Communication

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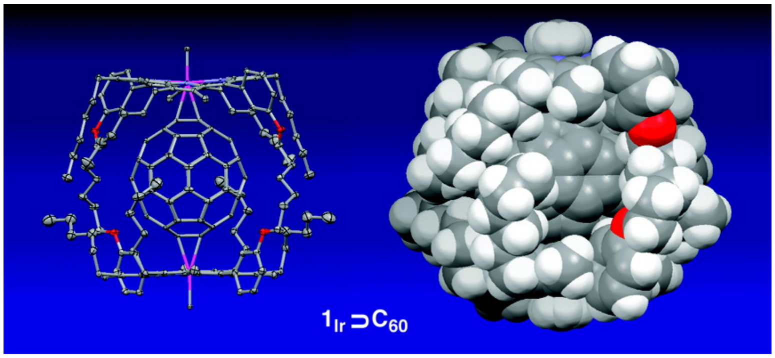

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Hosting Fullerenes by Dynamic Bond Formation with an Iridium Porphyrin Cyclic Dimer: A “Chemical Friction” for Rotary Guest Motions

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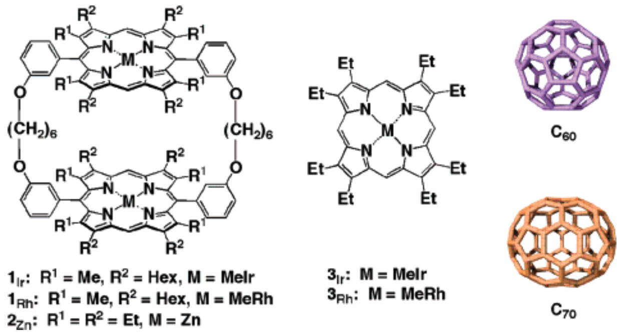
Cyclic hosts that strongly entrap fullerenes are highly important for selective extraction[1] and noncovalent modification[2] of such spherical carbon nanoclusters. Since our discovery of the hosting capability of a zinc porphyrin cyclic dimer in 1999,[3] various host molecules composed of multiple metalloporphyrin units have been reported, which can trap fullerenes in solution via van der Waals interactions.[4] Noteworthy is rhodium(III) porphyrin cyclic dimer $\mathbf{1_{Rh}}$ (Chart 1),[5] which is roughly 100 times more affinitive than its zinc porphyrin analogue toward fullerenes. The association constants (K_{assoc}) observed with C_{60} and C_{70} (10^7-10^8 M^{-1} in C_6H_6)[5a] have been the largest among those reported so far, suggesting a possible contribution of the metal centers of the host to the inclusion of fullerenes. Here we report an iridium version of $\mathbf{1_{Rh}}$ ($\mathbf{1_{Ir}}$; Chart 1) as an ultimate host that can entrap fullerenes by a “bond-forming interaction” and displays even 2−3 orders of magnitude greater K_{assoc} values than $\mathbf{1_{Rh}}$. This bond-forming interaction also forces C_{60} to be deformed and allows C_{70} to adopt an end-on orientation relative to the metalloporphyrin units. From restricted rotary motions of the guest fullerenes, we propose an interesting aspect of “chemical friction” on graphitic surfaces.

While group IX transition metal complexes of rhodium and iridium have been reported to form fullerene adducts,[6] the chemistry of iridium porphyrins has not been well-explored to date. Host $\mathbf{1_{Ir}}$ bears an axial methyl group at each iridium center, allowing for easy handling of the host molecule due to no ionization capability. Furthermore, the axial methyl groups possibly enhance the electron-donating ability of the host toward fullerenes and also serve as a probe for ^{1}H NMR spectroscopy. For the synthesis of $\mathbf{1_{Ir}}$,[7] our initial attempt, based on oxidative addition of a reduced form of $\mathbf{1_{Ir}}$ to MeI,[8b] was unsuccessful. However, we later found that iodoiridium(III) porphyrins readily undergo transmetalation with Me_3Al, allowing for the successful synthesis of $\mathbf{1_{Ir}}$ from its iodide precursor in a good yield (66%).

