Fullerenes

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Di- and Trinuclear [70]Fullerene Complexes: Syntheses and Metal–Metal Electronic Interactions**

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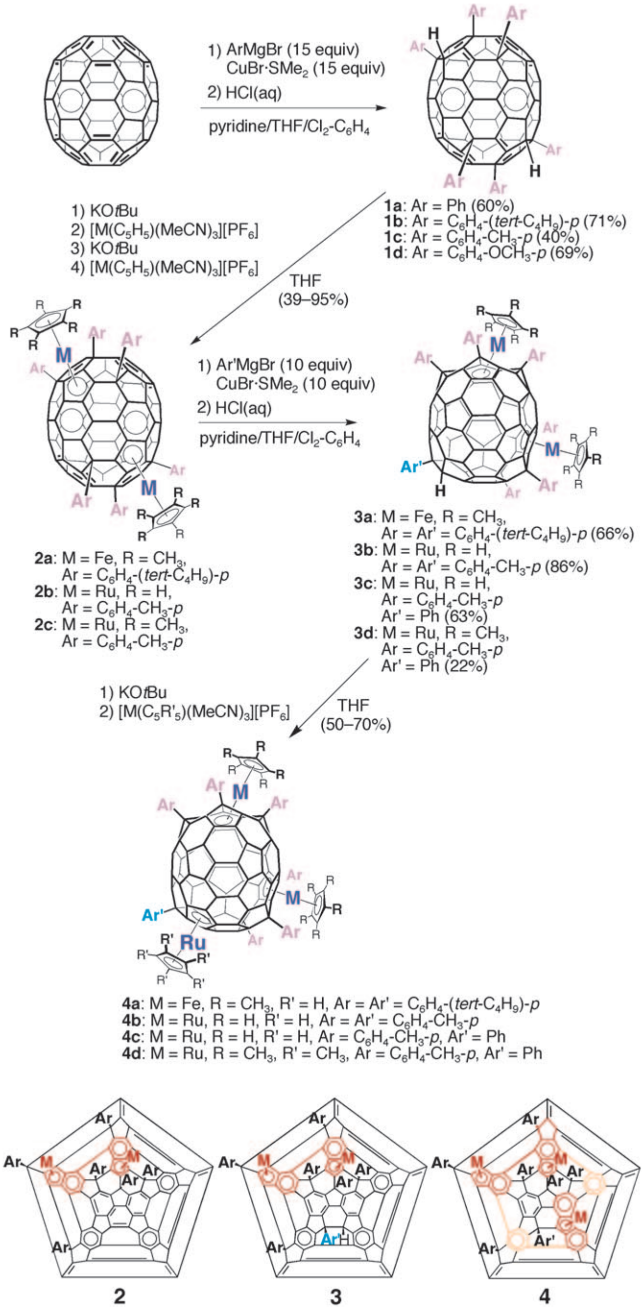
Transition-metal complexes of fullerenes are the molecules of interest in a variety of fields of chemistry.[1] Their multinuclear variants[2] are particularly interesting because of their rather unusual extended d–π–d conjugated system, in which the metal atoms interact with each other[3] through the semiconducting π system.[4] In this context, electronic interactions between multiple metal atoms across a π bridge is an interesting subject of study related to the development of molecular electronics.[5] With such interests in mind, we recently synthesized several stable mono- and dinuclear complexes of [60]fullerene[6,7] and reported on the unique photophysics of these molecules[8] as well as on their self-assembled monolayers on electrode surfaces.[9] We report herein the unique chemistry of di- and trinuclear [70]fullerene complexes **2** and **4** (Scheme 1), including regioselective sixfold addition of an arylcopper reagent to [70]fullerene to form **1**, regioselective addition of a seventh aryl group to the dinuclear complex **2** to form **3**, and the electronic communication among the metal atoms by way of the [70]fullerene conjugated π system.

