π-Bowl Complexes

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A Concave-Bound CpFe Complex of Sumanene as a Metal in a π Bowl**

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Coordination is one of the key modes in metal binding. A variety of planar π-conjugated compounds bind to metals in an η^n fashion. On the other hand, the way in which metals bind to curved carbon π surfaces has attracted continuous interest since the discovery of fullerenes and carbon nanotubes. To date, the *exo* π surfaces of fullerenes have been found to act as η^2-coordination ligands to various transition metals.[1] Other coordination modes in *exo* complexes were reported for modified fullerene π systems.[2] Fullerenes and carbon nanotubes are also known to form endohedral metal complexes to provide potentially useful materials in carbon chemistry.[3] In the coordination chemistry of fullerene fragments, called "buckybowls" or bowl-shaped hydrocarbons, there is the intriguing issue of the preference for metal binding to the convex surface versus the concave one (Figure 1 A,B), which was first addressed by the computational study of hemifullerene ($C_{30}H_{12}$) in 1993.[4] To date, few coordination complexes of buckybowls, such as corannulene (a C_{20} subunit of C_{60}, Figure 1 D), have been prepared and characterized.[5] Convex binding, including η^1, η^2, and η^6-coordination modes, was displayed in the X-ray crystal structures of some monometalated corannulene complexes.[5a,k,m–q] Recent theoretical studies on complexes of corannulene and its derivatives using density functional theory also indicated preferential convex binding to transition metals.[6] On the other hand, both convex and concave binding of ruthenium(II) to corannulene or tetramethylcorannulene with η^6 coordination has been reported.[5f,p,k] Furthermore, tri- and tetrametalation of corannulenes and hemifullerene were achieved under gas-phase deposition reactions; metal centers were bound to both convex and concave faces with η^2 binding.[5e,j,g,r] However, a concave-selective coordination complex has never been isolated or predicted by molecular calculations, except in ab initio studies on the binding of alkali-metal cations and Ga^+ to hemifullerene.[7] Concave coordination is considered to provide a route toward the synthesis of inclusion complexes of fullerenes or carbon nanotubes, which have potential applications in various fields, such as molecular electronics[8] and magnetic resonance imaging.[9]

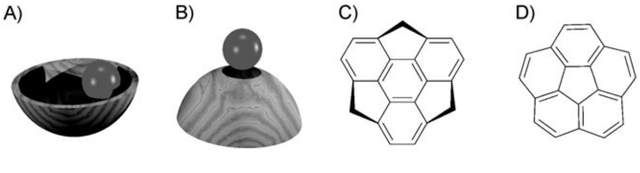
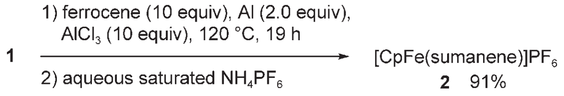


Figure 1. Schematic illustrations of A) concave and B) convex binding of a metal to a buckybowl. C) Sumanene (**1**, $C_{21}H_{12}$). D) Corannulene ($C_{20}H_{10}$).

Sumanene (**1**, $C_{21}H_{12}$, Figure 1 C) is the key C_{3v} symmetric partial structure of C_{60} and was first synthesized in 2003.[10] It has a deeper bowl (1.11 Å) than corannulene and exhibits slow bowl-to-bowl inversion. Furthermore, facile derivatization is permitted by nucleophilic bond formation with the benzylic carbanions.[11] Various coordination modes, including η^1, η^2, η^4, η^5, and η^6, are conceivable with sumanene, but its coordination chemistry with transition metals has been limited to a computational study that predicts convex binding of $\{Pt(PH_3)_2\}$ in an η^2 fashion.[12] From this point of view, it is challenging to "catch" a metal in the bowl. Herein, we report the first synthesis of the concave-binding complex of sumanene with $\{CpFe\}^+$ ($Cp = C_5H_5$).

