

## Stereochemical Inversion of a Coordinated, Curved Hydrocarbon: Syntheses and Structures of *exo*- and *endo*-[Ru( $\eta^6$ -fluoradene)( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] [CF<sub>3</sub>SO<sub>3</sub>]

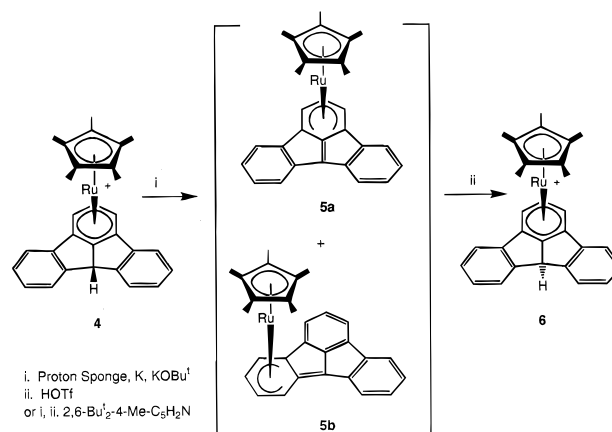
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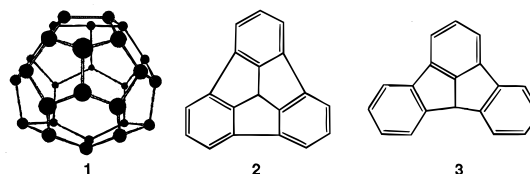
Chemists have long been interested in nonplanar hydrocarbons such as strained cycloalkenes,<sup>1–3</sup> in which the inside and outside surfaces have different chemical and physical properties. Fullerenes are an extreme example, forming very strong endohedral complexes<sup>4–15</sup> such as La@C<sub>82</sub><sup>8,9,16</sup> but weak exohedral metal complexes such as [Pt( $\eta^2$ -C<sub>60</sub>)(PPh<sub>3</sub>)<sub>2</sub>].<sup>17–19</sup> The weakness of exohedral binding has been attributed to the splayed-out orientation of the lobes of the external, radial p-orbitals, which do not overlap effectively in a polyhaptic fashion with the d-orbitals of a metal.<sup>20</sup>  $\pi$ -Orbital axis vector (POAV1) analysis gives a simple description of the curvature in  $\pi$ -conjugated systems.<sup>21–23</sup> The local curvature of a carbon atom is described by the pyramidalization angle  $\theta_p$ , defined as  $\theta_{ox} - 90^\circ$  where  $\theta_{ox}$  is the angle made by the three  $\sigma$ -bonds of a tricoordinate carbon atom to a common vector that originates at the carbon atom. Carbon atoms with maximum curvature are generally the most reactive. Further, Klärner et al. recently suggested, on the basis of semiempirical MO calculations, that the concave (*endo*) surface of a curved, nonconjugated aromatic hydrocarbon will display a much more negative electrostatic potential than the convex (*exo*) surface.<sup>24</sup>

### Scheme 1



We are investigating *endo*- and *exo*-complexes of curved hydrocarbons that model some features of metal–fullerene complexes. Labile [Ru( $\eta^6$ -corannulene)(Cp\*)][OTf] (Cp\* =  $\eta$ -C<sub>5</sub>-Me<sub>5</sub>, OTf = CF<sub>3</sub>SO<sub>3</sub>) has a rapidly inverting corannulene ligand.<sup>25</sup> One of the five-membered ring C–C bonds along the rim of the “buckybowl” compound C<sub>30</sub>H<sub>12</sub> oxidatively adds to Pt to form a novel  $\eta^2$ - $\sigma$ -bonded complex rather than a  $\pi$ -complex.<sup>26</sup>

C<sub>28</sub> (1) is the smallest even-numbered cluster that forms with special abundance in condensing carbon vapors.<sup>27</sup> T<sub>d</sub>-C<sub>28</sub> is constructed of 12 pentagons and 4 hexagons, with a quintet (<sup>5</sup>A<sub>2</sub>) ground state. C<sub>28</sub> can be stabilized in the gas phase as C<sub>28</sub>X<sub>4</sub> by addition of a monovalent atom such as H to each vertex, or by encapsulation of a tetravalent atom to give, e.g., U@C<sub>28</sub>.<sup>7,27–30</sup>