The first step of the synthesis is the copper-mediated[10] sixfold addition of arylmagnesium bromide to [70]fullerene to produce hexaaryl adducts $C_{70}Ar_6H_2$ (**1a–d**; Scheme 1) in the presence of pyridine,[11] without which the reaction stops after threefold addition.[12] The formation of six C–C bonds took place in one step in 40–71 % yield of isolated product on a 1 g scale. Other side products were unidentified insoluble products and adducts bearing more than six aryl groups. The mechanism of the high regioselectivity is unknown at this time. Repeated deprotonation of **1** (KO*t*Bu) and treatment with a cationic cyclopentadienyl complex (e.g., $[FeCp^*(MeCN)_3]PF_6$; $Cp^* = C_5Me_5$) produced the dinuclear complexes $[\{M(C_5R_5)\}_2\{C_{70}Ar_6\}]$ (**2a–c**). They are chiral and were obtained as corresponding racemates. We determined unambiguously the positions of the addends by X-ray crystallographic analysis of the diprotio compound **1a** and its diiron and diruthenium complexes **2a** and **2b** (Figure 1a,b; the



Scheme 1. Syntheses and Schlegel diagrams of di- and trinuclear [70]fullerene complexes.

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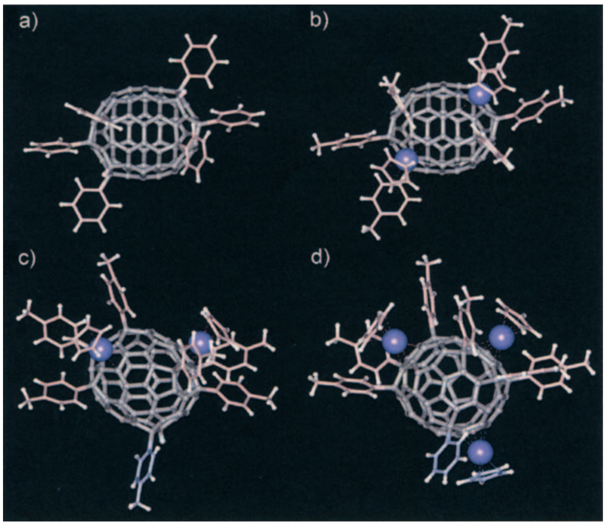

Figure 1. X-ray crystal structures of hexa- and heptaaryl [70]fullerenes and their di- and trinuclear complexes. Coloring corresponds to that in Scheme 1. a) Hexaphenyl adduct **1a**. b) Diruthenium complex **2b**. c) Hepta-aryladduct **3b**. The seventh aryl group is shown in light blue. d) Triruthenium complex **4c**.

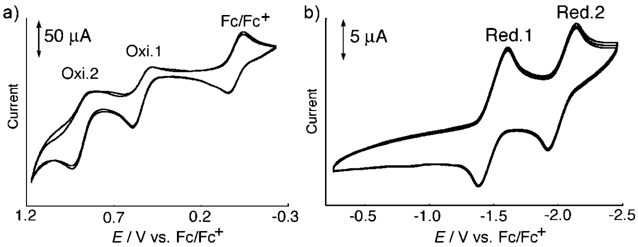

Figure 2. Electrochemistry of the diruthenium complex **2b**. a) Cyclic voltammogram of the electrochemical quasi-reversible oxidation of **2b**. The difference in the intensity of the anodic and cathodic scans suggests that the process is chemically irreversible. Half-wave oxidation potentials can be estimated to be 540 and 880 mV (vs. Fc/Fc^+). The ferrocene/ferrocenium couple is the internal standard. The measurement was performed in CH_2Cl_2 containing equimolar amounts of $[FeCp_2]$ and $[nBu_4N][B\{C_6H_3\text{-}(CF_3)_2\text{-}3,5\}_4]$ (0.1 M) as an electrolyte, which was crucial for the successful measurements.[17] The sweep started from −230 mV and moved towards the positive direction. b) Cyclic voltammogram of the reversible reduction of **2b** in THF containing nBu_4NClO_4.

structure of **2a** is in the Supporting Information). The ferrocene and ruthenocene moieties show the bonding characteristics of an η^5-indenyl metal complex (Scheme 1, top).[10] The two η^5-indenyl metal units are part of a biphenyl motif on the fullerene surface (colored red in the Schlegel diagram in Scheme 1, bottom).

