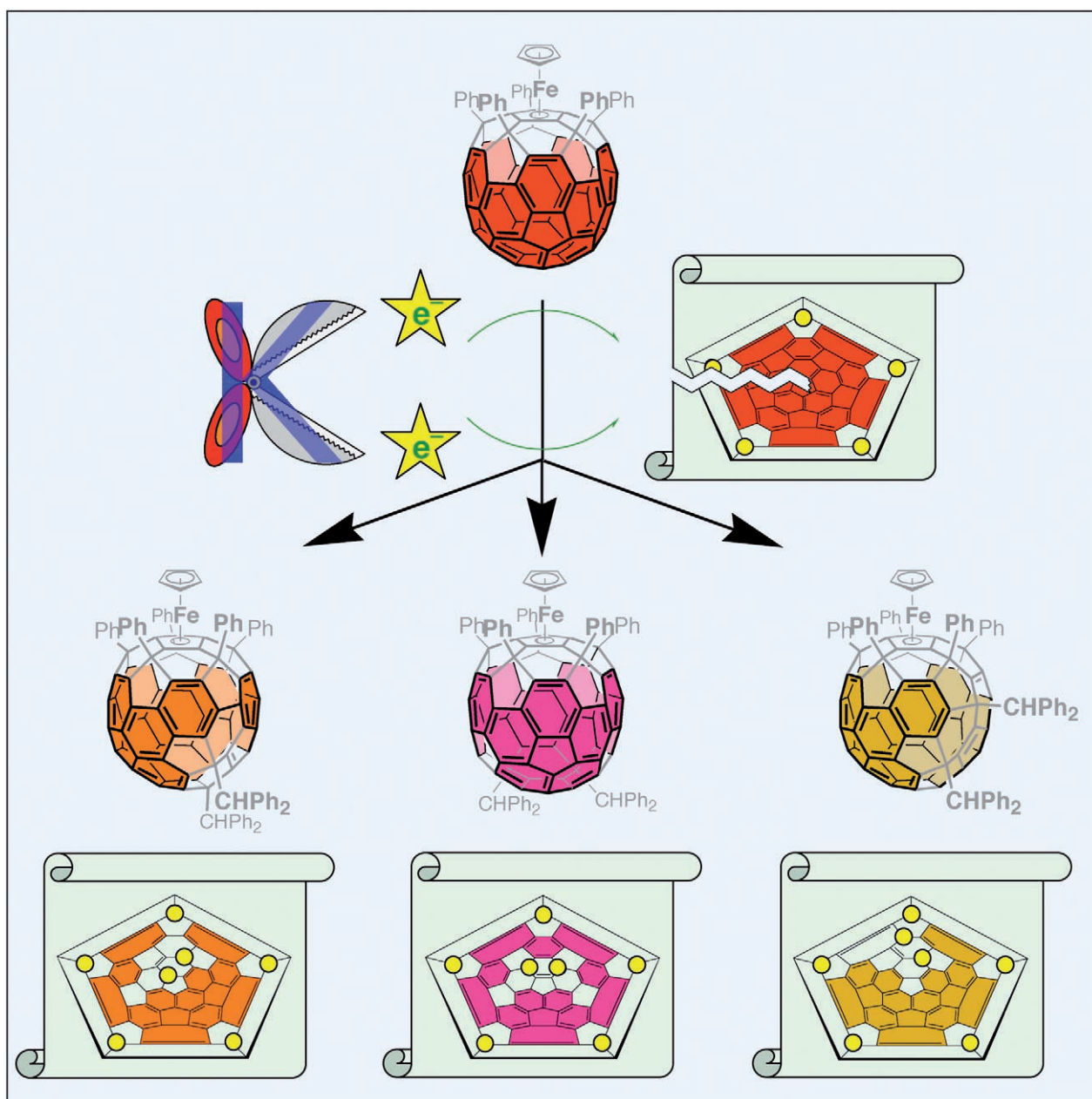


Hoop-Shaped Condensed Aromatic Systems: Synthesis and Structure of Iron- and Ruthenium-Hepta(organo)[60]fullerene Complexes

Yutaka Matsuo,^[a] Takeshi Fujita,^[b] and Eiichi Nakamura^{*[a, b]}



Abstract: Potassium reduction of iron- and ruthenium-penta(organo)[60]fullerene complexes, $[\text{M}(\eta^5\text{-C}_{60}\text{R}_5)(\eta^5\text{-Cp})]$ (**1a**: $\text{M}=\text{Fe}$, $\text{R}=\text{Ph}$; **1b**: $\text{M}=\text{Fe}$, $\text{R}=\text{Me}$; **1c**: $\text{M}=\text{Ru}$, $\text{R}=\text{Ph}$; **1d**: $\text{M}=\text{Ru}$, $\text{R}=\text{Me}$; $\text{Cp}=\text{C}_5\text{H}_5$) gave mono- and dianions of these complexes. Treatment of the dianion **1a** with α -bromodiphen-

ylmethane gave three different iron-hepta(organo)[60]fullerenes, $[\text{Fe}\{\eta^5\text{-C}_{60}\text{Ph}_5(\text{CHPh}_2)_2\}(\eta^5\text{-Cp})]$, as a mixture

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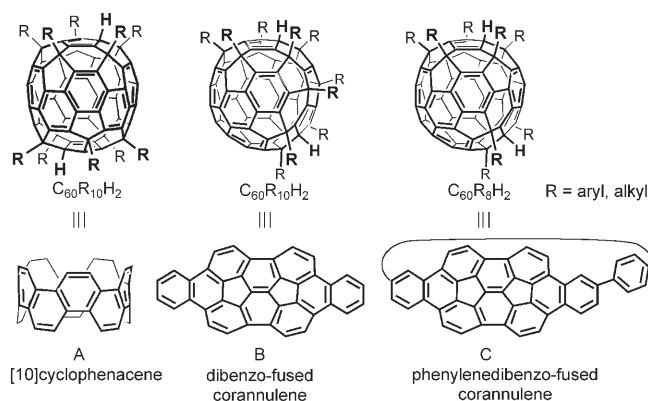
of regioisomers. All three compounds were fully characterized by physical methods, including X-ray crystallography and electrochemical measurements. One of the three compounds contains a new hoop-shaped condensed aromatic system.

Introduction

Multifunctionalization of fullerene by the introduction of organic and inorganic groups is an important subject of chemical research in several respects.^[1] For instance, the resulting multifunctionalized nanosized products can be further integrated to make submicron structures, which can be used in biological and materials applications.^[2–4] Furthermore, selective multifunctionalization enables selective detracting of the spherical conjugation system of the fullerene, which produces new curved π -conjugated systems. The latter possibility has been demonstrated by us^[5–7] and others.^[8] For example, we used nucleophilic multiple addition reactions of organocopper reagents^[9] for the synthesis of new hoop- and bowl-shaped aromatic systems, that is, [10]cyclophenacenes^[10] (A) and fused corannulenes^[11,12] (B and C; Scheme 1).

Addition of a nucleophile to fullerene is one method of achieving multifunctionalization; electrophilic alkylation of fullerene anion is another.^[13] For instance, fullerene dianion, C_{60}^{2-} , reacts with benzyl bromide to give $\text{C}_{60}(\text{CH}_2\text{Ph})_2$.^[13b] Related bis-additions to organo[60]fullerene derivatives also give structurally more complex and useful functionalized fullerenes.^[5d] Herein we report the chemical reduction of metal-pentaphenyl[60]fullerene complexes and utilization of the resulting dianions in electrophilic addition to obtain multifunctionalized metal-heptaorgano[60]fullerenes that

contain a new hoop-shaped aromatic system. The metal atom serves as an electrochemical probe for the study of the electronic structures of the π -electron-conjugated systems in the fullerene core.



