Synthesis and Characterization of a Zirconium Complex Containing a Corannulene-Based Ligand

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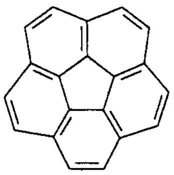
Summary: Exo-(η^5-$C_{20}H_{17}$)(η^5-C_5H_5)$ZrCl_2$ has been synthesized using partially hydrogenated corannulene as an η^5-ligand. The zirconium atom was determined to be bound to the exo face of the bowl-shaped ligand by an X-ray diffraction study.

The chemistry of corannulene, $C_{20}H_{10}$ (**1**), the smallest curved subunit of C_{60} (buckminsterfullerene), has received a great deal of attention in recent years.[1−4] This increase in interest is due in part to recent improvements in the synthesis of **1**.[5−9]



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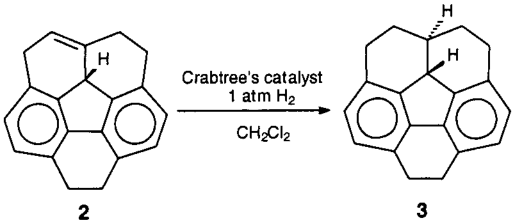
With the increased accessibility to **1**, there have been reports on the reduction chemistry of **1**,[10] the syntheses of new baskets and cyclophane corannulene based structures,[11] and host−guest fullerene complexes based on corannulene.[12] Another developing area of buckybowl chemistry is the coordination chemistry of buckybowls with transition metals. There have been a few reports of reactions of transition-metal complexes with buckybowls.[13,14] One example is that by O'Connor and coworkers, who have reported the [(η^6-corannulene)Ru(Cp*)]PF_6 complex.[13]

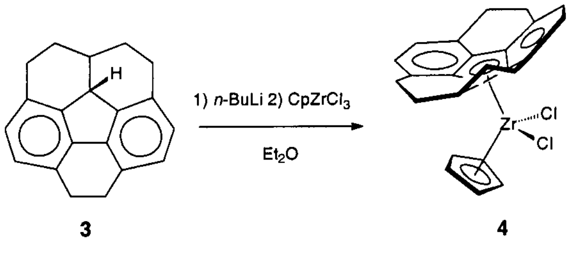
We were interested in determining whether a partially hydrogenated corannulene would be able to function as a curved fluorenyl anion analogue with unique steric properties due to the curvature of the ligand. As a starting point, we chose to use the partially hydrogenated corannulene hexahydrocorannulene ($C_{20}H_{16}$, **2**), which was reported by Rabideau and co-workers.[15] **2** is obtained in good yield by reaction of corannulene at −33 °C with a Na/THF/NH_3 mixture followed by an inverse aqueous ammonium chloride quench. Hydrogenation of the isolated double bond in **2** using Crabtree's catalyst and 1 atm of hydrogen gas yields octahydrocorannulene ($C_{20}H_{18}$, **3**) (eq 1).



(1)

The ^{1}H and ^{13}C NMR spectroscopic data are consistent with **3** being the hydrogenated product.[16] The hydrogen atoms at the hydrogenated spoke of the bowl are assigned a trans configuration, due to $J_{H-H} = 13.2$ Hz. The aromatic portion of **3** represents a fluorene core and therefore should function as a curved fluorenyl ligand after deprotonation.

Deprotonation of **3** with *n*-BuLi in Et_2O followed by addition of $CpZrCl_3$ yields *exo*-(η^5-$C_{20}H_{17}$)(η^5-C_5H_5)$ZrCl_2$ (**4**) in 47% yield as a red solid (eq 2).



(2)

The bowl-shaped ligand has two sides due to the curvature of the molecule: an endo (concave) and an exo (convex) side. The zirconium atom was determined to be bound to the exo side of the bowl by an X-ray structure determination (Figure 1).[17]

The Zr−C bond lengths to the modified corannulene ligand range from 2.46 to 2.60 Å, which are similar to

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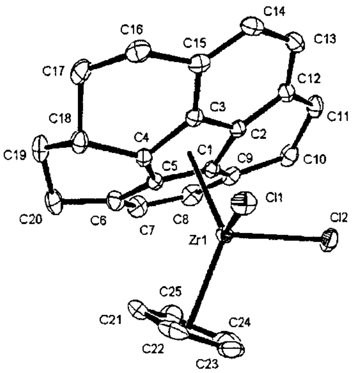

