and the simplicity of the signals for **2c**). To identify the first formed complex and estimate the propensity to isomerization, **1** and $RuCp^*(CH_3CN)_3OTf$ were allowed to react in methylene chloride-d_2 at −80 °C and monitored by ¹H NMR at −80 °C. At this temperature a 3 : 1 ratio of free **1** to **2b** is observed and shows no signs of isomerization over a period of 7 hours. Upon warming the solution to 25 °C the isomerization of **2b** to **2c** occurs in ~ 1 hour and stabilizes at a ratio of 2 : 1 for **2b:2c**. The rate of isomerization of **2b** to **2c** was determined in the presence of the residual acetonitrile, which may be serving as a catalyst for the isomerization, but under these conditions a lower limit of the barrier to metal arene migration is *ca.* 25 kcal mol⁻¹.

In the absence of X-ray quality crystals the diastereotopic protons, *endo* and *exo*, on the ethylene bridge of **1** provide a probe for *endo versus exo* facial complexation to the ruthenium fragment. Independent irradiation of the methyl protons of Cp*, and the upfield and downfield methylene protons of either **2b** or **2c**, shows no signal enhancements, which would be consistent with divergent *exo* facial binding at rings B and, C but as with any negative evidence this result is not conclusive. The similar and lower curvature of rings B and C correlates with the 2 : 1 ratio of isomers formed at equilibrium, indicative of a statistical distribution of B and C complexes. The formation of no isomer at ring A (**2a**) is not consistent with simple substituent steric arguments as even hexamethylbenzene forms a stable complex.[9,12] Some unique character of the environment at ring A must prohibit complexation. On the *endo* face that could be the severe steric clashing with the concave face, whereas on the *exo* face it likely stems from the poor orbital alignment.

To test this hypothesis on a computational level, the structure and energies of all six possible structures were calculated, using Cp instead of Cp* to spare some computer time. After probing many levels of theory, the B3LYP/GEN (MP2/GEN//B3LYP/GEN) basis set was found to perform well over a series of related compounds.[13] The relative energies of the isomers calculated on the basis of the most stable complex B-*exo* places all *endo* structures as well both
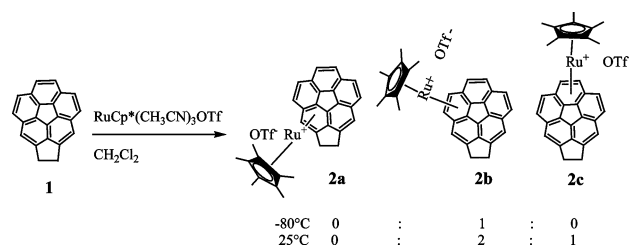

Fig. 1 Average POAV angles for each ring of acecorannulene (**1**) and corannulene (**3**) (POAV of C60 = 11.6°).

Fig. 2 Reaction of $RuCp^*(CH_3CN)_3OTf$ with acecorannulene.

A ring isomers higher than the level where there would be any observable population (*i.e.* > 3.0 kcal mol⁻¹; see Table 1).‡

The role of ring A in the complexation process is cryptic but can explain the initial formation of only complexes to ring B, as observed at −80 °C. The most stable η² complexes of fullerenes are the complexes in which the metal is coordinated to the most pyramidalized pair of carbons, with the most divergent pair of p-orbitals.[2] Given that η⁶ metal complexation is presumed to occur *via* a stepwise mechanism passing through η² and η⁴ complexes with sequential loss of ancillary ligands, the initially formed complex between **1** and RuCp*(CH₃CN)₂⁺ is presumed to be an η² complex to the pair of carbons with the most divergent pair of orbitals, carbons in ring A. Because more stable, higher hapticity complexes are accessible with **1** compared to fullerenes, the ruthenium fragment quickly slips to ring B, maintaining η² binding to the *exo* face during the slippage, forming a relatively stable η⁶ complex (**2b**) after loss of ligated acetonitrile. At low temperatures, the barrier for slippage from ring B to ring C (**2b** to **2c**) is too high therefore only one complex is observed. Upon warming a statistical mixture of complexes to rings B and C is observed, indicating little inherent selectivity for either ring. Because of the selectivity of η² complexes towards the most divergent (pyramidalized) pair of orbitals, as observed in fullerene chemistry, and the kinetic preference of RuCp* for ring B in **1**, *exo* facial binding in **2b** and **2c** can be surmised.

A qualitative trend is observed for the series of compounds studied (Fig. 3). The greater the curvature of the aromatic ring, the less stable an η⁶ complex is towards nucleophiles and oxygen. For RuCp*, the crossover between η⁶ and η⁴ or η² complexes occurs in rings with an average POAV angle greater than 5.3°. Future experiments should help elaborate the maximum amount of curvature allowed for η⁶ complexation.

Table 1 Relative computational energies for the six isomers of CpRu⁺ complexed to acecorannulene. Level: B3LYP/GEN (MP2/GEN//B3LYP/GEN)

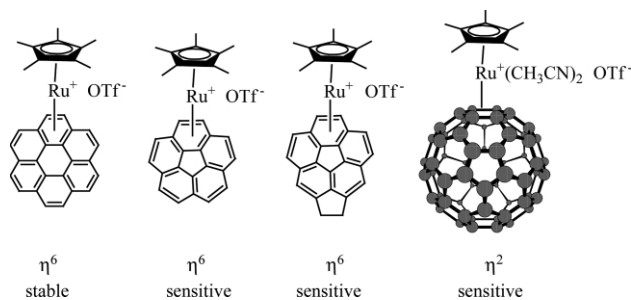| Isomer	*exo*/kcal mol⁻¹	*endo*/kcal mol⁻¹
2a	3.25 (2.1)	16.1 (10.3)
2b	0.0 (0.0)	12.2 (10.3)
2c	0.5 (0.4)	10.9 (7.8)

Fig. 3 Qualitative trend of hapticity and stability for ruthenium complexes.

Notes and references

‡ *Computational methods*: All calculations have been carried out using the GAMESS[14] software packages. The molecular structures were determined using a variety of levels of theory to establish self-consistency in terms of basis sets as well as effects of dynamic correlation. Hybrid density functional theory (HDFT) methods were employed using Becke's[15] 3 parameter hybrid exchange functional in combination with the nonlocal

correlation functional provided by the Lee–Yang–Parr expression,[16] B3LYP. Both the cc-pVDZ[17] and DZV(2d,p)[18] double-ζ basis sets were employed for all atoms except Ru, in which case the 3-21G(d)[19] and the more self-consistent Hay and Wadt relativistic effective core potential (RECP)[20] combination were used respectively with the former basis sets. These levels of theory were established as reliable for these compounds. The Hay–Wadt VDZ (n + 1) ECP, a (5s, 6p) → [3s, 3p] contraction, include an extra shell of electrons beyond what is traditionally available in effective core potentials. Elements including Ru include the 1-electron Darwin and mass–velocity relativistic corrections in their definitions. Full geometry optimizations were performed, and subsequent Hessians (matrix of second derivatives) were calculated to determine local minima (positive definite). From the fully optimized structures, single point energy computations were performed using the MP2[21] dynamic correlation treatment for additional comparisons against that provided by HDFT methods.

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