Scheme 1. Examples of selective destruction of π -conjugated systems of [60]fullerene.

Results and Discussion

Chemical Reduction of Penta(organo)[60]fullerene-Transition-Metal Complexes

The key initial finding in the present study is that we can achieve potassium reduction of transition-metal-organo[60]-fullerene complexes without undesirable loss of the metal atom from the fullerene core. We chose to study the reduction of buckyferrocene compounds, $[\text{Fe}(\eta^5\text{-C}_{60}\text{R}_5)(\eta^5\text{-Cp})]$ ($\text{Cp}=\text{C}_5\text{H}_5$; **1a**: $\text{R}=\text{Ph}$; **1b**: $\text{R}=\text{Me}$),^[14] and buckyruthenocenes, $[\text{Ru}(\eta^5\text{-C}_{60}\text{R}_5)(\eta^5\text{-Cp})]$ (**1c**: $\text{R}=\text{Ph}$; **1d**: $\text{R}=\text{Me}$),^[14d] because of their established stability.^[14a] Furthermore, their highly symmetric structures should help us to characterize the products, which we expected to be a mixture of compounds. According to the reduction potential of the bucky-metalloenes (**1d**: $E_{1/2}^{\text{red1}} = -1.43$ V, $E_{1/2}^{\text{red2}} = -2.01$ V vs. $\text{Fc}/$

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Fc^+ in THF; Fc =ferrocene), we used potassium metal as a reducing agent, whose reduction potential is about 3.0 V versus Fc/Fc^+ in THF.^[15]

Treatment of **1d** with nine equivalents of potassium metal in THF gave a reddish-black solution after 3 h, which then turned black-green after another 3 h. UV/Vis/NIR (near-IR) spectra (Figure 1) indicated the formation of monovalent

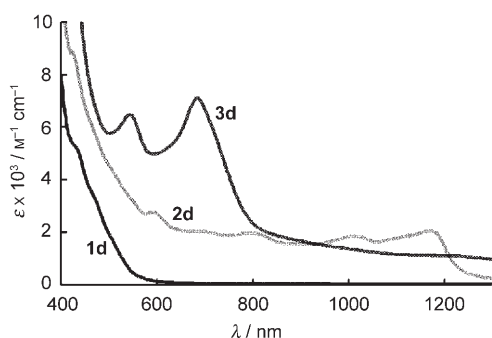
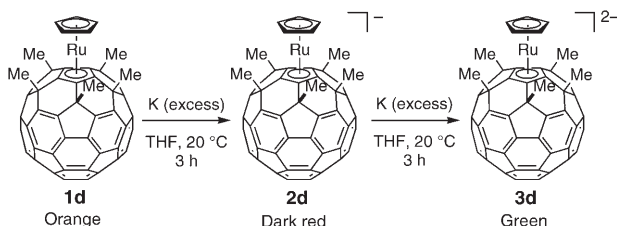


Figure 1. Absorption spectra of polyanions of buckyruthenocene: neutral compound **1d**, monoanion **2d**, and dianion **3d**.

$[\text{K}(\text{thf})_n][\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^5\text{-Cp})]$ (**2d**) during the first three hours, followed by divalent $[\text{K}_2(\text{thf})_n][\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^5\text{-Cp})]$ (**3d**) in the next three hours (Scheme 2), as judged by comparison with the spectra of the mono- and dianions of potas-



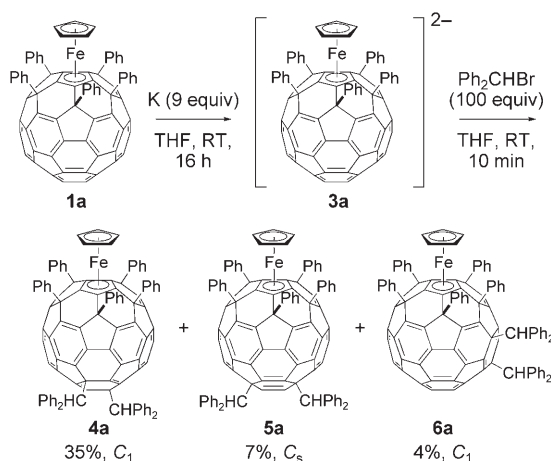
Scheme 2. Reduction of buckyruthenocene **1d** with potassium.

sium complexes of penta(aryl)[60]fullerenes (aryl=phenyl and biphenyl).^[5d] The absorption maxima of **2d** were at 592, 792, 1010, and 1174 nm, and the broad spectrum extended to the NIR region, which indicates the formation of an

open-shell structure, that is, a radical-anion species. Dianion **3d** showed absorption maxima at 544 and 684 nm. Compounds **2d** and **3d** are air- and moisture-sensitive and were immediately oxidized back to the neutral compound **1d** upon exposure to air. No NMR signals were observed for **3d**, probably due to contamination of the paramagnetic monoanion **2d**. The structural integrity of the original metal complex was retained in both anions, as judged by the structures of their derivatives (see below).

Synthesis and Structures of Three Hepta(organo)[60]fullerene–Metal Complexes

Divalent $[\text{K}_2(\text{thf})_n][\text{Fe}(\eta^5\text{-C}_{60}\text{Ph}_3)(\eta^5\text{-Cp})]$ (**3a**) was trapped in situ with an excess amount (100 equiv) of α -bromodiphenylmethane to give an orange-black crude product.^[16] The use of a large excess of the alkyl halide was essential, as the reaction otherwise afforded fullerene dimers.^[13b] After careful purification with preparative HPLC, three regioisomers of the iron-heptaorgano[60]fullerene complex $[\text{Fe}\{\eta^5\text{-C}_{60}\text{Ph}_5\text{-(CHPh}_2)_2\}(\eta^5\text{-Cp})]$ (**4a**, **5a**, and **6a**) were isolated in 35, 7, and 4% yield, respectively (Scheme 3). The reaction mechanism probably involves elec-



Scheme 3. Synthesis of three types of heptaadducts.

tron transfer from dianion **3a** to the alkyl halide to generate radical anion **2a** and an alkyl radical, followed by radical–radical coupling to give the anion of the monoalkylated product $[\text{Fe}\{\eta^5\text{-C}_{60}\text{Ph}_5\text{-(CHPh}_2)_2\}(\eta^5\text{-Cp})]$; this process is related to the mechanism of the dibenzoylation of C_{60} .^[13b] Next, a substitution reaction with the alkyl halide takes place to generate **4a**, **5a**, and **6a**. Application of this reaction to other iron and ruthenium complexes **1b**, **1c**, and **1d** afforded similarly alkylated products, $[\text{Fe}\{\eta^5\text{-C}_{60}\text{Me}_5\text{-(CHPh}_2)_2\}(\eta^5\text{-Cp})]$ (**4b**), $[\text{Ru}\{\eta^5\text{-C}_{60}\text{Ph}_5\text{-(CHPh}_2)_2\}(\eta^5\text{-Cp})]$ (**4c**), and $[\text{Ru}\{\eta^5\text{-C}_{60}\text{Me}_5\text{-(CHPh}_2)_2\}(\eta^5\text{-Cp})]$ (**4d**).

