624 *Organometallics* **2003,** *22,* 624−626

η^6-Corannulene Buckybowl Complexes of Iridium, Including Ring-to-Ring Migration

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Received December 17, 2002

*Summary: Corannulene ($C_{20}H_{10}$, **1**), a curved-surface fragment of buckminsterfullerene (C_{60}), forms an η^6-coordinated complex with Cp^*Ir^{2+}. The analogous 1,2,5,6-tetramethylcorannulene (**2**) complex, $Cp^*Ir(\eta^6\text{-}\mathbf{2})^{2+}$, initially forms three isomers, but migration of the Cp^*Ir^{2+} unit from a nonmethylated to a methylated ring gives two isomers in the final product.*

Much effort has been directed toward the synthesis of metal complexes of buckminsterfullerene[1] (C_{60}). In all of these compounds, the metal is bonded to two carbon atoms (η^2) shared between two six-menbered rings.[2] Considering the fact that buckminsterfullerene contains 20 six-membered rings, it is surprising that there are no complexes in which a metal coordinates in an η^6 fashion to one of them. Fragments of buckminsterfullerene, curved-surface polynuclear aromatic hydrocarbons (buckybowls), have been prepared, but only with considerable difficulty.[3] An example of such a buckybowl is corannulene ($C_{20}H_{10}$, **1**; Chart 1), the smallest of the buckybowls. It was first synthesized in 1966 by Barth & Lawton,[4] and its molecular structure was determined in 1976 by Hanson.[5] Recent improvements in its synthesis have made the study of its chemistry possible.[6]

Chart 1

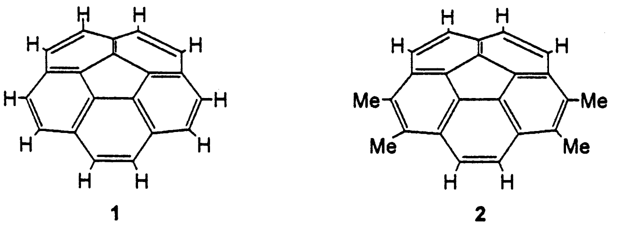
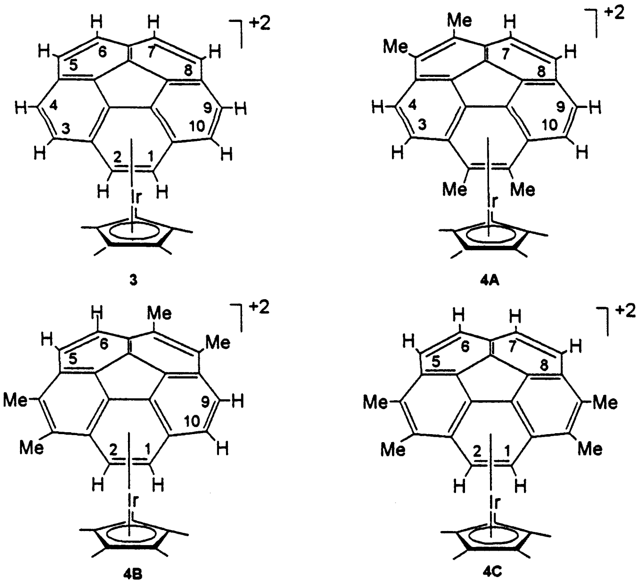


Chart 2. Structures of 3 and 4A−C



Only two transition-metal complexes of buckybowls have been reported. One, $[Pt(\eta^2{:}\sigma\text{-}C_{30}H_{12})(PPh_3)_2]$,[7] results from the insertion of Pt(0) into a C−C bond of $C_{30}H_{12}$. The other, $[Cp^*Ru(\eta^6\text{-}C_{20}H_{10})](O_3SCF_3)$,[8] resulting from η^6 coordination to corannulene (**1**), was insufficiently stable to be isolated but was characterized by NMR studies in solution. Previous attempts in our laboratory to prepare η^2-corannulene complexes with $CpM(CO)_2(THF)$ (M = Mn, Re) and $M(CO)_3(dppe)(NCMe)$ (M = Mo, W) were unsuccessful,[9] even though these same complexes form stable adducts with C_{60}.[1] Attempts to form η^6 complexes of **1** by reaction with $M(CO)_3(NCMe)_3$ (M = Cr, W) were also unsuccessful.[9] Here, we report reactions of the acetone complex $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ with two different buckybowls: corannulene (**1**) and 1,2,5,6-tetramethylcorannulene (**2**; Chart 1). In addition, we report the first ring-to-ring migration of a metal on either a buckyball or a buckybowl surface.