Figure 1. ORTEP plot of **4** (30% probability level).

those of the analogous zirconium fluorenyl complexes $(\eta^5\text{-9-R-C}_{13}H_8)(\eta^5\text{-C}_5H_5)ZrCl_2$, reported by Alt and co-workers.[18,19] The Zr−C4 bond distance is the shortest one (2.46 Å), which is similar to the Zr−C9 bond lengths in the analogous zirconium fluorenyl complexes (2.40−2.49 Å). Another feature of the structure is that the $C_{20}H_{17}$(C)−Zr−Cp(C)[20] angle (128.8°) is in the same range as the centroid−Zr−centroid angles for the reported fluorenyl Cp complexes (129.8−131.2°). This indicates that the bowl-shaped ligand has the same spatial occupancy around zirconium as the smaller fluorenyl ligand. The similarity in spatial demand, despite the $C_{20}H_{17}$ and fluorenyl anions being very dissimilar in size, is attributed to the fact that the metal is bound to the exo face of the bowl and, hence, the bowl curves away from the metal. Sawamura and co-workers saw a similar effect for their fullerene transition-metal complex *exo*-$(\eta^5\text{-C}_{60}Me_5)Rh(CO)_2$. Since the rhodium atom is bound to the exo face of a modified C_{60} molecule, the surrounding methyl groups are less sterically hindering than would be originally expected.[21] A list of selected bond lengths and angles of **4** are given in Table 1.

The curvature of the coordinated ligand was determined using the π-orbital axis vector (POAV1, $\theta_p = \theta_{\sigma\pi} - 90$) method.[22,23] The pyramidalization angles for the inside ring of the modified corannulene ligand are shown in Figure 2.

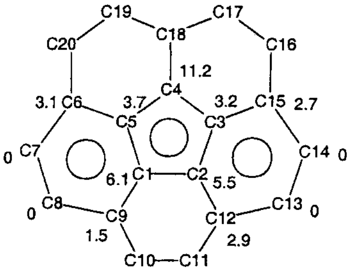

Figure 2. POAV1 angles (deg) of the corannulene-based ligand in **4**.

Table 1. Selected List of Bond Lengths (Å) and Angles (deg) for 4

Zr(1)-C(4)	2.464(2)	Zr(1)−C(21)	2.474(3)
Zr(1)−C(1)	2.544(2)	Zr(1)−C(25)	2.477(3)
Zr(1)−C(5)	2.576(2)	Zr(1)−C(23)	2.492(2)
Zr(1)−C(2)	2.576(2)	Zr(1)−C(24)	2.473(3)
Zr(1)−C(3)	2.602(2)	Zr(1)−C(22)	2.494(3)
C(9)−C(1)−C(5)	124.6(2)	C(5)−C(4)−C(3)	104.77(18)
C(9)−C(1)−C(2)	124.6(2)	C(5)−C(4)−C(18)	122.33(19)
C(5)−C(1)−C(2)	107.3(2)	C(3)−C(4)−C(18)	121.7(2)
C(12)−C(2)−C(3)	124.4(2)	C(1)−C(5)−C(6)	121.3(2)
C(12)−C(2)−C(1)	125.5(2)	C(1)−C(5)−C(4)	109.51(19)
C(3)−C(2)−C(1)	107.29(19)	C(6)−C(5)−C(4)	127.9(2)
C(2)−C(3)−C(15)	121.5(2)	$C_{20}H_{17}$(C)−Zr−Cp(C)	128.8
C(2)−C(3)−C(4)	109.46(19)		
C(15)−C(3)-C(4)	128.1(2)		

C4 has the largest θ_p angle of 11.2°, while C3 and C5 have the smallest pyramidalization angles of 3.2 and 3.7°, respectively. The average pyramidalization angle of the inner Cp core is 5.9°, compared with that of corannulene, which is calculated to be 8.7°.[23] This decrease in average pyramidalization angle indicates that hydrogenation of corannulene reduces the curvature of the bowl.

It is also interesting to note that the substituted fluorenyl ligand in $(\eta^5\text{-9-}i\text{Pr-C}_{13}H_8)(\eta^5\text{-C}_5H_5)ZrCl_2$ reported by Alt and co-workers is very slightly curved away from the zirconium center with an average POAV1 angle of 2.25°.[19] The carbon with the attached isopropyl group in the fluorenyl ligand displays the largest θ_p angle of 6.3°, while the rest of the carbons in the middle ring have θ_p values between 1.9 and 0.6°. Since our corannulene-based ligand is more constricted due to the bowl geometry, it displays a greater curvature than the analogous unrestricted fluorenyl ligands.