The colors of the solutions of **4a**, **5a**, and **6a** were brown, pale red, and yellow, respectively. Figure 2 shows the absorption spectra of **4a**, **5a**, and **6a**. Compound **4a** exhibited an absorption maximum at 385 nm with an extended absorp-

Abstract in Japanese:

五重付加型[60]フラーレン鉄およびルテニウム錯体に対し、カリウムを作用させることにより還元を行い、モノアニオンおよびジアニオンを得た。ジアニオンと臭化ジフェニルメタンの反応により、三種類の七重付加型[60]フラーレン鉄錯体 $[\text{Fe}\{\eta^5\text{-C}_{60}\text{Ph}_5\text{-(CHPh}_2)_2\}(\eta^5\text{-Cp})]$ を位置異性体の混合物として得た。三種類の化合物の同定は X 線結晶構造解析および電気化学測定によって行った。量子化学計算により三種類の七重付加体の持つ π 電子共役系に関する詳しい知見を得た。三種類の π 電子共役系のうちの一つは新しいベルト状の縮合環芳香族構造を有する興味深い化合物である。

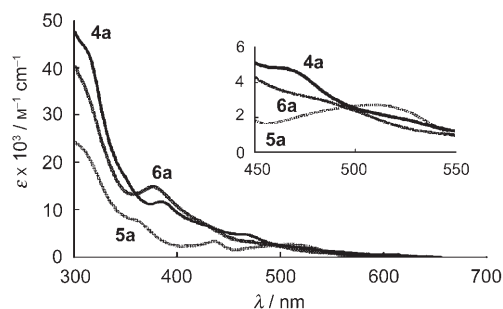


Figure 2. Absorption spectra of 6.4×10^{-6} M solutions of **4a**, **5a**, and **6a** in THF.

tion band toward 600 nm, whereas compound **5a** showed an absorption peak at 436 nm and a broad absorption band at 510 nm. The spectrum of **6a** displayed a peak at 376 nm and an extended absorption band. Thus, the absorption spectra of **4a** and **6a** are similar, but that of **5a** is different. In the ^1H NMR spectra of **4a**, **5a**, and **6a**, singlet signals were observed at 3.15, 3.22, and 2.89 ppm, respectively, due to the Cp ligand. Compounds **4a** and **6a** exhibited two singlet signals for the methine protons in the two diphenylmethyl groups (**4a**: 5.21 and 5.64 ppm; **6a**: 3.10 and 4.59 ppm), whereas the methine signal for **5a** appeared as one singlet signal (5.20 ppm). This indicates that **4a** and **6a** have C_1 symmetry and **5a** has C_s symmetry. The ^{13}C NMR data for **4a**, **5a**, and **6a** are also consistent with the assigned symmetry. The number of carbon signals due to noncoordinating sp^2 -hybridized carbon atoms are 48, 25, and 48 for **4a**, **5a**, and **6a**, respectively.

Unambiguous structure determination of **4a**, **5a**, and **6a** was achieved by X-ray crystallographic analysis (Figures 3–5). Single crystals were obtained by slow diffusion of ethanol in a solution of **4a** in CS_2 , a solution of **5a** in *p*-xylene, and a solution of **6a** in toluene. In the structures of **4a** and **5a**, two diphenylmethyl groups are attached in a 1,4 manner to hexagons that are located next to the bottom pentagon. On

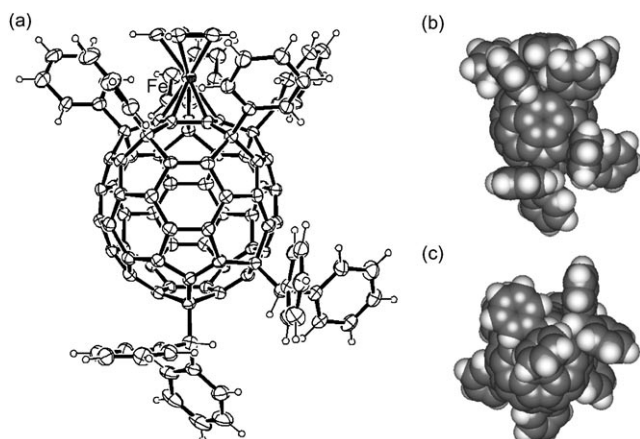


Figure 3. Crystal structure of **4a**(CS_2)₂. a) ORTEP drawing. Ellipsoids are drawn at the 30% probability level. CS_2 molecules found in the unit cell are omitted for clarity. b) Side view of Corey–Pauling–Koltun (CPK) model. c) Bottom view of CPK model.

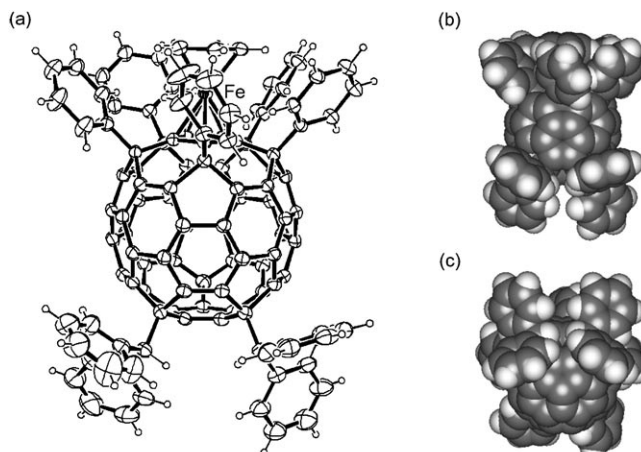


Figure 4. Crystal structure of **5a**(*p*-xylene)_{0.5}. a) ORTEP drawing. Ellipsoids are drawn at the 30% probability level. *p*-Xylene molecules found in the unit cell are omitted for clarity. b) Side view of CPK model. c) Bottom view of CPK model.

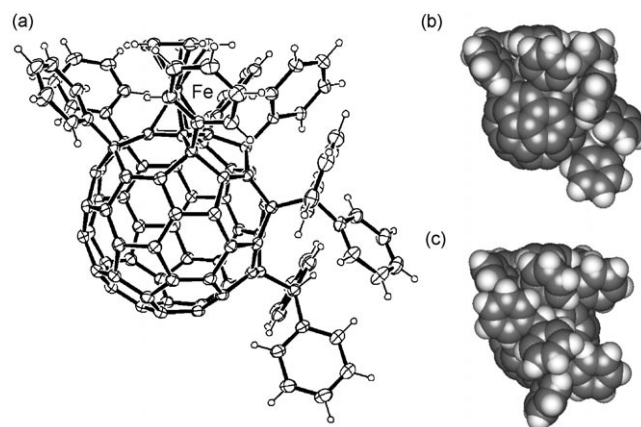


Figure 5. Crystal structure of **6a**(toluene)₃. a) ORTEP drawing. Ellipsoids are drawn at the 30% probability level. Toluene molecules found in the unit cell are omitted for clarity. b) Side view of the CPK model. c) Another side view of the CPK model.

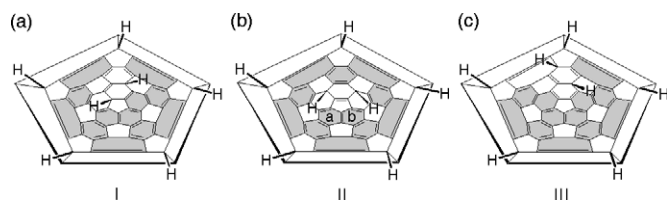
the other hand, in the structure of **6a**, two addends are placed in a 1,4 manner on one of the hexagons that is distant from the bottom pentagon. What is characteristic of these compounds is that the addends are so large that they define the outer shape of the molecules and physically enclose the conjugated π system on the fullerene core; this is an important issue given their application in solid-state electronic devices.

