Chiral Polyarenes

DOI: 10.1002/ange.200805567

A Chiral Concave-Bound Cyclopentadienyl Iron Complex of Sumanene**

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The characteristic properties of the curved π-conjugated systems of fullerenes and carbon nanotubes make them ideal for application to the area of functional materials. Molecules that consist of fragments of C_{60}, that is, "buckybowls", "geodesic polyarenes", or "π bowls", can be considered to represent another class of curved π-conjugated materials, which is represented by corannulene ($C_{20}H_{10}$) and sumanene (**1**, $C_{21}H_{12}$; Figure 1 a). The C_{3v}-symmetric π bowl **1**, which was first reported by our group, is characterized by its three benzylic positions;[1] we have investigated its structure, generation of anion species, electrophilic substitution, bowl-to-bowl inversion dynamics, and application for organic electrical materials.[2]

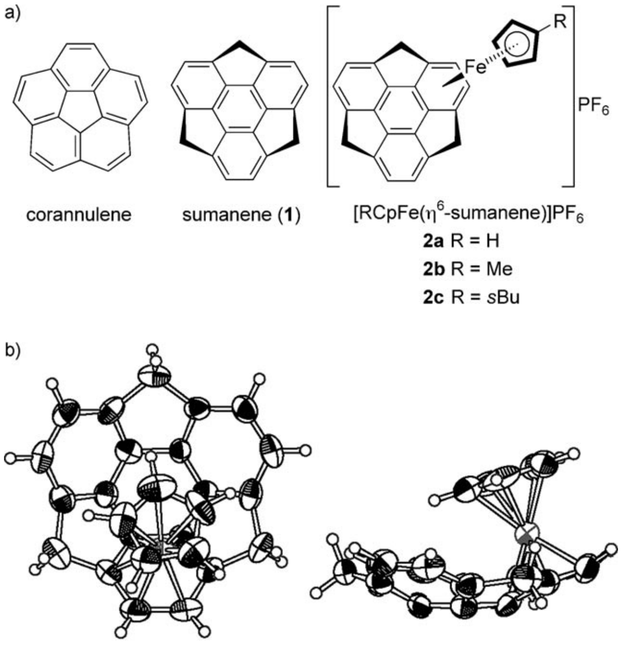

Figure 1. a) Corannulene, sumanene (**1**), and [RCpFe(η^6-sumanene)]PF_6 (**2a**–**c**). b) X-ray crystal structure of **2a** with thermal ellipsoids set at 40% probability (PF_6 ion omitted for clarity): Top view (left) and side view (right).

From a coordination chemistry viewpoint, π bowls are unique ligands because they can provide not only convex surfaces but also open concave surfaces for metal binding. π-Bowl complexes of various metals in several coordination modes have been prepared and characterized for over a decade.[3] Recently, the first concave-selective binding complex [CpFe(η^6-sumanene)]PF_6 (**2a**, Cp = C_5H_5) was demonstrated in both solution and solid states, by using NMR spectroscopy and X-ray crystallography, respectively (Figure 1 b). It is also the first example of a $CpFe^+$ complex of π bowls.[4] These findings prompted us to investigate the substituent effect on the Cp ring for face selectivity and the restricted rotation of the Cp moiety because of the steric repulsion between the substituent and bowl-shaped ligand. In addition, if a chiral substituent is introduced onto the Cp ring, the sumanene ligand might also be desymmetrized by complexation.[5] Such chiral complexes are expected to act as a model structure of chiral endohedral metallofullerene, an asymmetric organometallic catalyst, or a molecular recognition unit. However, there are no reports to date of chiral π-bowl complexes.[6] Herein, we describe the synthesis and structure of the monoalkyl-substituted [CpFe(η^6-sumanene)]$^+$ complexes **2b** and **2c**, and the first chiral π-bowl complex (*S*)-**2c**.