Analogous to $\mathbf{1_{Rh}}$, $\mathbf{1_{Ir}}$ in C_6D_6 at 25 °C displayed a complicated ^{1}H NMR spectrum due to the presence of some conformational isomers.[5a,7] For example, the Me−Ir and meso protons of $\mathbf{1_{Ir}}$ showed multiple singlet signals at δ −6.50 to −5.98 and δ 9.89 to 10.04 ppm, respectively. However, upon mixing with C_{60}, the spectrum became much simplified to give single Me−Ir and meso-H signals at δ −5.65 and 10.11 ppm, respectively.[7] Spectroscopic titration of $\mathbf{1_{Ir}}$ with C_{60} in C_6H_6 at 25 °C resulted in a red shift of the Soret absorption band of $\mathbf{1_{Ir}}$ from 400 to 414 nm with a decrease in intensity, characteristic of the inclusion of fullerenes.[7] The 1:1 stoichiometry, as expected for $\mathbf{1_{Ir}}\supset C_{60}$, was supported by plotting the absorbance changes (ΔAbs) at 400 nm versus $[C_{60}]/[\mathbf{1_{Ir}}]$.[7] However, the K_{assoc} value in C_6H_6 was too large to evaluate accurately ($K_{\text{assoc}} > 10^9$ M^{-1}) from this titration profile.[7] Hence, 1,2-dichlorobenzene (DCB), a much better solvent for fullerenes, was used, so that the K_{assoc} value was properly reduced to a reliable range (1.3×10^8 M^{-1}).[7] Nevertheless, this value is still extraordinary, when compared to the K_{assoc} of reference $\mathbf{1_{Rh}}$, which is only 3.4×10^5 M^{-1} in DCB[7] (2.4×10^7 M^{-1} in C_6H_6).[5a] In fact, 1:1 mixing of $\mathbf{1_{Ir}}$ with $\mathbf{1_{Rh}}\supset C_{60}$ in C_6D_6 at 25 °C resulted in a rapid transfer of C_{60} from $\mathbf{1_{Rh}}$ to $\mathbf{1_{Ir}}$.[7] While metalloporphyrin monomers such as $\mathbf{3_{Rh}}$[8a] (Chart 1) hardly interact with fullerenes in solution, monomer $\mathbf{3_{Ir}}$,[8b] in sharp contrast, showed a distinct absorption spectral change upon mixing with C_{60} in C_6H_6.[7]

Chart 1



After numerous trials, we successfully obtained a single crystal of $\mathbf{1_{Ir}}\supset C_{60}$ suitable for X-ray crystallography, by slow evaporation of a CH_2Cl_2 solution of an equimolar mixture of $\mathbf{1_{Ir}}$ and C_{60}. Figure 1 shows an ORTEP diagram of $\mathbf{1_{Ir}}\supset C_{60}$ at −180 °C, where $\mathbf{1_{Ir}}$ and C_{60} share a C_2 axis of $\mathbf{1_{Ir}}\supset C_{60}$. Two iridium atoms in $\mathbf{1_{Ir}}$ are located in this axis and bind to C_{60} from both of its sides. Each of these iridium centers, which are crystallographically nonequivalent, binds in an η^2 fashion to a 6:6 ring juncture C−C bond of C_{60}. The C(1)−C*(1) and C(30)−C*(30) distances of 1.424(4) and 1.425(4) Å, respectively, are definitely longer than the C−C bonds at 6:6 ring fusions (1.391(18) Å)[9] but shorter than those at 5:6 fusions (1.455(12) Å)[9] in intact C_{60}. Of interest, guest C_{60} is deformed to adopt an ellipsoidal shape,[6d] where the midpoints of the C(1)−C*(1) and C(30)−C*(30) bonds are 7.067 Å apart from one another, while the dimensions of C_{60} in the two orthogonal directions, perpendicular to the Ir−Ir axis (6.968 and 6.928 Å), are comparable to those of intact C_{60} (6.938 Å). In contrast, C_{60} in the cavity of zinc porphyrin $\mathbf{2_{Zn}}$ (Chart 1) displays neither bond-forming nor deformation signature.[5a]