One may categorize the location of the addends according to the position in the formation of the first C–C bond. The radical-coupling reaction of **3a** at the carbon atom in the bottom pentagon afforded **4a**, whereas that at the carbon atom next to the bottom pentagon afforded **5a**. When the radical-coupling reaction took place at a carbon atom distant from those at the bottom pentagon, **6a** formed. Given the assumption that the spin density resides largely at the bottom pentagon,^[5d] the predominance of **4a** over the other

two products can be rationalized. The geometry around the iron metal is similar to that of the parent buckyferrocene **1a**. Average Fe–C(fullerene) bond lengths for **4a**, **5a**, and **6a** are in the range 2.069–2.078 Å (**1a**: 2.084 Å), whereas average Fe–C(Cp) bond lengths are in the range 2.046–2.057 Å (**1a**: 2.062 Å).

Comparison of π -Electron-Conjugated Systems of Three Hepta(organo)[60]fullerene–Metal Complexes

Further investigations of the π -electron-conjugated systems of the three hepta(organo)[60]fullerene–metal complexes were performed with the aid of quantum-mechanical calculations. Here we discuss the structures and aromaticity by the use of model compounds in which the original carbon addends are replaced by hydrogen atoms, that is, [Fe(η^5 -C₆₀H₇)(η^5 -Cp)] (I, II, and III, corresponding to **4a**, **5a**, and **6a**; Scheme 4). The structures were energy-optimized with



Scheme 4. Aromaticity maps for model compounds of a) **4a**, b) **5a**, and c) **6a** (gray = aromatic, NICS < −4.0; white = non-aromatic, NICS > −4.0).

density functional theory by using the B3LYP hybrid functional^[17] with a basis set (denoted 631LAN) that consists of the LANL2DZ basis set, which includes a double- ζ valence basis set with the Hay and Wadt effective core potential (ECP)^[18] for Fe and the 6-31G* basis set^[19] for C and H. The calculated structures reasonably reproduced the X-ray structures of **4a**, **5a**, and **6a**. Average Fe–C(fullerene) bond lengths for **4a**, **5a**, and **6a** are in the range 2.104–2.108 Å (X-ray: 2.069–2.078 Å), whereas average Fe–C(Cp) lengths are in the range 2.074–2.077 Å (X-ray: 2.046–2.057 Å).

The nucleus-independent chemical-shift (NICS)^[20] calculations (GIAO-SCF/631LAN//HF/631LAN) performed on these optimized model structures gave us information about the aromaticity of the ring systems in these complex conjugated systems. The gray hexagons in Scheme 4 are those rings that showed aromaticity. In model II, one circular row of the hoop-shaped condensed aromatic network [10]cyclophenacene can be identified, which is supplemented by the two benzene rings a and b. The other two model compounds I and III contain a corannulene system.

The similarities of and differences between these models appear to account for the resemblance of the UV/Vis spectra of **4a** and **6a** (Figure 2) and for their difference from the spectrum of **5a**. The broad absorption band at 510 nm can probably be attributed to the cyclic π -conjugated system of **5a**. Electronic structures calculated from the model compounds also suggested the similarity between I and III. In

both I and III, the lowest-unoccupied molecular orbital (LUMO), highest-occupied molecular orbital (HOMO), HOMO-1, HOMO-4, and HOMO-5 are located at the fullerene moieties, and HOMO-2 and HOMO-3 are localized at the iron atoms (see Supporting Information, Figures S1 and S3). On the other hand, in II, the LUMO, HOMO, HOMO-1, and HOMO-2 comprise the π orbitals of the fullerene, and HOMO-4 and HOMO-5 comprise the d orbitals of the iron center (Figure S2). The energy-level diagrams of I and III (Figure S4) resemble each other but not that of II. The HOMO–LUMO gap of II (2.73 eV) is narrower than those of I and III (2.76 and 2.78 eV, respectively). A narrow HOMO–LUMO gap was also found for the [10]cyclophenacene we reported previously.^[5c]

Electrochemistry of Three Hepta(organo)[60]fullerene–Metal Complexes

Cyclic voltammetry (CV) gave information about the degree of π -electron conjugation of the three heptaadducts **4a**, **5a**, and **6a**. Here the iron atom can act as a sensitive probe for investigation of each curved π system. Generally speaking, the metal atoms coordinated to the fullerene core tend to be oxidized at high potentials because of the electron-withdrawing nature of the fullerene ligands. For example, buckyferrocene **1a** is much more difficult to oxidize than ordinary ferrocene (**1a**: $E_{1/2}^{\text{ox1}} = 0.50$ V vs. Fc/Fc⁺). Compounds **4a**, **5a**, and **6a** showed reversible one-electron oxidation corresponding to the oxidation of the iron atoms at $E_{1/2}^{\text{ox1}} = 0.50$, 0.45, and 0.44 V versus Fc/Fc⁺, respectively (Figure 6). Compound **4a** has a higher oxidation potential than **5a** and **6a**. This result suggests that the π -electron-conjugated system of **4a** is the most-electron-withdrawing among the three and that the electron-withdrawing nature of the bowl-shaped π -conjugated systems is generally stronger than that of the cyclic π -conjugated systems. As for **6a**, its weaker electron-withdrawing nature may be attributed to its small π -conjugated system relative to those of **4a** and **5a**.

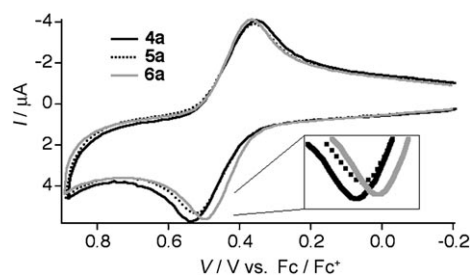


Figure 6. Cyclic voltammograms of heptaadducts **4a**, **5a**, and **6a**. All measurements were performed in 0.3 mM THF containing 100 mM (*n*Bu₄N)(ClO₄) as supporting electrolyte.

Conclusions

We have demonstrated that buckymetalloenes **1a–d** can be reduced without loss of the metal atoms. Furthermore, the

resulting dianions **3a–d** can be alkylated to produce a new hoop-shaped π -electron-conjugated system. This compound represents a second example of hoop-shaped condensed aromatics and exhibits spectral and electronic properties similar to the first [10]cyclophenacene derivative we reported recently.^[5] The heptaadducts and their conjugated systems reported in this paper are unavailable by nucleophilic addition to the buckymetalloocene, which produces octa- and decaadducts.^[5] We expect that the present synthetic methodology can be applied to other transition-metal complexes^[21] and metal-[70]fullerene compounds.^[22] Finally, we draw the readers' attention to the intriguing outer shape and the very large size of these molecules, which will be useful for the construction of even larger molecular systems.

Experimental Section

General

All manipulations were carried out with standard Schlenk techniques under argon. THF was purified and degassed by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. Compounds **1a–d** were prepared according to the previous report.^[14a,d,e] α -Bromodiphenylmethane was purchased from Tokyo Kasei Co. and was used as received.