Electrochemical measurements further support the structural data for the diruthenium complex **2b**. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **2b** in CH_2Cl_2 reveal two quasi-reversible one-electron oxidation waves arising from the two metal atoms at $E_{1/2} = 0.54$ and 0.88 V versus ferrocene/ferrocenium (Fc/Fc^+; Figure 2a). The potential difference[13] $\Delta E = 340$ mV is very large, because the two metallocene moieties are directly conjugated with each other through the [70]fullerene π system (Scheme 1 and Figure 1; cf. HOMO conjugation[14] for the dinuclear [60]fullerene system).[7,15] In the cathodic scan of **2b** in THF, two reversible one-electron reduction waves corresponding to stepwise two-electron reduction of the [70]fullerene core were observed ($E_{1/2} = -1.50$ and -2.06 V vs. Fc/Fc^+; Figure 2b). These values are comparable to those of the second and third one-electron reduction of [70]fullerene (−0.87, −1.44, and −1.93 V vs. Fc/Fc^+ in THF), thus indicating that the dinuclear hexaaryl [70]fullerene still possesses a high electron-accepting ability and stability to reduction—properties necessary for the fullerene to act as a viable device.[16]

The next challenge was the synthesis of triply substituted compounds, which we achieved in good yield and with high regioselectivity (Scheme 1). Introduction of the seventh aryl group to the diiron complex **2a** by addition of $\{C_6H_4\text{-}(tert\text{-}C_4H_9)\text{-}p\}MgBr$ in the presence of $CuBr{\cdot}SMe_2$ and pyridine took place selectively and afforded a single product, the heptaaryl compound $[(Cp^*Fe)_2(C_{70}\{C_6H_4\text{-}(tert\text{-}C_4H_9)\text{-}p\}_7H)]$ (**3a**) in 66% yield of isolated product. Analogous reactions afforded the ruthenium compounds **3b–d** regioselectively in 63–86% yield. The position of the Ar′ group in **3c** was determined by X-ray crystallographic analysis (Figure 1c). Further conversion of **3** to the corresponding trinuclear compounds **4** was achieved in a manner similar to the synthesis of **2**. A mixed diiron ruthenium compound $[(Cp^*Fe)_2(CpRu)(C_{70}Ar_7)]$ (**4a**; $Cp = C_5H_5$) was thus obtained in 50% yield (Scheme 1), in which the third ruthenium atom is coordinated by a fluorenyl motif (red in Scheme 1, bottom).

Triruthenium complexes **4b–d** were also synthesized from **3b–d** in a similar fashion. The X-ray structure of **4c** is shown in Figure 1d. As indicated by the Schlegel diagram in Scheme 1, the three metallocene groups (red) are conjugatively connected through a cyclic poly(*p*-phenylene) array (orange), as required for a three-way junction. The cyclic voltammogram of the trinuclear complex **4d** in CH_2Cl_2 exhibited a one-electron quasi-reversible or irreversible oxidation wave for each metal center ($E_{pa} = 0.39$, 0.65, and 0.85 V vs. Fc/Fc^+; the $E_{1/2}$ values (0.33, 0.55, and 0.82 V) are less certain owing to irreversible processes, Figure 3a). The first and the second oxidation events most likely occurred at the two indenyl moieties, because the fluorenyl unit is the most influenced by the strong electron-withdrawing nature of [70]fullerene, thus giving a higher oxidation potential. The stepwise oxidation with the large separations between the waves demonstrates the metal–metal interaction through the conjugated π-electron system of [70]fullerene. Reversible reduction of **4b** took place at −1.77 and −2.19 V versus Fc/Fc^+ in THF (Figure 3b), indicating that the trinuclear complex is still highly electron-accepting.