The metalation of sumanene was performed by ligand exchange with a cyclopentadienyl group of ferrocene. The reaction proceeded in the presence of aluminum powder and aluminum chloride without solvent under argon at 120 °C for 19 h. The counteranion of the crude complex was replaced by hexafluorophosphate, giving $[CpFe(sumanene)]PF_6$ (**2**) as an orange solid (Scheme 1) The use of excess ferrocene and aluminum chloride selectively afforded the desired monometalated complex in 91 % yield. Reaction in decahydronaphthalene as solvent did not yield **2**. The parent peak in the high-resolution FAB mass spectrum showed *m/z* 385.0677, corresponding to $[CpFe(sumanene)]^+$. This result is in sharp



Scheme 1. Synthesis of $[CpFe(sumanene)]PF_6$ (**2**).

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contrast with the dimetalation of fluorene ($C_{13}H_{10}$) and triphenylene ($C_{18}H_{12}$).[13]

The structure of **2** in solution was investigated using ^{1}H and ^{13}C NMR spectroscopy. Figure 2A shows the 600 MHz ^{1}H NMR spectrum of **2** at 298 K in CD_3CN. The aromatic sumanene proton signals split into two low-field doublets ($\delta = 7.69$ and 7.62 ppm, $J = 7.6$ Hz, H_b and H_c) and a singlet peak with a high-field shift ($\delta = 6.39$ ppm, H_a). This singlet can be assigned to the protons of the benzene ring coordinated to the $\{CpFe\}^+$ unit. These results indicate the selective binding of the Fe^{II} center to a flank benzene ring rather than the central (hub) benzene ring. The benzylic protons appear as two pairs of doublets in a 2:1 ratio ($J = 19.1$ Hz, 4H, H_d; $J = 20.1$ Hz, 2H, H_e). The high-field *endo* benzylic protons ($\delta = 4.96$ and 3.92 ppm, $H_{d_{endo}}$ and $H_{e_{endo}}$) and low-field *exo* benzylic protons ($\delta = 5.21$ and 4.94 ppm, $H_{d_{exo}}$ and $H_{e_{exo}}$) support the bowl-shaped structure, as observed with **1**. The *endo* proton at $\delta = 4.96$ ppm ($H_{d_{endo}}$) displays an exceptional low-field shift, thus suggesting the strong effect of the Fe^{II} center and indicating that the metal is present on the *endo* side of the sumanene skeleton. Only a singlet signal for the cyclopentadienyl protons was observed at 298 K, suggesting fast dynamic rotation at this temperature. The signal of the cyclopentadienyl protons H_f at $\delta = 3.26$ ppm was shifted approximately $\Delta\delta = 1.3$ ppm to higher field than the corresponding protons of $[CpFe(\eta^6\text{-fluorene})]PF_6$ and $[CpFe(\eta^6\text{-triphenylene})]PF_6$ ($\delta = 4.64$ and 4.45 ppm, respectively; see Figure S6 in the Supporting Information). This strong ring-current effect also supports the concave binding. Twelve signals were observed in the ^{13}C NMR spectrum, thus suggesting a C_s symmetric structure (see Figure S2 in the Supporting Information). The concave binding structure of **2** was furthermore confirmed by nuclear Overhauser effect (NOE) experiments. Irradiation of the cyclopentadienyl protons resulted in NOEs at the *endo* benzylic protons (2.6 % for each $H_{d_{endo}}$ and 3.0 % for $H_{e_{endo}}$) and sumanene aromatic protons (1.5 % for each H_a, 0.9 % for each H_b, and 0.7 % for each H_c), as shown in Figure 2B, whereas no NOE signals were observed with the corresponding *exo* protons ($H_{d_{exo}}$ and $H_{e_{exo}}$, see also Figure S3 in the Supporting Information). Variable-temperature NMR spectroscopy experiments were also conducted (see Figure S7 in the Supporting Information). At low temperature (243 K), small broadening of the peaks was observed, and at a high temperature (333 K) the couples of benzylic peaks were not closer together. These findings indicate slow bowl-to-bowl inversion in **2**.