HPLC analysis was performed on a Shimadzu LC-10A system equipped with an SPD-M10A diode-array detector and a Develosil RPFullerene column (4.6 \times 250 mm²). Preparative HPLC separations were performed by the use of a Develosil RPFullerene column (20 \times 250 mm²). ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded on a JEOL ECA500 spectrometer. ¹H NMR spectra in CDCl₃ were referenced internally to tetramethylsilane, and ¹³C NMR spectra to the solvent resonance. Full assignment of the ¹³C NMR signals was performed with the aid of 2D-HMQC (heteronuclear multiple-quantum coherence) and HMBC (heteronuclear multiple-bond correlation). Other spectra were recorded on the following instruments: IR spectra: Applied Systems Inc. React-IR 1000; UV/Vis/NIR spectra: JASCO V570; mass spectra: JEOL JMS-T100LC.

Electrochemical Measurements

Electrochemical measurements were performed with a Hokuto HZ-5000 voltammetric analyzer. A glassy-carbon electrode was used as the working electrode. The counterelectrode was a platinum coil, and the reference electrode was an Ag/Ag⁺ electrode. CV was performed at a scan rate of 100 mVs⁻¹. All half-wave potentials $E_{1/2} = (E_{pc} + E_{pa})/2$, in which E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc⁺.

Theoretical Calculations

All theoretical calculations were performed with the Gaussian 03 package.^[23] The B3LYP calculation with a basis set (denoted 631LAN) that consists of the LANL2DZ basis set, which includes a double- ζ valence basis set with the Hay and Wadt ECP for Fe and the 6-31G* basis set for C and H, was used for the geometry optimization of model compounds (I, II, and III). The NICS values at the ring centers were calculated at the GIAO-SCF/631LAN//HF/631LAN level for the B3LYP/631LAN geometries.

Syntheses

4a, **5a**, and **6a**: Microcrystalline solids of **1a** (194 mg, 0.158 mmol) and potassium metal (55.6 mg, 1.42 mmol), which was washed with dried THF, were placed in a Schlenk tube. THF (28 mL) was added to the mixture at room temperature to start the reduction process. After the mixture was stirred for 16 h at room temperature, a black-green solution was

obtained. The solution was transferred to another Schlenk tube by canula under argon. α -Bromodiphenylmethane (3.91 g, 15.8 mmol) was added to the solution at room temperature, the color of which immediately changed to dark red. After the mixture was stirred for 10 min, ethanol (0.02 mL) was added dropwise. THF was removed under reduced pressure, and the resulting dark-red oily liquid was washed with methanol to afford a brown solid. The solid was dissolved in toluene, the solution was filtered through a pad of silica gel (CS₂/toluene = 10:0.8:2), and purification by HPLC (toluene/acetonitrile = 3:7) was performed. Brown, dark-pink, and yellow fractions appeared in this order and were collected and dried under reduced pressure to give **4a** (86.9 mg, 0.0556 mmol, 35%) as brown microcrystals, **5a** (17.9 mg, 0.0114 mmol, 7%) as dark-pink microcrystals, and **6a** (10.7 mg, 0.0069 mmol, 4%) as dark-yellow microcrystals. Crystallization was performed by slow diffusion of ethanol in a solution of **4a** in CS₂, a solution of **5a** in *p*-xylene, and a solution of **6a** in toluene.

4a: IR (powder): $\tilde{\nu}$ = 3056 (w), 3026 (w), 1600 (w), 1582 (w), 1493 (m), 1447 cm⁻¹ (m); ¹H NMR (CDCl₃, 500 MHz): δ = 3.15 (s, 5H, Cp), 5.21 (s, 1H, CH), 5.64 (s, 1H, CH), 7.20–7.46 (m, 5H, *p*-PhC₆₀); 10H, *m*-PhC₆₀; 4H, *p*-PhCH; 4H, *m*-PhCH), 7.57–7.60 (m, 4H, *m*-PhCH), 7.68 (d, *J* = 7.5 Hz, 2H, *o*-PhCH), 7.71 (d, *J* = 6.3 Hz, 2H, *o*-PhC₆₀), 7.72 (d, *J* = 7.5 Hz, 2H, *o*-PhC₆₀), 7.83 (d, *J* = 8.6 Hz, 2H, *o*-PhCH), 7.85 (d, *J* = 9.2 Hz, 2H, *o*-PhC₆₀), 8.05 (d, *J* = 7.5 Hz, 2H, *o*-PhC₆₀), 8.07 (d, *J* = 9.2 Hz, 2H, *o*-PhC₆₀), 8.20 (d, *J* = 7.5 Hz, 2H, *o*-PhCH), 8.35 ppm (d, *J* = 7.5 Hz, 2H, *o*-PhCH); ¹³C NMR (CDCl₃, 125 MHz): δ = 58.0 (C(sp³)Ph), 58.3 (C(sp³)Ph), 58.6 (C(sp³)Ph), 58.7 (C(sp³)Ph), 58.8 (C(sp³)Ph), 62.1 (C(sp³)CH), 63.4 (C(sp³)CH), 65.0 (CH), 65.6 (CH), 73.3 (Cp), 91.6 (FCp), 92.4 (FCp), 92.5 (FCp), 92.6 (FCp), 93.4 (FCp), 127.3, 127.3, 127.4, 127.4, 127.6, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 128.3, 128.5, 128.7, 128.9, 129.0, 129.1, 129.2, 129.4, 129.5, 129.6, 130.3, 130.3, 130.9 (*p*-PhC₆₀, *m*-PhC₆₀, *o*-PhC₆₀, *m*-PhCH, *o*-PhCH, *p*-PhCH), 137.9, 139.0, 139.7, 140.4, 140.6, 140.7, 141.2, 141.5, 142.5, 142.8, 143.4, 143.5, 143.6, 143.7, 143.7, 143.7, 143.8, 143.9, 144.1, 144.4, 144.5, 144.5, 144.7, 144.7, 145.4, 145.4, 146.1, 146.1, 146.6, 146.9, 146.9, 147.5, 147.5, 147.8, 148.4, 148.9, 148.9, 149.0, 149.6, 149.7, 149.8, 149.9, 150.5, 150.7, 151.5, 151.7, 152.2, 152.6, 153.0, 153.3, 153.4, 153.6, 154.9, 155.0, 155.4, 156.3, 161.4 ppm (*i*-PhC₆₀, *i*-PhCH, C(sp²)); HRMS (positive atmospheric-pressure chemical ionization; APCI+): *m/z* calcd for C₁₂₁H₅₂Fe: 1560.3418 [*M*]⁺; found: 1560.3373.

5a: IR (powder): $\tilde{\nu}$ = 3056 (w), 3025 (w), 1600 (w), 1582 (w), 1493 (m), 1445 cm⁻¹ (m); ¹H NMR (CDCl₃, 500 MHz): δ = 3.22 (s, 5H, Cp), 5.20 (s, 2H, CH), 7.17–7.39 (m, 21H, Ph), 7.46–7.49 (m, 2H, Ph), 7.58–7.61 (m, 4H, Ph), 7.72–7.73 (m, 4H, *o*-PhCH), 7.83–7.84 (m, 2H, *o*-PhC₆₀), 7.91–7.93 (m, 8H, *o*-PhC₆₀), 8.14–8.15 ppm (m, 4H, *o*-PhCH); ¹³C NMR (CDCl₃, 125 MHz): δ = 58.4 (2C, C(sp³)Ph), 58.7 (2C, C(sp³)Ph), 59.1 (1C, C(sp³)Ph), 63.0 (2C, C(sp³)CH), 65.0 (2C, CH), 73.3 (5C, Cp), 93.6 (2C, FCp), 93.7 (2C, FCp), 93.9 (1C, FCp), 127.3, 127.5, 127.6, 127.6, 127.7, 127.7, 127.8, 128.3, 128.8, 129.2, 129.3, 129.3, 129.9, 130.1 (*p*-PhC₆₀, *m*-PhC₆₀, *o*-PhC₆₀, *m*-PhCH, *o*-PhCH, *p*-PhCH), 139.8, 140.6, 142.8, 142.9, 143.1, 143.2, 143.3, 143.4, 143.6, 144.0, 144.7, 144.7, 144.9, 145.0, 145.1, 145.1, 145.9, 147.2, 147.3, 148.7, 149.7, 150.8, 151.2, 151.6, 153.0, 153.2, 153.2, 155.0, 155.8, 159.1 ppm (*i*-PhC₆₀, *i*-PhCH, C(sp²)); HRMS (APCI+): *m/z* calcd for C₁₂₁H₅₂Fe: 1560.3418 [*M*]⁺; found: 1560.3357.