It is known that $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ reacts with a variety of arenes to form η^6-arene complexes[10] of the type $[Cp^*Ir(\eta^6\text{-arene})](BF_4)_2$. The synthesis of $[Cp^*Ir(\eta^6\text{-}C_{20}H_{10})](BF_4)_2$ (**3**; Chart 2) by reaction of $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ (0.020 mmol) with **1** (0.040 mmol)

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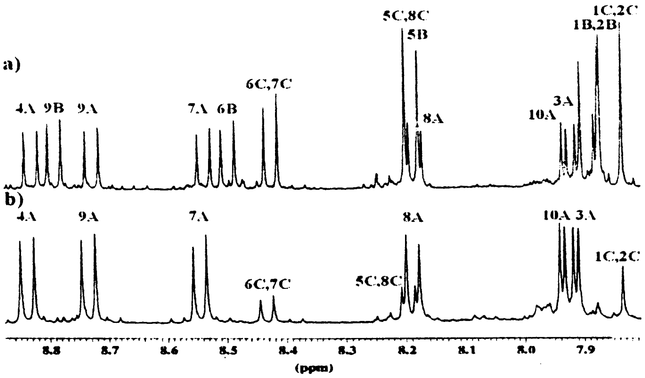

Figure 1. ^{1}H NMR spectra in the corannulene region of isomers **4** formed in the reaction of $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ with **2** at room temperature in CD_3NO_2: (a) 15 min; (b) 6 h. The peak assignments A−C refer to isomers **4A**−**C**.

under an Ar atmosphere is quantitative in CD_3NO_2 solvent at room temperature within 5 min. Although **3** is stable in CD_3NO_2 and can be precipitated by addition of CH_2Cl_2, it is too air-sensitive to give satisfactory elemental analyses. It is soluble in acetone and methanol, but the solvent displaces the corannulene ligand immediately. The characterization of **3** in CD_3NO_2 is based on its ^{1}H,[11] $^{13}C\{^1H\}$,[12] COSY, and NOESY NMR spectra, as discussed below.

The reaction of $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ (0.020 mmol) with **2** (0.042 mmol) is carried out using the same conditions as those used with **1**, under an Ar atmosphere, in CD_3NO_2 at room temperature. After 3 min, three complexes (isomers) are observed by ^{1}H NMR studies: **4A**, **4B**, and **4C** (Chart 2). The ratio among them is 23:61:16 (**4A**:**4B**:**4C**). After 15 min, the ratio is 36:43:21 (Figure 1). After 6 h, isomer **4B** has disappeared and the ratio between **4A** and **4C** is 88:12 (Figure 1). This ratio does not change within the next 24 h, or even within 1 month. When the reaction of $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ with **2** is carried out at 101 °C for 3 h, **4B** is not observed and the ratio **4A**:**4C** is the same (88:12) as that reached after 24 h at room temperature. While **4** could be precipitated from CH_2Cl_2 with hexanes, it was too air-sensitive to give satisfactory elemental analyses. However, the three isomers in CD_3NO_2 were fully characterized by their ^{1}H,[13−15] $^{13}C\{^1H\}$,[16] COSY, and NOESY NMR and mass[17] spectra.