The NMR spectroscopic data of **4** are consistent with the assigned structure,[24] and the ^{13}C chemical shift of C4 (δ 103.98 ppm) is in the expected range (δ ~100 ppm) for an η^5 binding of the zirconium atom by the $C_{20}H_{17}$ ligand.[25]

Corannulene is estimated to undergo a bowl-to-bowl inversion process with $\Delta G^\ddagger \approx 10-11$ kcal/mol, based on a substituted corannulene having $\Delta G^\ddagger = 10.2 \pm 0.2$ kcal/mol.[26] The inversion barriers of partially hydrogenated corannulenes (di- and tetrahydrocorannulenes) have

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(16) NMR spectroscopic data for **3**: ^1H NMR ($CDCl_3$, 20 °C) δ 6.86 (d, 2H, $J = 7.6$ Hz), 6.71 (d, 2H, $J = 7.6$ Hz), 4.00 (d, 1H, $J = 13.2$ Hz), 3.32 (m, 2H), 2.74 (m, 5H), 2.50 (m, 2H), 2.16 (m, 2H), 0.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 20 °C) δ 151.19 (quat C), 141.47 (quat C), 137.17 (quat C), 129.52 (quat C), 125.57 (CH), 123.81 (CH), 40.27 (CH), 33.15 (CH_2), 30.06 (CH), 28.88 (CH_2), 26.92 (CH_2).

(17) Crystal data for **4**: $C_{25}H_{22}Cl_2Zr$ (fw = 484.25), red plate, monoclinic, $P2_1/n$ (No. 14), $a = 12.6274(6)$ Å, $b = 10.4427(5)$ Å, $c = 15.2552(7)$ Å, $\beta = 94.2260(10)°$, $V = 2006.14(16)$ Å^3, $D_{calcd} = 1.604$ g/cm^3 ($Z = 4$), $R = 0.0242$, $R_w = 0.0584$ (on all F^2, all data), $R = 0.0223$, $R_w = 0.0574$ (on F, $I > 2\sigma(I)$), GOF = 1.046. All other details are provided in the Supporting Information.

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(20) $C_{20}H_{17}$(C) = centroid of the $C_{20}H_{17}$ ligand, Cp(C) = centroid of the C_5H_5 ligand.

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(24) NMR spectroscopic data for **4**: ^1H NMR (CD_2Cl_2, 20 °C) δ 6.96 (d, 2H, $J = 6.9$ Hz), 6.86 (d, 2H, $J = 6.9$ Hz), 6.10 (s, 5H, Cp), 3.63 (m, 2H), 3.40 (m, 1H), 3.14 (m, 2H), 3.01 (m, 2H), 2.82 (m, 2H), 2.51 (m, 2H), 0.93 (m, 2H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 140.33 (quat C), 135.74 (quat C), 134.53 (quat C), 127.23 (quat C), 125.47 (CH), 121.78 (CH), 116.96, (Cp), 103.58 (quat C), 35.33 (CH_2), 31.50 (CH), 29.05 (CH_2), 28.33 (CH_2).

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also been reported to be in the 6−8.5 kcal/mol range.[27] We conducted a variable-temperature ^{1}H NMR spectroscopic study on **4** to determine whether the bowl ligand was undergoing a similar bowl-to-bowl inversion process. We observed no change in the ^{1}H NMR spectrum by cooling a solution of **4** to −80 °C (CD_2Cl_2) or heating to 100 °C (toluene-d_8). This means that **4** is undergoing a rapid inversion that we are unable to detect, is undergoing slow inversion but the minor endo isomer is too low in concentration to detect using the 300 MHz spectrometer, or is not inverting. We are currently attempting to resolve this issue by synthesizing the analogous endo complex to compare the reactivity with that of the exo isomer. If the ligand was rapidly inverting on the NMR spectrometer time scale, we would expect the chemistry of the endo and exo complexes to be similar.

The organometallic chemistry of buckybowls has only begun to be explored in recent years. We hope that this exciting area of chemistry will continue to grow and be developed as improved synthetic methods of the fullerene fragments are reported.

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Supporting Information Available: Text giving experimental details and spectroscopic data for **3** and **4** and tables giving X-ray structural data for **4**. This material is available free of charge via the Internet at: http://pubs.acs.org.

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