6a: IR (powder): $\tilde{\nu}$ = 3056 (w), 3025 (w), 1598 (w), 1582 (w), 1493 (m), 1445 cm⁻¹ (m); ¹H NMR (CDCl₃, 500 MHz): δ = 2.89 (s, 5H, Cp), 3.10 (s, 1H, CH), 4.59 (s, 1H, CH), 6.68 (d, *J* = 8.1 Hz, 2H, Ph), 7.00–7.49 (m, 33H, Ph), 7.56 (t, *J* = 7.5 Hz, 1H, Ph), 7.78 (d, *J* = 7.5 Hz, 2H, Ph), 7.82–7.86 (m, 4H, Ph), 7.97–7.99 ppm (m, 3H, Ph); ¹³C NMR (CDCl₃, 125 MHz): δ = 54.5 (C(sp³)Ph), 55.9 (C(sp³)Ph), 57.4 (C(sp³)Ph), 57.8 (C(sp³)Ph), 58.1 (C(sp³)Ph), 60.4 (C(sp³)CH), 60.6 (C(sp³)CH), 61.5 (CH), 61.9 (CH), 72.9 (Cp), 89.7 (FCp), 90.1 (FCp), 91.0 (FCp), 92.6 (FCp), 95.1 (FCp), 126.6, 126.9, 127.0, 127.1, 127.2, 127.3, 127.5, 127.5, 127.5, 127.6, 127.6, 127.7, 127.7, 127.9, 128.0, 128.3, 128.4, 129.1, 129.2, 129.2, 129.5, 130.5, 130.9, 131.2, 132.3 (*p*-PhC₆₀, *m*-PhC₆₀, *o*-PhC₆₀, *m*-PhCH, *o*-PhCH, *p*-PhCH), 137.7, 139.2, 139.3, 139.6, 139.8, 140.6, 141.2, 141.4, 141.5, 142.9, 143.0, 143.0, 143.3, 143.5, 143.6, 144.2, 144.3, 144.5, 144.6, 144.6, 144.7, 144.9, 145.1, 145.4, 145.4, 145.5, 145.6, 145.6, 145.7, 146.0, 146.2, 146.8, 146.9, 147.1, 147.3, 147.5, 148.1, 148.2, 148.6, 148.6, 148.8, 149.0, 149.7, 150.5, 151.1, 151.2, 151.6, 151.9, 152.1, 152.3, 152.7, 155.1,

155.5, 156.8, 156.9, 157.4, 158.4 ppm (*i*-PhC₆₀, *i*-PhCH, C(sp²)); HRMS (APCI+): *m/z* calcd for C₁₂₁H₅₂Fe: 1560.3418 [*M*]⁺; found 1560.3401.

4b: This compound was synthesized in the same manner as **4a**. From [Fe(η⁵-C₆₀Me₃)(η⁵-C₅H₅)] (49.3 mg, 0.0538 mmol), potassium metal (14.7 mg, 0.376 mmol), and α-bromodiphenylmethane (1.33 g, 5.38 mmol), **4b** (23.5 mg, 0.0188 mmol, 35%) was obtained as brown microcrystals. ¹H NMR (CDCl₃, 500 MHz): δ = 2.16 (s, 3H, CH₃), 2.29 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.52 (s, 3H, CH₃), 2.59 (s, 3H, CH₃), 4.77 (s, 5H, Cp), 5.16 (s, 1H, CH), 5.54 (s, 1H, CH), 7.21–7.24 (m, 2H, *p*-Ph), 7.30–7.34 (m, 4H, *m*-Ph), 7.36–7.41 (m, 2H, *p*-Ph), 7.51–7.56 (m, 4H, *m*-Ph), 7.66 (d, *J* = 7.5 Hz, 2H, *o*-Ph), 7.82 (d, *J* = 7.5 Hz, 2H, *o*-Ph), 8.13 (d, *J* = 8.0 Hz, 2H, *o*-Ph), 8.32 ppm (d, *J* = 8.0 Hz, 2H, *o*-Ph); ¹³C NMR (CDCl₃, 125 MHz): δ = 29.2 (CH₃), 29.5 (CH₃), 29.6 (CH₃), 29.6 (CH₃), 29.9 (CH₃), 49.8 (C(sp³)CH₃), 49.9 (C(sp³)CH₃), 50.4 (C(sp³)CH₃), 50.5 (C(sp³)CH₃), 50.6 (C(sp³)CH₃), 61.8 (C(sp³)CH), 63.1 (C(sp³)CH), 65.0 (CH), 65.5 (CH), 68.5 (Cp), 90.2 (FCp), 91.3 (FCp), 91.3 (FCp), 91.3 (FCp), 92.6 (FCp), 127.2 (*p*-Ph), 127.2 (*p*-Ph), 127.4 (*p*-Ph), 127.4 (*p*-Ph), 128.2 (*m*-Ph), 128.4 (*m*-Ph), 128.6 (*m*-Ph), 128.8 (*m*-Ph), 129.6 (*o*-Ph), 130.3 (*o*-Ph), 130.3 (*o*-Ph), 130.8 (*o*-Ph), 138.0, 139.1, 139.9, 140.3, 140.7, 140.7, 141.1, 141.3, 142.2, 142.6, 143.3, 143.5, 143.8, 143.9, 144.2, 144.3, 144.6, 144.6, 144.8, 144.9, 145.4, 145.5, 145.5, 146.7, 147.0, 147.0, 147.1, 147.2, 147.6, 148.1, 148.6, 148.7, 148.7, 149.4, 149.4, 149.9, 150.6, 151.6, 152.1, 152.4, 152.7, 153.4, 153.7, 154.4, 154.8, 155.0, 155.4, 155.5, 157.1, 157.6, 158.4, 161.0 ppm (*i*-PhC₆₀, *i*-PhCH, C(sp²)).