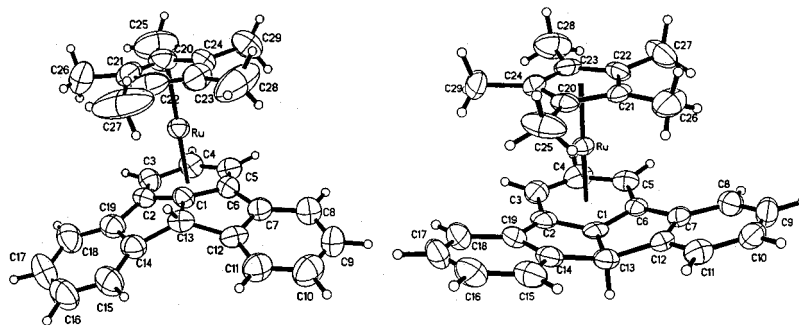


The unknown hydrocarbon C<sub>19</sub>H<sub>10</sub> (2)<sup>31</sup> would be a good model for one corner of C<sub>28</sub>. Opening one arene–arene bond leads to fluoradene (C<sub>19</sub>H<sub>12</sub>, 3),<sup>32</sup> with distinct *endo* and *exo* faces. Its coordination chemistry is nearly unexplored. Cr coordinates to a non-central ring in [Cr(CO)<sub>5</sub>( $\eta^6$ -fluoradene)], but *endo*- vs *exo*-stereochemistry was not determined.<sup>33</sup> Crystallographically characterized [Re(CO)<sub>5</sub>( $\eta^1$ -fluoradenyl)] has a  $\sigma$ -bond to the central, aliphatic carbon atom; [Mn(CO)<sub>5</sub>( $\eta^5$ -fluoradenyl)] was spectroscopically characterized.<sup>34</sup>

The reaction of [Ru(MeCN)<sub>3</sub>(Cp\*)][OTf] with fluoradene (3) in CH<sub>2</sub>Cl<sub>2</sub> gives *exo*-[Ru( $\eta^6$ -fluoradene)(Cp\*)][CF<sub>3</sub>SO<sub>3</sub>] (4) in 79% yield (Scheme 1).<sup>35</sup> <sup>1</sup>H NMR analysis shows traces of other

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**Figure 1.** Perspective drawings of the cations of **4** and **6**. Ellipsoids correspond to 50% probability contours of atomic displacement.

isomers. Compound **4** does not exchange with other arene ligands or acetonitrile in  $\text{CH}_2\text{Cl}_2$  at room temperature, nor with 7b-d-fluoradene or 7b-isopropylfluoradene in refluxing THF. Deprotonation of **4** with 1,8-bis(dimethylamino)naphthalene (Proton Sponge), K, or  $\text{KOCMe}_3$  in THF gives very reactive  $[\text{Ru}(\text{Cp}^*)(\eta^5\text{-fluoradényl})]$  (**5**).<sup>36</sup>  $^1\text{H}$  NMR indicates two isomers with  $\text{Cp}^*$  resonances at  $\delta$  0.82 (**5a**) and 0.84 (**5b**), the ratio depending upon the base and reaction conditions. One equivalent of Proton Sponge in  $\text{CD}_2\text{Cl}_2$  gives a **5a/5b** ratio of 20:1, whereas excess  $\text{KOCMe}_3$  in THF gives a 1.7:1 ratio. The  $^1\text{H}$  NMR spectrum of **5a** indicates a plane of symmetry, which **5b** lacks. Presumably ruthenium is  $\eta^5$ -coordinated to a planar fluoradényl ligand in **5**.

Protonation of **5** with trifluoromethanesulfonic acid in  $\text{CH}_2\text{Cl}_2$  gives *endo*- $[\text{Ru}(\eta^6\text{-fluoradene})(\text{Cp}^*)][\text{CF}_3\text{SO}_3]$  (**6**).<sup>37</sup> The conversion of **4** to **6** can also be quantitatively effected by catalytic 2,6-di-*tert*-butyl-4-methylpyridine in  $\text{CD}_2\text{Cl}_2$ . Monitoring by  $^1\text{H}$  NMR shows exclusive formation of **6** in 6 h at room temperature.

X-ray crystallography confirms that the  $[\text{Ru}(\text{Cp}^*)]^+$  center is  $\eta^6$ -coordinated to the exo face of the central arene ring of fluoradene in **4** and the endo face in **6**.<sup>38</sup> Bonding parameters are similar to several other  $[\text{Ru}(\eta^6\text{-arene})(\text{Cp}^*)]^+$  complexes.<sup>39</sup> The distance between the  $\text{Cp}^*$  centroid and the  $\eta^6$ -arene centroid is

(35) Reaction of  $[\text{Ru}(\text{Cp}^*)(\text{MeCN})_3][\text{OTf}]$  (0.360 g, 0.710 mmol) with fluoradene (0.360 g, 1.50 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) for 4 h at 0 °C, followed by precipitation from THF/ $\text{Et}_2\text{O}$  gave pale yellow crystals of **4** (0.350 g, 79%). Selected NMR data:  $^1\text{H}$  (200 MHz,  $\text{CDCl}_3$ ,  $\delta_{\text{H}}$ ) 1.79 (s, 15H,  $\text{Cp}^*$ ), 4.31 (s, 1H),  $^{13}\text{C}$  (100.6 MHz,  $\text{CDCl}_3$ ,  $\delta_{\text{C}}$ ) 10.4 (Me of  $\text{Cp}^*$ ), 52.8 (C7b), 80.4 (C2), 85.4 (C1/C3), 94.7 ( $\text{Cp}^*$ ), 109.8, 110.8 (C3a/C11b, C11c).