In summary, we have developed a strategy for selective synthesis of new classes of [70]fullerene derivatives **1** to **4** possessing many organic and metallic substituents in structurally defined positions. The synthesis has been achieved with a high level of regiocontrol and with minimal synthetic effort, and the multinuclear compounds are thermally stable in air. Not only their molecular structures are striking but their electronic properties are unique in that the metal atoms electronically communicate with each other. The new synthetic strategy has made possible the installation of organic

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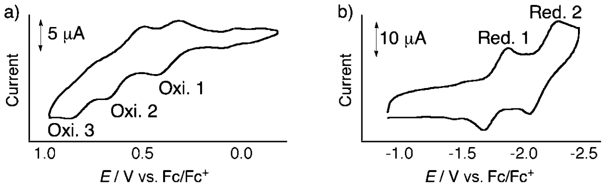

Figure 3. Electrochemistry of the triruthenium complex **4d**. a) Cyclic voltammogram of the three-electron oxidation of **4d**. The measurement was performed in CH_2Cl_2 containing $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{B}\{\mathrm{C}_6\mathrm{H}_3\text{-}(\mathrm{CF}_3)_2\text{-}3,5\}_4]$ (0.1 M) as an electrolyte. b) Cyclic voltammogram of the reversible reduction of **4d** in THF containing $n\mathrm{Bu}_4\mathrm{NClO}_4$.

groups surrounding each metal center,[10,18,19] and these groups may serve as scaffolds for organizing the molecules in two- or three-dimensional space, which is necessary for applications in molecular electronics.[9,13,20]

Experimental Section

1b: $[\mathrm{C}_6\mathrm{H}_4\text{-}(tert\text{-}\mathrm{C}_4\mathrm{H}_9)\text{-}4]\mathrm{MgBr}$ in THF (0.88 M, 20.2 mL, 17.9 mmol) was added to $\mathrm{CuBr{\cdot}SMe_2}$ (3.64 g, 17.9 mmol) in pyridine (200 mL) at 28 °C. After stirring for 10 min at 40 °C, a degassed solution of C_{70} (1.00 g, 1.19 mmol) in *o*-dichlorobenzene (200 mL) was added. The multiple addition reaction was complete within 6 h. The reaction mixture was quenched with HCl(aq). Pyridine and THF were removed under vacuum. The crude mixture was dissolved in toluene and filtered through a pad of silica gel (toluene). The solution was concentrated to a small volume, and the products were precipitated by addition of MeOH to obtain a dark red solid. The crystals were washed thoroughly with MeOH and dried under vacuum. Analytically pure $\mathrm{C}_{70}[\mathrm{C}_6\mathrm{H}_4\text{-}(tert\text{-}\mathrm{C}_4\mathrm{H}_9)\text{-}4]_6\mathrm{H}_2$ (1.39 g, 71 % yield) was obtained after purification with HPLC (RPFullerene, 250 mm, toluene/acetonitrile = 1:1).

2a: KO*t*Bu (1.0 M in THF, 80 μL, 80 μmol) was added to **1b** (120 mg, 73.0 μmol) in THF (12 mL) at 28 °C. $[\mathrm{FeCp^*(CH_3CN)_3}]\mathrm{PF_6}$ (0.10 M in CH_3CN, 0.85 mL, 85 μmol) was added to the reaction mixture. After stirring for 5 min at 28 °C, additional KO*t*Bu (1.0 M in THF, 80 μL, 80 μmol) and $[\mathrm{FeCp^*(CH_3CN)_3}]\mathrm{PF_6}$ (0.10 M in CH_3CN, 0.85 mL, 85 μmol) was added to the mixture. After further stirring for 5 min, solvents were removed under vacuum. The black residue was dissolved in hexane and purified by the silica gel column chromatography (hexane/toluene = 1:0; ca. 9:1 as eluent). The solvents were evaporated. Recrystallization from toluene/MeOH gave black plate crystals of **2a** (57.8 mg, 39 % yield).

Experimental details for compounds **1a**,**c**,**d**, **2b**,**c**, **3a**,**d**, and **4a–d** and X-ray data are supplied in the Supporting Information.

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