4c: This compound was synthesized in the same manner as **4a**. From [Ru(η⁵-C₆₀Ph₃)(η⁵-C₅H₅)] (35.8 mg, 0.0281 mmol), potassium metal (7.7 mg, 0.20 mmol), and α-bromodiphenylmethane (695 mg, 2.81 mmol), **4c** (10.7 mg, 0.00666 mmol, 24%) was obtained as brown microcrystals. ¹H NMR (CDCl₃, 500 MHz): δ = 3.53 (s, 5H, Cp), 5.23 (s, 1H, CH), 5.67 (s, 1H, CH), 7.22–7.85 (m, 5H, *p*-C₆₀Ph; 10H, *m*-C₆₀Ph; 10H, *o*-C₆₀Ph; 4H, *p*-CHPh₂; 8H, *m*-CHPh₂; 4H, *o*-CHPh₂), 8.22 (d, *J* = 7.5 Hz, 2H, *o*-CHPh₂), 8.38 ppm (d, *J* = 8.0 Hz, 2H, *o*-CHPh₂); ¹³C NMR (CDCl₃, 125 MHz): δ = 57.7 (C(sp³)Ph), 58.1 (C(sp³)Ph), 58.4 (C(sp³)Ph), 58.5 (C(sp³)Ph), 58.6 (C(sp³)Ph), 62.1 (C(sp³)CH), 63.4 (C(sp³)CH), 65.0 (CH), 65.6 (CH), 77.3 (Cp), 98.6 (FCp), 99.2 (FCp), 99.5 (FCp), 99.5 (FCp), 100.3 (FCp), 127.2, 127.3, 127.3, 127.3, 127.3, 127.4, 127.4, 127.4, 127.5, 127.5, 127.6, 127.6, 128.3, 128.5, 128.6, 128.7, 128.8, 128.8, 128.9, 129.1, 129.2, 129.6, 130.3, 130.3, 130.9 (*p*-PhC₆₀, *m*-PhC₆₀, *o*-PhC₆₀, *m*-PhCH, *o*-PhCH, *p*-PhCH), 138.2, 139.2, 139.7, 140.5, 140.6, 140.7, 141.2, 141.5, 142.5, 143.1, 143.5, 143.7, 144.0, 144.2, 144.2, 144.2, 144.3, 144.4, 144.4, 144.5, 144.6, 144.7, 144.9, 144.9, 145.3, 145.6, 146.1, 146.2, 146.8, 147.1, 147.2, 147.6, 147.6, 147.9, 148.4, 148.9, 148.9, 149.0, 149.7, 149.7, 149.8, 149.9, 150.4, 150.8, 151.5, 151.8, 152.0, 152.7, 152.9, 153.3, 153.3, 153.8, 154.8, 155.1, 155.4, 156.3, 161.5 ppm (*i*-PhC₆₀, *i*-PhCH, C(sp²)).

4d: This compound was synthesized in the same manner as **4a**. From [Ru(η⁵-C₆₀Me₃)(η⁵-C₅H₅)] (19.7 mg, 0.0205 mmol), potassium metal (5.6 mg, 0.14 mmol), and α-bromodiphenylmethane (506 mg, 2.05 mmol), **4d** (9.3 mg, 0.0072 mmol, 35%) was obtained as brown microcrystals. ¹H NMR (CDCl₃, 500 MHz): δ = 1.93 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 2.29 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 5.08 (s, 5H, Cp), 5.21 (s, 1H, CH), 5.59 (s, 1H, CH), 7.23–7.26 (m, 2H, *p*-Ph), 7.33–7.35 (m, 4H, *m*-Ph), 7.40–7.44 (m, 2H, *p*-Ph), 7.55–7.59 (m, 4H, *m*-Ph), 7.70 (d, *J* = 7.5 Hz, 2H, *o*-Ph), 7.86 (d, *J* = 7.5 Hz, 2H, *o*-Ph), 8.17 (d, *J* = 7.5 Hz, 2H, *o*-Ph), 8.35 ppm (d, *J* = 7.5 Hz, 2H, *o*-Ph); ¹³C NMR (CDCl₃, 125 MHz): δ = 30.9 (CH₃), 31.0 (CH₃), 31.2 (CH₃), 31.3 (CH₃), 31.5 (CH₃), 47.4 (C(sp³)CH), 47.7 (C(sp³)CH), 49.8 (C(sp³)CH₃), 49.8 (C(sp³)CH₃), 50.3 (C(sp³)CH₃), 50.3 (C(sp³)CH₃), 50.4 (C(sp³)CH₃), 58.5 (CH), 59.5 (CH), 71.1 (Cp), 96.4 (FCp), 97.5 (FCp), 97.6 (FCp), 97.6 (FCp), 98.7 (FCp), 127.0, 127.2, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 130.5, 131.0, 131.1, 131.4 (*p*-Ph, *m*-Ph, *o*-Ph), 135.8, 137.0, 137.7, 139.5, 139.5, 141.3, 141.9, 142.4, 143.4, 143.4, 143.6, 144.0, 144.2, 144.2, 144.8, 144.8, 145.1, 145.1, 145.4, 146.2, 146.8, 147.0, 147.3, 147.6, 147.7, 147.8, 147.9, 148.3, 148.7, 149.0, 149.2, 149.2, 149.2, 149.4, 149.4, 151.0, 151.8, 151.9, 152.0, 152.7, 153.1, 153.7, 154.5, 155.1, 155.4, 155.5, 155.5, 156.6, 157.3, 158.3, 158.6, 164.3 ppm (*i*-PhC₆₀, *i*-PhCH, C(sp²)).

X-ray Crystallographic Analysis

Crystals of **4a**, **5a**, and **6a** suitable for X-ray diffraction were mounted on a MacScience DIP2030 imaging plate diffractometer for data collection with MoK_α (graphite-monochromated, λ = 0.71069 Å) radiation. The structures of **4a**, **5a**, and **6a** were solved by direct methods (SIR97).^[24] The positional and thermal parameters of the non-hydrogen atoms were refined anisotropically on *F*² by the full-matrix least-squares method with SHELXS-97.^[25] Hydrogen atoms were placed at calculated positions and refined with the riding model on their corresponding carbon atoms. In the subsequent refinement, the function Σ(*wF*_o² − *wF*_c²)² was minimized, in which |*F*_o| and |*F*_c| are the observed and calculated structure-factor amplitudes, respectively. The agreement indices are defined as *R*1 = Σ(|*F*_o| − |*F*_c|)/Σ|*F*_o| and *wR*2 = [Σ(*wF*_o² − *wF*_c²)²/Σ(*wF*_o⁴)]^{1/2}. CCDC-643455 (**4a**), -643456 (**5a**), and -643457 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif.