(36) Reaction of **4** (0.125 g, 0.200 mmol) with 1,8-bis(dimethylamino)-naphthalene (0.043 g, 0.20 mmol) in THF (25 mL) for 1 h, followed by evaporation of the purple solution, extraction with benzene (50 mL), filtration, evaporation, and trituration with pentane (20 mL) gave **5** (0.060 g, 60%) as a red-brown solid. Selected  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta_{\text{H}}$ ): 0.82 (s, 15H,  $\text{Cp}^*$ ). Similar treatment with K,  $\text{KOCMe}_3$ , or  $\text{K}[\text{C}_{19}\text{H}_{11}]$  in THF gave two isomers of **5** with  $\delta_{\text{H}}$  ( $\text{Cp}^*$ ) 0.82 and 0.84.

(37) Reaction of **4** (0.150 g, 0.240 mmol) with K (0.020 g, 0.50 mmol) in refluxing THF (15 mL) followed by evaporation, extraction with  $\text{CH}_2\text{Cl}_2$  (10 mL), addition of HOTf (0.10 mL, 1.1 mmol), and precipitation with  $\text{Et}_2\text{O}$  (30 mL) gave **6** (0.075 g, 50%). Selected NMR data:  $^1\text{H}$  (200 MHz,  $\text{CDCl}_3$ ,  $\delta_{\text{H}}$ ) 1.13 (s, 15H,  $\text{C}_3\text{Me}_5$ ), 4.54 (s, 1 H).  $^{13}\text{C}$  (100.6 MHz,  $\text{CDCl}_3$ ,  $\delta_{\text{C}}$ ) 14.0 (Me of  $\text{Cp}^*$ ), 72.5 (C7b), 79.6 (C2), 86.2 (C1/C3), 88.1 ( $\text{Cp}^*$ ), 88.9 (C11c). Treatment of **4** (0.006 g, 0.01 mmol) with a catalytic 2,6-di-*tert*-butyl-4-methylpyridine in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) converted **4** completely to **6** in 6 h.

(38) Single crystals from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . Enraf-Nonius CAD-4, Mo K $\alpha$  radiation,  $2\theta$  range 4–50°, empirical absorption correction, calculated H atoms. **4**:  $Cc$ ,  $Z = 4$ , 5100 data, 2221 unique with  $I > 2\sigma(I)$ , 343 variables,  $R(2\sigma) = 2.8\%$ ,  $wR(\text{all data}) = 8.3\%$ . **6**:  $Pna2_1$ ,  $Z = 4$ , 2385 data, 1928 unique with  $I > 2\sigma(I)$ , 343 variables,  $R(2\sigma) = 3.2\%$ ,  $wR(\text{all data}) = 8.6\%$ .

3.54(1) Å in both **4** and **6**, but the Ru atom is 0.038(8) Å closer to arene and 0.031(8) Å further from  $\text{Cp}^*$  in **6** compared to **4**. Apparently the interligand distance is limited by steric constraints, but Ru interacts more strongly with the tipped-in endo p-orbitals in **6** than the splayed-out exo p-orbitals in **4**. The stronger arene–Ru bonding makes **6** the thermodynamically favored product. The pyramidalization angles from POAV1 analysis of **4** and **6** reveal that the most pyramidalized carbon atom of the coordinated arene ring of **4** has  $\theta_p = 4.6^\circ$ , smaller than free fluoradene's value of  $7.9^\circ$ . The fluoradene ligand is slightly flattened in **6**, with the coordinated arene ring having a maximum  $\theta_p$  of  $6.1^\circ$ .

The reaction sequence **3**  $\rightarrow$  **4**  $\rightarrow$  **5**  $\rightarrow$  **6** results in a stereochemical inversion of fluoradene. Complex **4** is kinetically favored by the greater accessibility of the exo face of fluoradene to the ruthenium center. The fluoradényl ligand of **5** is presumably planar, as reported for the sandwich structure of  $[\text{Li}_2(\mu_2\text{-}\eta^6\text{-C}_{19}\text{H}_{11})_2]^+\text{C}_6\text{H}_6$ .<sup>40</sup> Protonation of **5** to give **6** is favored, with the acid approaching the fluoradényl ligand from the less crowded exo-face.

We are seeking to further characterize intermediate **5**, and to determine whether bulky substituents on the aliphatic carbon of fluoradene can be used to force initial endo-coordination of ruthenium.

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**Supporting Information Available:** Preparation and spectroscopic data for **4**, **5**, and **6**; tables of crystallographic details including atomic coordinates, equivalent  $U$  values, anisotropic  $U$  values, bond lengths and angles, atom-numbering scheme, and perspective drawings for structures of **4** and **6** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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