The synthesis of the methyl-substituted complex [MeCpFe(η^6-sumanene)]PF_6 (**2b**) was first investigated. Alkyl-substituted CpFe(η^6-arene) cationic complexes are known to be synthesized by ligand exchange of 1,1′-dialkylated ferrocene.[7] Sumanene (**1**) was treated with 1,1′-dimethylferrocene in the presence of two equivalents of aluminum powder and five equivalents of aluminum chloride without solvent at 120 °C under argon to give the corresponding complex **2b** in quantitative yield [Eq. (1)]. Although the solubility of the nonsubstituted complex **2a** in organic solvents is quite poor (**2a** is only soluble in acetonitrile, acetone, and DMF), **2b** is moderately soluble in dichloromethane and slightly soluble in THF. This increased solubility appears to arise from the presence of the methyl group.

The ^{1}H NMR spectrum of **2b** in [D$_6$]acetone is shown in Figure 2 (top spectrum). All aromatic protons (H_a, H_b, and H_c) and benzylic protons (H_d and H_e) were observed in **2a**, which shows approximate C_s symmetry. The chemical shift of H_a on the coordinated benzene ring is 0.12 ppm higher than that of **2a**. This shift is considered to be influenced by the electron-donating effect from the methyl group. Irradiation of

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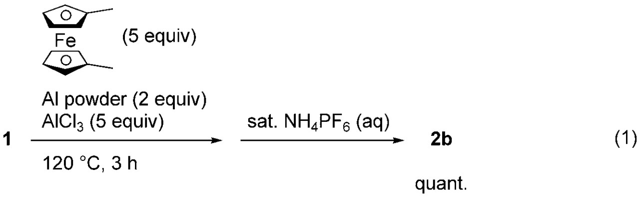
[**] We thank Toshiko Muneishi for recording the NMR spectra. H.S. expresses his special thanks to the Global Center of Excellence (GCOE) program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University. This work was financially supported in part by Research Capability Development Project from Frontier Research Center, Graduate School of Engineering, Osaka University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805567.



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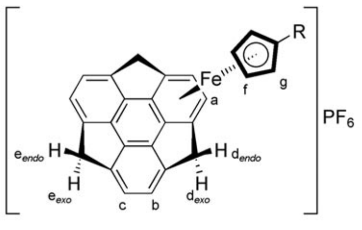


2a: R = H
2b: R = Me

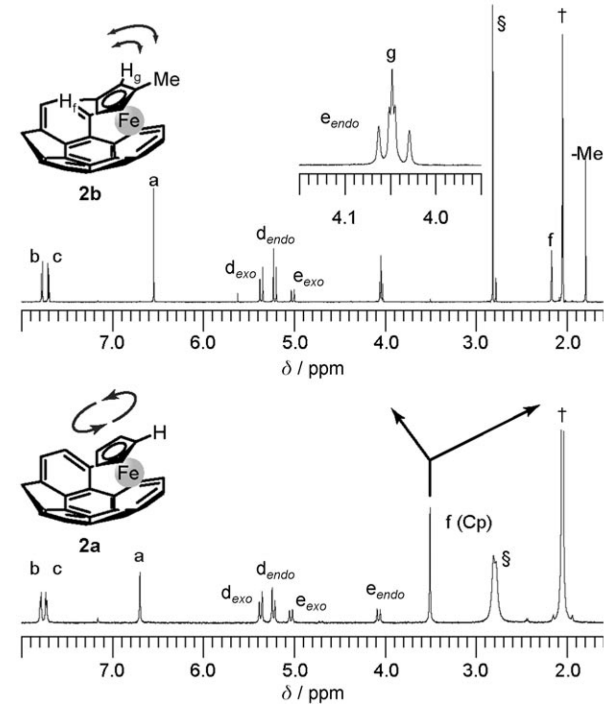


Figure 2. Selected regions of ^{1}H NMR spectra of **2a** (bottom) and **2b** (top; 600 MHz, [D$_6$]acetone). † = Residual solvent peak, § = water.