Table 1. ^{1}H NMR Spectra of 3 and 4A−C in the Corannulene Region (CD_3NO_2, ppm)

H position	3	4A	4B	4C
1	7.98 (s)		7.88 (d)	7.81 (s)
2	7.98 (s)		7.87 (d)	7.81 (s)
3	7.97 (d)	7.91 (d)		
4	8.74 (d)	8.82 (d)		
5	8.18 (d)		8.18 (d)	8.18 (d)
6	8.46 (d)		8.54 (d)	8.43 (d)
7	8.46 (d)	8.53 (d)		8.43 (d)
8	8.18 (d)	8.17 (d)		8.18 (d)
9	8.74 (d)	8.72 (d)	8.84 (d)	
10	7.97 (d)	7.92 (d)	7.90 (d)	

^{1}H NMR signals for comparable protons in **3** and **4** in the corannulene region, assigned from COSY and NOESY NMR studies, have very similar chemical shifts (Table 1). The protons on the carbons coordinated to Ir (positions 1 and 2) are in the range 7.98−7.81 ppm; they are singlets (**3** and **4C**) or doublets (**4B**), depending on the symmetry of the isomer. Protons on carbons not bonded to Ir are AB systems with coupling constants of 9 Hz. Their chemical shift ranges depend on their distance from the Ir atom. The ranges are 7.97−7.90 ppm (positions 3 and 10), 8.84−8.72 ppm (positions 4 and 9), 8.18−8.17 ppm (positions 5 and 8), and 8.54−8.43 ppm (positions 6 and 7). The $^{13}C\{^1H\}$ NMR spectra of **3**[12] and **4A**[16] show signals between 115.7 and 92.4 ppm assigned to the carbons bonded directly to the Ir. These signals are upfield with respect to the free ligands (e.g. 136.3, 132.0, and 128.2 ppm for **1**), as is typically observed in simple iridium arene complexes.[10] This indicates clearly that iridium is η^6-coordinated to one of the six-membered rings of the ligand.

The stabilities of $[Cp^*Ir(\eta^6\text{-arene})](BF_4)_2$ complexes are greater when the arenes are alkyl-substituted.[10] The reaction of $[Cp^*Ir(OCMe_2)_3](BF_4)_2$ with **2** initially (within 3 min) gives, as the major product, isomer **4B**, in which the Cp^*Ir^{2+} unit is coordinated to a nonmethylated ring. However, it is followed by the isomerization of **4B** to the more stable isomer **4A**, in which the Cp^*Ir^{2+} unit is coordinated to one of the methylated rings. It is not known whether this isomerization occurs by migration on the surface of **2** or by dissociation of Cp^*Ir^{2+} from **2**.

Reactions of the final **4A**:**4C** (88:12) mixture with excess benzene or acetone (10 equiv) in CD_3NO_2 at room temperature result in complete substitution of **2** by benzene within 6 h and by acetone within 4 h. Isomer **4C** disappears somewhat more quickly than **4A** in both reactions, which indicates that the corannulene ligand **2** is more labile in **4C**, where the $CpIr^{2+}$ unit is coordinated to a nonmethylated ring.

Considering the strong tendency of $[Cp^*Ir(OCMe_2)_3]^{2+}$ to form η^6 complexes with **1** and **2**, the reaction with C_{60} was attempted. Due to the insolubility of C_{60} in CH_3NO_2, $CHCl_2CHCl_2$ was used as the solvent; there was no ^{13}C NMR evidence for the formation of a Cp^*Ir^{2+} complex with C_{60}.

In conclusion, buckminsterfullerene C_{60} coordinates to a variety of mononuclear metal complexes through

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(11) ^{1}H NMR for **3** (400.13 MHz, CD_3NO_2, room temperature): δ 8.74 (d, $J_{HH} = 9$ Hz, $C_{20}H_{10}$, 2H), 8.46 (d, $J_{HH} = 9$ Hz, $C_{20}H_{10}$, 2H), 8.18 (d, $J_{HH} = 9$ Hz, $C_{20}H_{10}$, 2H), 7.98 (s, $C_{20}H_{10}$, 2H), 7.97 (d, $J_{HH} = 9$ Hz, $C_{20}H_{10}$, 2H), 2.06 (s, Cp*, 15H) ppm.

(12) $^{13}C\{^1H\}$ NMR for **3** (100.61 MHz, CD_3NO_2, room temperature): δ 143.7 (C4,9), 134.1 (C6,7), 131.8 (C5,8), 121.1 (C3,10), 115.1 (C−Ir), 105.0 (Cp*), 99.4 (C−Ir), 92.4 (C1,2), 9.98 (Cp*Me), 144.6, 136.6, 136.0, 134.6 (C4a, C6a, C8a, C10d, C10e, C10f) ppm.