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- [1] a) R. Taylor, *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*, Imperial College Press, London, **1999**; b) A. Hirsch, M. Brettreich, *Fullerenes, Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**; c) C. Thilgen, F. Diederich, *Chem. Rev.* **2006**, *106*, 5049–5135.
- [2] a) N. Martin, L. Sanchez, B. Illescas, I. Perez, *Chem. Rev.* **1998**, *98*, 2527–2548; b) J. F. Nierengarten, N. Armaroli, G. Accorsi, Y. Rio, J. F. Eckert, *Chem. Eur. J.* **2003**, *9*, 37–41; c) H. Imahori, S. Fukuzumi, *Adv. Funct. Mater.* **2004**, *14*, 525–536; d) D. M. Guldi, F. Zerbetto, V. Georgakilas, M. Prato, *Acc. Chem. Res.* **2005**, *38*, 38–43.
- [3] a) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato, E. Nakamura, *Nature* **2002**, *419*, 702–705; b) Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 432–433; c) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 9586–9587; d) Y.-W. Zhong, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 3052–3053.
- [4] a) M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe, E. Nakamura, S.-Q. Zhou, B. Chu, *Chem. Lett.* **2000**, 1098–1099; b) S. Zhou, C. Burger, B. Chu, M. Sawamura, M. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe, E. Nakamura, *Science* **2001**, *291*, 1944–1947; c) E. Nakamura, H. Isobe, *Acc. Chem. Res.* **2003**, *36*, 807–815.
- [5] a) E. Nakamura, K. Tahara, Y. Matsuo, M. Sawamura, *J. Am. Chem. Soc.* **2003**, *125*, 2834–2835; b) Y. Matsuo, K. Tahara, E. Nakamura, *Org. Lett.* **2003**, *5*, 3181–3184; c) Y. Matsuo, K. Tahara, M. Sawamura, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 8725–8734; d) Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 8457–8466; e) Y. Matsuo, K. Tahara, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 7154–7155.
- [6] a) R. Hoffmann, *Int. J. Phil. Chem.* **2003**, *9*, 7–10; b) L. T. Scott, *Angew. Chem.* **2003**, *115*, 4265–4267; *Angew. Chem. Int. Ed.* **2003**, *42*, 4133–4135; c) M. Randić, *Chem. Rev.* **2003**, *103*, 3449–3606.
- [7] Y. Matsuo, E. Nakamura in *Functional Organic Materials: Syntheses, Strategies and Applications* (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, **2006**, pp. 59–80.
- [8] a) G. Schick, M. Levitus, L. Kvetko, B. A. Johnson, I. Lamparth, R. Lunkwitz, B. Ma, S. I. Khan, M. A. Garcia-Garibay, Y. Rubin, *J. Am. Chem. Soc.* **1999**, *121*, 3246–3247; b) K. Hutchison, J. Gao, G. Schick, Y. Rubin, F. Wudl, *J. Am. Chem. Soc.* **1999**, *121*, 5611–5612.
- [9] a) M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 12850–12851; b) H. Iikura, S. Mori, M. Sawamura, E. Naka-

- mura, *J. Org. Chem.* **1997**, *62*, 7912–7913; c) M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, E. Nakamura, *J. Organomet. Chem.* **2000**, *599*, 32–36; d) M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, E. Nakamura, *Chem. Lett.* **2000**, 270–271; e) Y. Matsuo, A. Muramatsu, K. Tahara, M. Koide, E. Nakamura, *Org. Synth.* **2006**, *83*, 80–87.
- [10] a) E. Heilbronner, *Helv. Chim. Acta* **1954**, *37*, 921–935; b) F. Vögtle, *Top. Curr. Chem.* **1983**, *115*, 157–159; c) A. Schröder, H.-B. Meckelburger, F. Vögtle, *Top. Curr. Chem.* **1994**, *172*, 179–201; d) J. Aihara, *J. Chem. Soc. Perkin Trans. 2* **1994**, 971–974; e) L. Türker, *THEOCHEM* **1999**, *491*, 275–280.
- [11] a) R. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380–381; b) R. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1971**, *93*, 1730–1745; c) L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082–7084; d) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldrige, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 1921–1923; e) G. Zimmermann, U. Nuechter, S. Hagen, M. Nuechter, *Tetrahedron Lett.* **1994**, *35*, 4747–4750; f) P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235–242.
- [12] a) P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, R. Sygula, *J. Am. Chem. Soc.* **1994**, *116*, 7891–7892; b) A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1999**, *121*, 7800–7803; c) S. Hagen, M. S. Bratcher, M. S. Erickson, G. Zimmermann, L. T. Scott, *Angew. Chem.* **1997**, *109*, 407–409; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 406–408; d) G. Mehta, G. Panda, *Chem. Commun.* **1997**, 2081–2082; e) A. Sygula, Z. Marcinow, F. R. Fronczek, I. Guzei, P. W. Rabideau, *Chem. Commun.* **2000**, 2439–2440.
- [13] a) C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones, K. M. Kadish, *J. Am. Chem. Soc.* **1993**, *115*, 8505–8506; b) R. Subramanian, M. K. Kadish, N. M. Vijayashree, X. Gao, T. M. Jones, D. M. Miller, K. L. Krause, T. Suenobu, S. Fukuzumi, *J. Phys. Chem.* **1996**, *100*, 16327–16335; c) S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa, K. M. Kadish, *J. Am. Chem. Soc.* **1998**, *120*, 9220–9227; d) F. Cheng, Y. Murata, K. Komatsu, *Org. Lett.* **2002**, *4*, 2541–2544; e) S. Miki, M. Kitao, K. Fukunishi, *Tetrahedron Lett.* **1996**, *37*, 2049–2052; f) E. Allard, L. Rivi  re, J. Delaunay, D. Dubois, J. Cousseau, *Tetrahedron Lett.* **1999**, *40*, 7223–7226; g) E. Allard, J. Delaunay, F. Cheng, J. Cousseau, J. Ord  na, J. Gar  n, *Org. Lett.* **2001**, *3*, 3503–3506; h) E. Allard, J. Delaunay, J. Cousseau, *Org. Lett.* **2003**, *5*, 2239–2242; i) Y.-H. Zhu, L.-C. Song, Q.-M. Hu, C.-M. Li, *Org. Lett.* **1999**, *1*, 1693–1695; j) Y. Chi, J. B. Bhonsle, T. Canteenwala, J.-P. Huang, J. Shiea, B.-J. Chen, L. Y. Chiang, *Chem. Lett.* **1998**, 465–466; k) T. Canteenwala, P. A. Padmawar, L. Y. Chiang, *J. Am. Chem. Soc.* **2005**, *127*, 26–27.
- [14] a) M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaoka, E. Nakamura, *J. Am. Chem. Soc.* **2002**, *124*, 9354–9355; b) E. Nakamura, *Pure Appl. Chem.* **2003**, *75*, 427–434; c) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 13974–13975; d) Y. Matsuo, Y. Kuninobu, S. Ito, E. Nakamura, *Chem. Lett.* **2004**, *33*, 68–69; e) R. H. Herber, I. Nowik, Y. Matsuo, M. Toganoh, Y. Kuninobu, E. Nakamura, *Inorg. Chem.* **2005**, *44*, 5629–5635; f) Y. Matsuo, H. Isobe, T. Tanaka, Y. Murata, M. Murata, K. Komatsu, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17148–17149.
- [15] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.
- [16] Reduction potentials for **1a**: $E_{1/2}^{\text{red1}} = -1.36$, $E_{1/2}^{\text{red2}} = -1.95$ V versus Fc/Fc⁺ in THF.
- [17] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [18] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 299–310.
- [19] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, **1986**.
- [20] a) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318; b) M. B  hl, A. Hirsch, *Chem. Rev.* **2001**, *101*, 1153–1184.
- [21] a) M. Sawamura, Y. Kuninobu, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 12407–12408; b) Y. Matsuo, E. Nakamura, *Organometallics* **2003**, *22*, 2554–2563; c) Y. Kuninobu, Y. Matsuo, M. Toganoh, M. Sawamura, E. Nakamura, *Organometallics* **2004**, *23*, 3259–3266; d) Y. Matsuo, A. Iwashita, E. Nakamura, *Organometallics* **2005**, *24*, 89–95; e) Y.-W. Zhong, Y. Matsuo, E. Nakamura, *Chem. Asian J.* **2007**, *2*, 358–366.
- [22] a) M. Sawamura, H. Iikura, A. Hirai, E. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 8285–8286; b) M. Sawamura, M. Toganoh, H. Iikura, Y. Matsuo, A. Hirai, E. Nakamura, *J. Mater. Chem.* **2002**, *12*, 2109–2115; c) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Organomet. Chem.* **2003**, *683*, 295–300.
- [23] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT (USA), **2004**.
- [24] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
- [25] G. M. Sheldrick, Programs for Crystal-Structure Analysis (Release 972), University of G  ttingen, G  ttingen (Germany), **1998**.

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