the methyl group resulted in nuclear Overhauser effect (nOe) signals at H_a, $H_{d\,endo}$, and H_g. On the other hand, no nOe signals were observed at H_b and H_c (see the Supporting Information). These results indicate that the iron center is located on the concave face of the sumanene skeleton, and the methyl group positions are located far from H_b and H_c. The Cp protons of **2b** split into two peaks, H_f and H_g. The chemical shift of H_f on the Cp ring is $\delta = 2.17$ ppm, which is at a higher field than those of the corresponding Cp protons for **2a** ($\delta = 3.51$ ppm). The observed stronger ring-current effect from the sumanene bowl suggests that H_f is located on the inside of the concave face of the bowl structure. On the other hand, H_g appears at a lower field ($\delta = 4.05$ ppm) than the Cp protons for **2a**. The conformation of the Cp ring of **2b** was also determined by HMQC and HMBC experiments (see the Supporting Information). Variable-temperature ^{1}H NMR spectra in [D$_6$]acetone exhibited a low-field shift of H_f and a high-field shift of H_g when the temperature was raised from −60 to 45 °C (see the Supporting Information). These shifts arise from the change of the shielding effect of the sumanene bowl by partially restricted thermal rotation of the Cp ring (Figure 2). The protons on the sumanene skeleton did not change at the temperature of measurement, which indicates very slow or no bowl-to-bowl inversion.

Complex **2b** was recrystallized from a saturated solution of acetone to give single crystals as orange blocks. In the X-ray crystallographic analysis,[8] ORTEP diagrams clearly show concave-selective coordination (Figure 3). Elongation of the bond lengths of C8–C9, C7–C21, and C22–C23 in the coordinated benzene rings compared to the nonsubstituted complex **2a** was observed. Furthermore, C7–C8 and C9–C23 are also longer than the corresponding bonds of **2a** (bond-length data are shown in the Supporting Information). The bowl depth, which is defined as the perpendicular distance from the center of the hub benzene ring (C22–C27) to the rim carbon atoms, is 0.98 Å at the coordinated side (C7 and C8). The bowl depths of the noncoordinated side are 1.13 Å (C12 and C13) and 1.09 Å (C17 and C18), which are almost the same as observed with **2a**. The conformation of the methyl group on the Cp ring induces the desymmetrization in the solid state, which indicates the presence of atropisomers. One molecule of acetone is observed per molecule of the complex and two types of the asymmetric columnar stacked structures are present in the crystal packing. (Figure 4).[9] One column consists of the same atropisomer, which is stacked in the same direction as observed with **2a**. On the other hand, the adjacent column consists of the other atropisomer with the stacking in the opposite direction. The distance between the Cp ring and hub benzene ring of the adjacent molecule is 3.5 Å, which is larger than that of **2a** (3.3 Å).

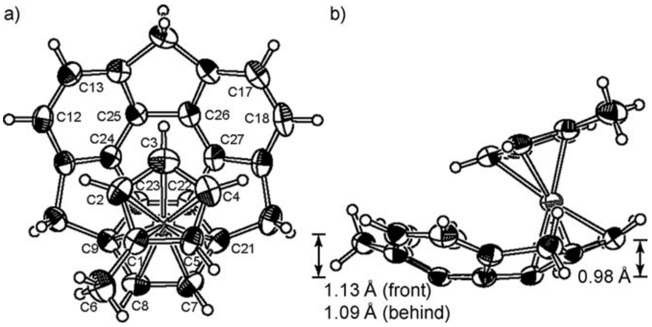


Figure 3. Crystal structure of the cation of **2b** with thermal ellipsoids set at 40 % probability (the PF$_6$ ion and acetone are omitted for clarity). a) Top view with numbering and b) side view with bowl depth.