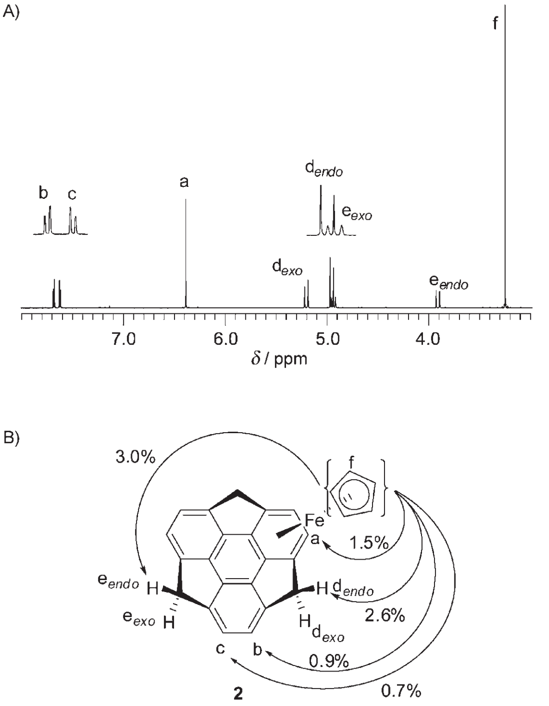

Figure 2. A) ^{1}H NMR spectrum of **2** (600 MHz, CD_3CN). B) NOEs in **2**.

Complex **2** was recrystallized from a saturated solution of propionitrile to give single crystals as orange platelets, which were subjected to X-ray crystallographic analysis.[14] The crystal structure belongs to the monoclinic crystal system. ORTEP diagrams are illustrated in Figure 3A,B and clearly show the concave binding of the cyclopentadienyl iron moiety to a flank benzene ring of **2**. Figure 3C,D shows the bond lengths of **2**. In the iron-coordinated flank benzene ring, the bond lengths C7–C21, C26–C19, and C6–C20 increased by 0.02–0.04 Å compared to the corresponding bonds in uncoordinated flank benzene rings. Conversely, C6–C7 and C21–C26 decreased by 0.02–0.03 Å (Figure 3C). On the other hand, C19–C20 exhibits a longer bond (1.42 Å). Other C–C bonds in the sumanene skeleton were almost in agreement with the trends of the bond alternations of **1** (bond lengths of **1** are shown in blue, Figure 3C). The Fe–C bonds from the iron center to the six-membered ring (C6, C7, C19, and C20) range from 2.01 to 2.07 Å. Although the distances to the hub carbon atoms (C21 and C26) are a little longer (2.136 and 2.135 Å, respectively), the coordination can be considered almost η^6 coordination (Figure 3D). Such concave η^6 coordination is thus achieved in the curved π-conjugated carbon system for the first time. The cyclopentadienyl ring is tilted 6° to the iron-bound benzene ring, perhaps because of steric repulsion with the sumanene skeleton. The bowl depth was measured as a perpendicular distance from the center of the hub benzene ring (C21–C26) to the rim carbon atoms of the aromatic rings. A small amount of bowl flattening was observed around the coordinated side (C6, C20; ca. 0.99 Å);[15] in contrast, the bowl depth at the other side (C10, C11, C15, and C16; 1.07 to 1.13 Å) was almost the same as found for **1** (1.11 Å, Figure 3B). Haddon's π-orbital axis vector (POAV) analysis[16] reveals that the uncomplexed hub carbons atoms (C23 and C25) are pyramidalized to 8.5 and 9.1°, which is undistinguishable from the values of **1** (ca. 8.8°). On the other hand, smaller and larger values were observed at C24 and C22, respectively (8.2° and 9.5°). The Fe-bound hub carbon atoms (C21 and C26) have POAV angles of 6.9 and 7.5°, respectively, showing the flattening found in the bowl depth (Figure 3C). The hexafluorophosphate counteranion was disordered in the crystal, and four fluorine atoms were refined with an occupancy factor of 0.5:0.5. The crystal structure for one arrangement is shown in Figure 3E,F. Columnar stacking was observed; partial π–π orbital overlap