(13) ^{1}H NMR for **4A** (400.13 MHz, CD_3NO_2, room temperature): δ 8.82 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 8.72 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 8.53 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 8.17 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 7.92 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 7.91 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 3.05 (s, $C_{20}H_6Me_4$, 3H), 3.04 (s, $C_{20}H_6Me_4$, 3H), 2.90 (s, $C_{20}H_6Me_4$, 3H), 2.89 (s, $C_{20}H_6Me_4$, 3H), 1.89 (s, Cp*, 15H) ppm.

(14) ^{1}H NMR for **4B** (400.13 MHz, CD_3NO_2, room temperature): δ 8.84 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 8.54 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 8.18 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 1H), 7.90 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 2H), 7.88 (d, AB, $J_{HH} = 2$ Hz, $C_{20}H_6Me_4$, 1H), 7.87 (d, AB, $J_{HH} = 2$ Hz, $C_{20}H_6Me_4$, 1H), 2.98 (s, $C_{20}H_6Me_4$, 6H), 2.85 (s, $C_{20}H_6Me_4$, 6H) 2.02 (s, Cp*, 15H) ppm.

(15) ^{1}H NMR for **4C** (400.13 MHz, CD_3NO_2, room temperature): δ 8.43 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 2H), 8.18 (d, $J_{HH} = 9$ Hz, $C_{20}H_6Me_4$, 2H), 7.81 (s, $C_{20}H_6Me_4$, 2H), 2.96 (s, $C_{20}H_6Me_4$, 6H), 2.89 (s, $C_{20}H_6Me_4$, 6H), 2.03 (s, Cp*, 15H) ppm.

(16) $^{13}C\{^1H\}$ NMR for **4A** (100.61 MHz, CD_3NO_2, room temperature): δ 143.4 (C9), 141.8 (C4), 132.5 (C7), 131.7 (C8), 119.8 (C3), 119.6 (C10), 115.7 (C−Ir), 114.6 (C−Ir), 107.3 (C−Ir), 106.9 (C−Ir), 103.5 (Cp*), 98.8 (C−Ir), 98.3 (C−Ir), 16.2 (Me), 15.6 (Me), 14.8 (Me), 9.27 (Cp*Me), 142.7, 142.6, 139.9, 137.1, 136.2, 135.0, 134.1 (C5, C6, C4a, C6a, C8a, C10d, C10e, C10f) ppm.

(17) MS for **4**: m/z 317 ($[Cp^*Ir(C_{24}H_{18})]^{2+}$), electrospray in CD_3NO_2.

two carbon atoms (η^2) but is not known to coordinate η^6 to any metal fragment, including Cp*Ir^{2+}. On the other hand, the curved-surface corannulene buckybowls **1** and **2** do not coordinate in an η^2 fashion to metal fragments, even those (CpM(CO)$_2$, where M = Mn, Re, and M(CO)$_3$-(dppe), where M = Mo, W) that form η^2 complexes with C$_{60}$.[1] However, **1** and **2** do coordinate in an η^6 manner to electrophilic fragments such as Cp*Ir^{2+} and Cp*Ru$^+$.[8] Thus, C$_{60}$ and corannulene, with very similar structural features, have very different preferences for metal complex coordination: C$_{60}$ prefers η^2 binding, while corannulenes (**1** and **2**) prefer η^6 coordination. We are continuing to explore buckybowls and their coordination to electrophilic transition-metal complexes.

Acknowledgment. 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-7405-Eng-82 with Iowa State University. We thank Dr. Z. Marcinow for helping us with the synthesis of **2**.

Supporting Information Available: Text and figures giving synthetic procedures and spectra for **3** (^{1}H, ^{13}C{^{1}H}, COSY, NOESY) and for the mixture of isomers **4A** and **4C** (^{1}H, ^{13}C{^{1}H}, COSY, NOESY). This material is available free of charge via the Internet at http://pubs.acs.org.

OM021012R