Synthesis of the *sec*-butyl-substituted complex **2c** was also carried out to afford the asymmetric π-bowl complex. First, the diastereomeric mixtures (*dl*/*meso*) of 1,1′-di(*sec*-butyl)-ferrocene (**3**) were synthesized by borane reduction of the diol **4**[10] in high yield (Scheme 1a). Optically active (*S*,*S*)-**3**

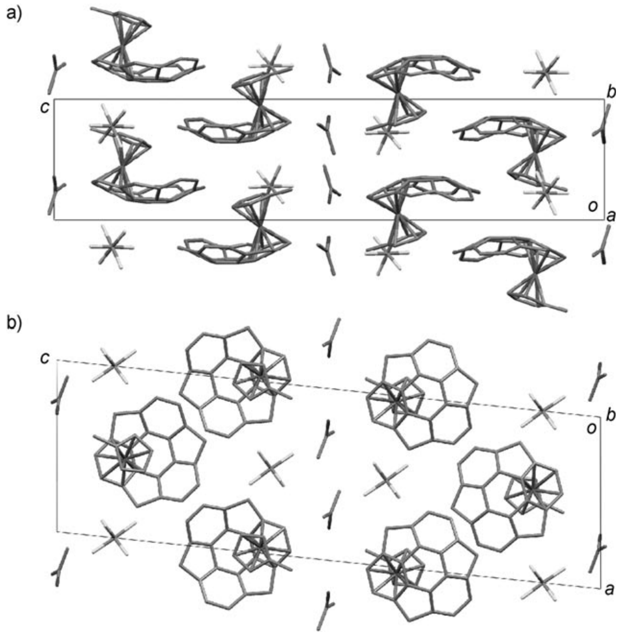
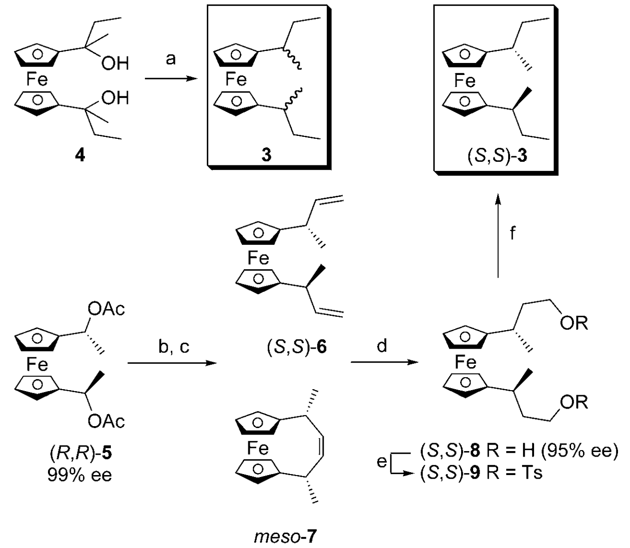


Figure 4. Crystal cell and packing structure of **2b** (H atoms are omitted for clarity): a) Side view and b) top view.



Scheme 1. Synthesis of **3** and optically active (*S*,*S*)-**3**. a) $BH_3{\cdot}SMe_2$ (9.0 equiv), THF, 60 °C, 90 h, 98 %; b) $H_2C{=}CHMgCl$ (2.6 equiv), $ZnCl_2$ (5.2 equiv), Et_2O, −78 °C→RT, 12 h, 49 % ((*S*,*S*)-**6**/*meso*-**6** ≈ 5/1); c) Grubbs catalyst 1st generation (0.03 equiv), CH_2Cl_2, RT, 12 h, quant. ((*S*,*S*)-**6**/(*S*,*S*)-**7**/*meso*-**7** ≈ 5:trace:1); d) 9-BBN·THF (3.0 equiv), THF, 50 °C, 12 h; then, NaOH (aq, 6 M), H_2O_2 (30 %), 0→50 °C, 6 h, 82 % (from isolated (*S*,*S*)-**6**) (95 % *ee*); e) TsCl (4.0 equiv), Et_3N (4.0 equiv), DMAP (0.4 equiv), CH_2Cl_2, RT, 90 min, 72 %; f) $LiAlH_4$ (4.0 equiv), Et_2O, 0 °C→reflux, 3 h, 74 %. 9-BBN = 9-borabicyclo[3.3.1]nonane, DMAP = *N*,*N*-dimethyl-4-aminopyridine, Ts = 4-toluenesulfonyl.