We investigated the rotational dynamics of included C_{60}. If guest C_{60} rotates freely, all of its carbon atoms should be identical to one another, thereby giving rise to a single ^{13}C NMR signal. On the other hand, if the bond formation between $\mathbf{1_{Ir}}$ and C_{60}, as observed in the crystalline state (Figure 1), occurs in solution, the rotation of C_{60} may be decelerated, resulting in broadening or even multiplication of its ^{13}C NMR signal. At 20 °C in toluene-d_8,

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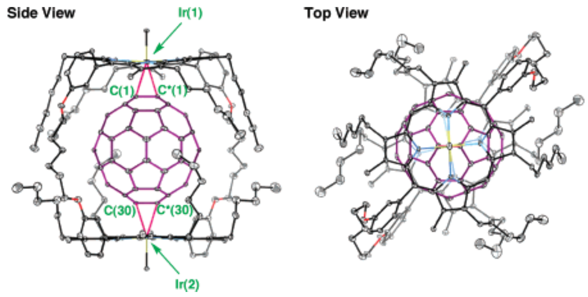

Figure 1. ORTEP diagram of $\mathbf{1}_{\mathbf{Ir}}{\supset}C_{60}{\cdot}(CH_2Cl_2)_4$ at −180 °C (50% thermal ellipsoids). The solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir(1)−C(1), 2.430(3); Ir(2)−C(30), 2.399(2); C(1)−C*(1), 1.424(4); C(30)−C*(30), 1.425(4).

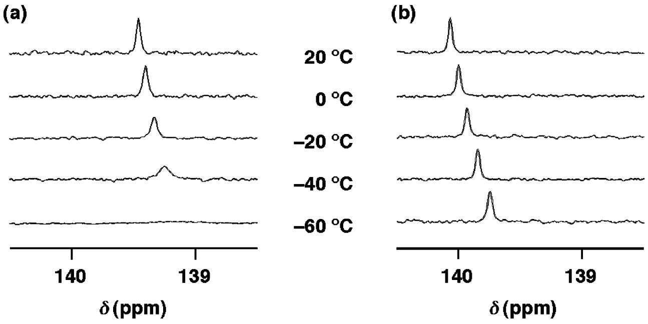

Figure 2. Variable-temperature ^{13}C NMR spectra in toluene-d_8 of C_{60} in (a) $\mathbf{1}_{\mathbf{Ir}}{\supset}C_{60}$ and (b) $\mathbf{1}_{\mathbf{Rh}}{\supset}C_{60}$. The inclusion complexes were prepared by mixing ^{13}C-enriched C_{60} with 1.5 equiv of **1**.

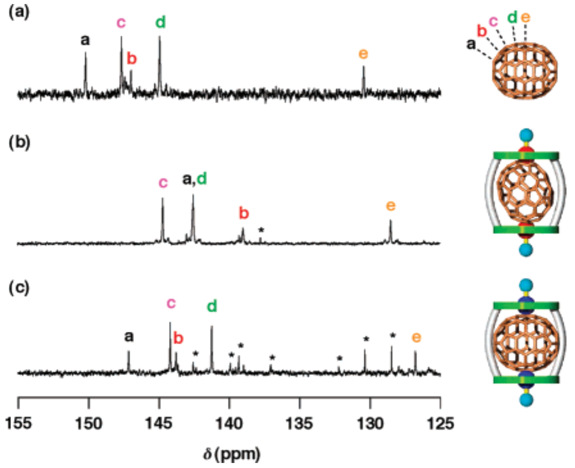

Figure 3. ^{13}C NMR spectra (δ 125−155 ppm) in $CDCl_3/CS_2$ (1/1 v/v) at 25 °C of (a) C_{70} alone, (b) $\mathbf{1}_{\mathbf{Ir}}{\supset}C_{70}$, and (c) $\mathbf{1}_{\mathbf{Rh}}{\supset}C_{70}$. The inclusion complexes were prepared by mixing ^{13}C-enriched C_{70} with 2.0 equiv of **1**. Asterisked signals originate from the host molecules.