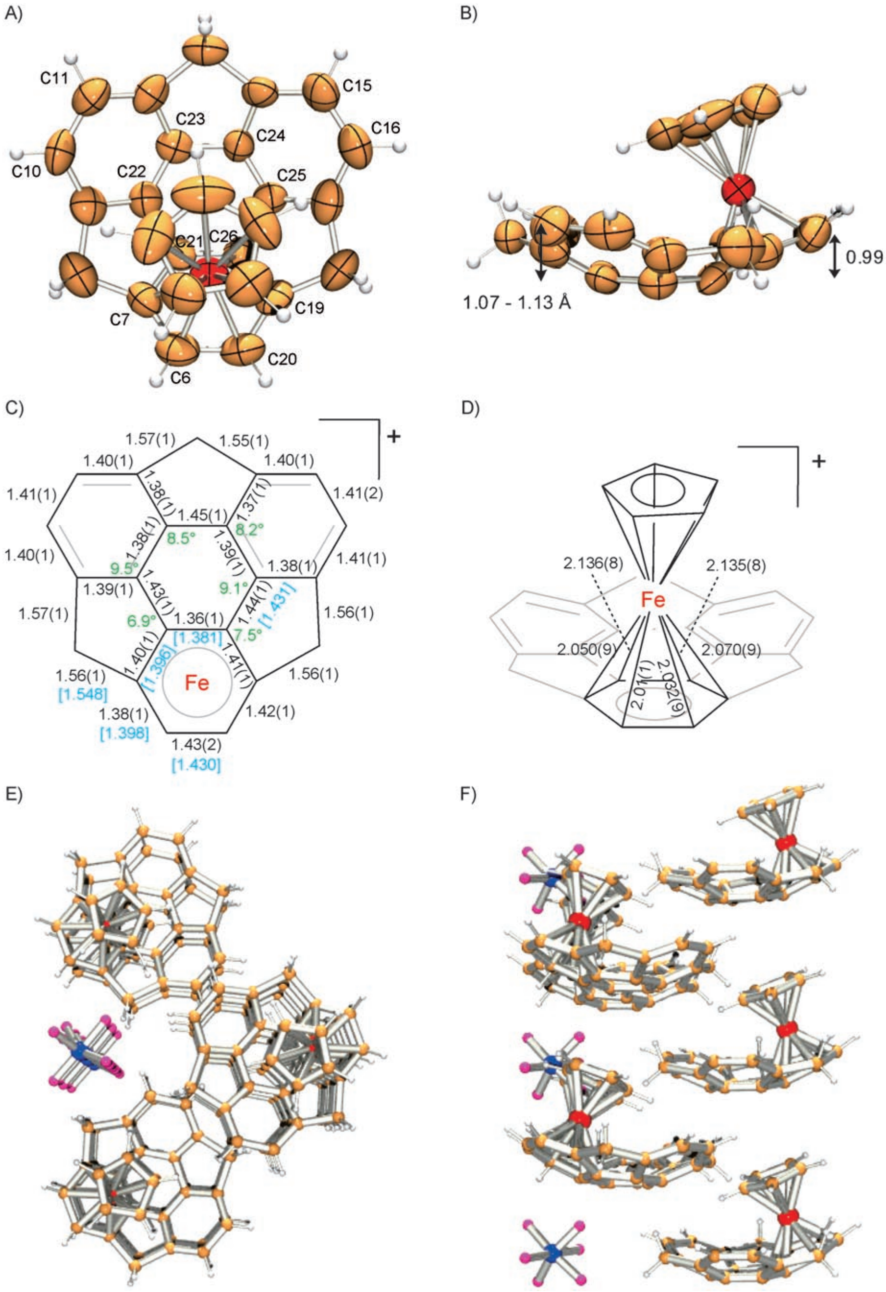

Figure 3. A), B) Crystal structure of the cation of **2** with thermal ellipsoids set at 50% probablility; top view with numbering (A) and side view with bowl depth (B). C), D) Bond lengths (in Å) and POAV angles (shown in green) for the cation of **2**. The bond lengths of **1** are shown in square brackets in blue. E), F) Top and side views, respectively, of the packing structure of **2**. Fe red, C orange, H white, P blue, F purple.

is probable between the cyclopentadienyl and hub benzene rings of adjacent molecules, which are separated by a distance of 3.3–3.9 Å. Hexafluorophosphate anions are positioned in the molecular gaps.