was synthesized from (*R*,*R*)-1,1′-bis(1-acetoxyethyl)ferrocene (*R*,*R*)-**5** in four steps (Scheme 1 b). The stereospecific vinylation[11] of ((*R*,*R*)-**5**) and subsequent kinetic resolution in the ring-closing metathesis gave (*S*,*S*)-**6** and *meso*-**7**.[12] Hydroboration of the mixtures with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by treatment by aqueous NaOH and H_2O_2, afforded the corresponding diol (*S*,*S*)-**8**, whilst *meso*-**7** did not react under these conditions. HPLC analysis on a chiral stationary phase[13] of (*S*,*S*)-**8** showed an *ee* value of 95 %. Tosylation and $LiAlH_4$ reduction occurred in moderate yields without racemization. Complexation reactions with **3** and (*S*,*S*)-**3** were performed to afford *rac*-**2c** and (*S*)-**2c**, respectively, both in 60 % yield [Eq. (2)].

$$\mathbf{1} \xrightarrow[\text{120 °C, 1 h}]{\substack{\mathbf{3}\text{ or }(S,S)\text{-}\mathbf{3}\text{ (5 equiv)} \\ \text{Al powder (2 equiv)} \\ \text{AlCl}_3\text{ (5 equiv)}}} \xrightarrow{\text{sat. NH}_4\text{PF}_6\text{ (aq)}} \underset{60\%}{rac\text{-}\mathbf{2c}\text{ or }(S)\text{-}\mathbf{2c}} \qquad (2)$$

The ^1H NMR spectra of **2c** in CD_2Cl_2 showed a desymmetric structure (Figure 5 a). All the Cp protons were observed as magnetically different peaks at $\delta = 1.79$, 2.06, 3.68, and 3.86 ppm. Furthermore, the peaks of *endo*-benzylic $H_{d_{endo}}$ and rim H_a on the coordinated benzene ring split because of the effect from the *sec*-butyl-substituted CpFe unit. Concave-face selective coordination is indicated by the selective splitting of $H_{d_{endo}}$ protons. The chiral sumanene complex (*S*)-**2c** with $[\alpha]_D^{19} = +104.1°$ (*c* 0.54, $CHCl_3$) was obtained by ligand exchange with optically active (*S*,*S*)-**3**. The circular dichroism spectrum of (*S*)-**2c** exhibited the positive Cotton effects at 272, 303, and 517 nm (Figure 5 b). The

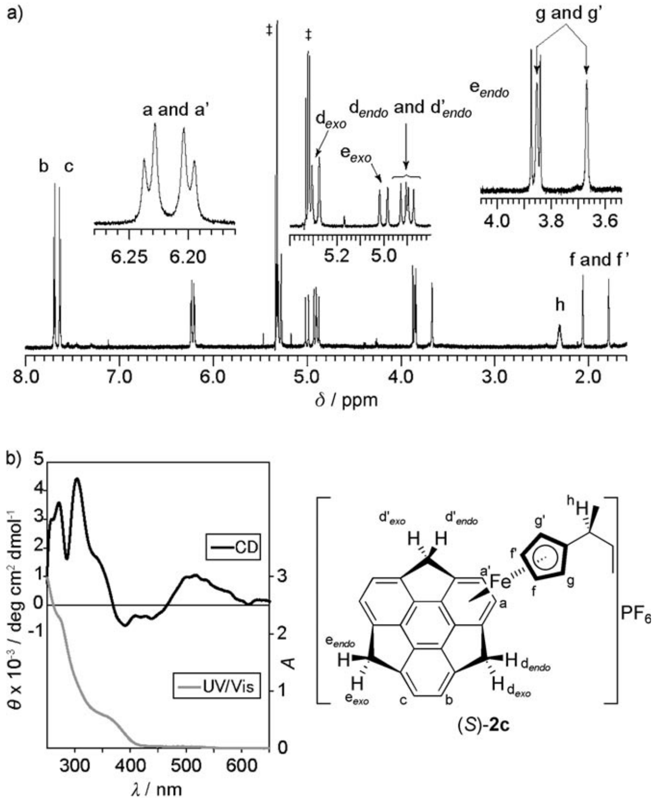


Figure 5. a) Selected regions of the ^1H NMR spectra of (*S*)-**2c** (600 MHz, CD_2Cl_2). ‡ = Residual solvent peak. b) UV/Vis (gray) and circular dichroism (CD, black) spectra of (*S*)-**2c** (1.0×10^{-4} M in CH_2Cl_2).