$\mathbf{1}_{\mathbf{Ir}}{\supset}C_{60}$ showed a single C_{60} signal at δ 139.5 ppm with a half-width ($W^{1/2}$) value of 5.2 Hz (Figure 2a). Upon cooling, this signal obviously became broader and gave, at −60 °C, a $W^{1/2}$ value (60.2 Hz) that is nearly 12 times as large as that at 20 °C. Thus, the bond-forming host/guest interaction in $\mathbf{1}_{\mathbf{Ir}}{\supset}C_{60}$ indeed operates, though dynamically, in solution and gives rise to a chemical friction on the rotary guest motion. In contrast, the $W^{1/2}$ value of the C_{60} signal due to $\mathbf{1}_{\mathbf{Rh}}{\supset}C_{60}$ hardly changed upon cooling from 20 (5.2 Hz) to −60 °C (6.2 Hz) (Figure 2b).

Unlike C_{60}, C_{70} adopts an ellipsoidal shape, where the double bonds at its poles are rather isolated electronically from the others (Figure 3a).[10] If the iridium centers of $\mathbf{1}_{\mathbf{Ir}}$ prefer such π-electron-rich C═C bonds,[6b,c] guest C_{70} could adopt an end-on orientation relative to the metalloporphyrin units. On the other hand, a side-on orientation of C_{70} may occur[5a] if van der Waals interactions are dominant over the bond formation. When ^{13}C-enriched C_{70} was allowed to complex with $\mathbf{1}_{\mathbf{Ir}}$ in $CDCl_3/CS_2$ (1/1 v/v), all the ^{13}C signals due to guest C_{70} shifted upfield at 25 °C (Figure 3b). Since the upfield shift was more pronounced for the carbon atoms at the poles ($\Delta\delta = -7.7, -8.0$ ppm) than at the equatorial positions ($\Delta\delta = -3.0, -2.5, -2.0$ ppm), guest C_{70} most likely adopts an end-on orientation relative to the metalloporphyrin units. This is in sharp contrast with $\mathbf{1}_{\mathbf{Rh}}{\supset}C_{70}$ (Figure 3c), where a side-on orientation is preferred for guest C_{70},[11] thereby resulting in slightly but definitely greater chemical shift changes for the carbon atoms at the equatorial positions ($\Delta\delta = -3.4, -3.7, -3.6$ ppm) than at the poles ($\Delta\delta = -3.0, -3.2$ ppm).[5a] Interestingly, while the order of the magnitudes of Δδ for $\mathbf{1}_{\mathbf{Ir}}{\supset}C_{70}$ was unchanged upon cooling from 50 to −60 °C,[7] some of the C_{70} signals, most explicitly, due to carbon atoms a and b interactive with the iridium centers, were broadened significantly.[7] Hence, included C_{70} hardly rotates along its shorter axis but can rotate thermally along its longer axis as a consequence of the slipping of the iridium centers from one C═C bond to the neighboring ones at the pole positions of C_{70}. Thus, as expected, the chemical friction for C_{70} is not isotropic.

In conclusion, $\mathbf{1}_{\mathbf{Ir}}$ serves as the novel bond-forming cyclic host for fullerenes, featuring the largest association constants among those reported to date. This bond formation also causes an ellipsoidal deformation of C_{60} and an end-on orientation of C_{70} relative to the metalloporphyrin units. Furthermore, the restricted rotary motions of C_{60} and C_{70} within the cavity of $\mathbf{1}_{\mathbf{Ir}}$ provide an interesting aspect of chemical friction on graphitic surfaces with different curvatures. Interaction of metalloradical species,[12] possibly derived from $\mathbf{1}_{\mathbf{Ir}}$ and $\mathbf{1}_{\mathbf{Rh}}$, with fullerenes and carbon nanotubes is one of the subjects worthy of further investigation.

Supporting Information Available: Synthesis of $\mathbf{1}_{\mathbf{Ir}}$, analytical data of mixtures of $\mathbf{1}_{\mathbf{Ir}}$, $\mathbf{1}_{\mathbf{Rh}}$, and $\mathbf{3}_{\mathbf{Ir}}$ with fullerenes, and crystallographic data of $\mathbf{1}_{\mathbf{Ir}}{\supset}C_{60}{\cdot}(CH_2Cl_2)_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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