In conclusion, the concave-bound π-bowl complex of sumanene as a sole diastereomer was synthesized and characterized by NMR spectroscopy and X-ray crystallographic analysis. Furthermore, in bowl-shaped aromatic hydrocarbon complexes, it is the first example of a cyclopentadienyl iron complex. These results are expected to widen the scope of π-conjugated complexes possessing curved π surfaces and permit the synthesis of useful materials, including endohedral metallofullerenes.

Experimental Section

A dried flask equipped with a magnetic stirring bar was charged with sumanene (**1**, 42.0 mg, 0.159 mmol), ferrocene (295 mg, 1.59 mmol), aluminum powder (8.6 mg, 0.318 mmol), and aluminum chloride (212 mg, 1.59 mmol). After evacuation and several argon purges, the flask was heated to 120 °C and stirred for 19 h under argon. The blue-green melt was cooled to room temperature. Water (30 mL) and toluene (30 mL) were added to the reaction mixture. The organic layer was extracted with water (2 × 20 mL). The combined aqueous layer was washed with toluene (4 × 20 mL) and filtered through filter paper. Saturated NH_4PF_6(aq) was added to the filtrate to give a white-brown precipitate. The precipitate was collected by filtration on a membrane filter (mixed cellulose ester) and dried under reduced pressure. The solid was suspended in THF, and the suspension was filtered through a membrane filter (polytetrafluoroethylene). The residue was dried under vacuum to give pure **2** as an orange powder (77.0 mg, 0.145 mmol, 91 %). For recrystallization, a hot propionitrile solution of **2** (about 90 °C) was cooled to 4 °C and kept in the refrigerator for two days to give orange platelets, which were used for X-ray structural analysis. Complex **2** is very light-sensitive in solution. Most operations were carried out in the dark. IR (KBr): $\tilde{\nu} = 1418, 1391, 838, 557\ \text{cm}^{-1}$; ^{1}H NMR (600 MHz, CD_3CN): $\delta = 3.26$ (s, 5H; f), 3.92 (d, $J = 20.10$ Hz, 1H; e_{endo}), 4.94 (d, $J = 20.10$ Hz; 1H; e_{exo}), 4.96 (d, $J = 19.12$ Hz, 2H; d_{endo}), 5.21 (d, $J = 19.12$ Hz, 2H; d_{exo}), 6.39 (s, 2H; a), 7.62 (d, $J = 7.58$ Hz, 2H; c), 7.69 ppm (d, $J = 7.58$ Hz, 2H; b); ^{13}C NMR (150 MHz): $\delta = 43.3$, 46.8, 78.6, 82.5, 102.7, 111.4, 128.0, 129.4, 144.0, 151.2, 151.6, 152.1 ppm, assigned with HMQC and HMBC analysis (see the Supporting Information); HRMS (FAB) calcd for $C_{26}H_{17}Fe$ $[(M-PF_6)^+]$: 385.0674, found: 385.0677.

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[14] Crystal data for **2**: monoclinic, space group $P2_1/c$ (#14), $a = 10.524(1)$, $b = 7.1348(6)$, $c = 26.871(2)$ Å, $\beta = 91.340(3)°$, $V = 2017.2(3)$ Å^3, $Z = 4$; $R1 = 0.098$; $wR2 = 0.295$. Further details are given in the Supporting Information.

[15] In the case of $[\{(C_5Me_5)Ru\}_2]$, μ_2-η^6,η^6-corannulene or tetramethylcorannulene, the significant flattening of a curved surface was reported, see references [5f] and [5k].

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