appearance of the Cotton effect at 272 nm indicates the desymmetrization of the sumanene ligand.

In summary, we have successfully synthesized two monoalkyl-substituted CpFe–sumanene complexes **2b**, **2c**, and (*S*)-**2c**. These complexes exhibited concave-face selective coordination, where the rotation of the Cp ring is restricted. Two asymmetric columnar stacked structures are revealed in the X-ray crystallographic analysis of **2b**. Chiral (*S*)-**2c** shows magnetic and optical desymmetrization in the sumanene ligand. It should be noted that this is the first chiral complex of a π-bowl ligand.

Experimental Section

A dried round-bottomed flask equipped with a magnetic stirring bar was charged with sumanene (**1**, 52.8 mg, 0.200 mmol), 1,1′-dimethylferrocene (224 mg, 1.00 mmol), aluminum powder (10.8 mg, 0.400 mmol), and aluminum chloride (133 mg, 0.500 mmol). After evacuation and purging several times with argon, the flask was heated to 120 °C and stirred for 3 h under argon. The blue-green melt was cooled to 0 °C. Water (30 mL) and toluene (30 mL) were added. The organic layer was extracted with water (3 × 20 mL). The combined aqueous layers were washed with toluene (3 × 20 mL) and filtered through a filter paper. An aqueous saturated NH_4PF_6 solution was added to the filtrate and the resulting orange precipitate was collected on a membrane filter (mixed cellulose ester) and dried in vacuo to give **2b** as an orange solid (108 mg, 0.200 mmol, quantitative yield). For recrystallization, a hot solution of **2b** (about 50 °C) in acetone was cooled to 4 °C and refrigerated for 3 h to give orange blocks. The crystals thus obtained were used for X-ray structural analysis. The complex **2b** is light-sensitive in coordinating solvents, therefore manipulations were carried out in the dark whenever possible. IR (KBr) 2954, 1652, 1397, 998, 952, 840 cm^{-1}; ^{1}H NMR (600 MHz, $[D_6]$acetone): $\delta = 1.80$ (s, 3 H, H_h), 2.17 (t, 2 H, $J = 1.9$ Hz, H_f), 4.05 (d, 1 H, $J = 20.3$ Hz, $H_{e\,endo}$), 4.05 (t, 2 H, $J = 1.9$ Hz, H_g), 5.02 (d, 1 H, $J = 20.3$ Hz, $H_{e\,exo}$), 5.21 (d, 2 H, $J = 19.0$ Hz, $H_{d\,endo}$), 5.36 (d, 2 H, $J = 19.0$ Hz, $H_{d\,exo}$), 6.55 (s, 2 H, H_a), 7.71 (d, 2 H, $J = 7.8$ Hz, H_c), 7.77 ppm (d, 2 H, $J = 7.8$ Hz, H_b); ^{13}C NMR (150 MHz, $[D_6]$acetone): $\delta = 12.0$, 43.1, 46.6, 78.6, 80.1, 85.1, 94.3, 102.4, 110.8, 128.0, 129.2, 140.1, 151.1, 151.5, 152.1 ppm, assigned with nOe, HMQC, and HMBC analyses (see the Supporting Information); HRMS (FAB) calcd for $C_{27}H_{19}Fe$ $[(M-PF_6)^+]$: 399.0836, found: 399.0840.

Received: November 14, 2008

Keywords: arene ligands · atropisomerism · chirality · coordination modes · metallocenes

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