



Synthesis of a superphane dimer—a metallocenophane with four metal centers

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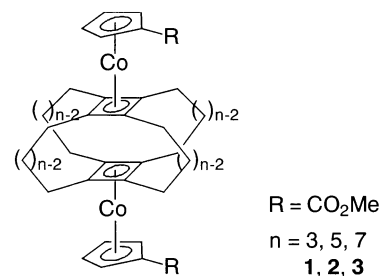
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Abstract—The first dimeric bis(η^5 -cyclopentadienyl- η^4 -cyclobutadienyl-cobalt)superphane has been synthesized. It represents a metallocenophane with four cobalt centers which are electrochemically active. Cyclic voltammetric (CV) studies revealed two reversible oxidation potentials at 500 and 870 mV and two irreversible peaks at 1050 and 1280 mV, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

The nature of electron transfer between well separated donor and acceptor sites has been attracting great attention for nearly 40 years.^{1,2} There are different approaches to study this process: either one considers model systems as close as possible to reality or very simple systems which capture only the essence. The latter avenue has been taken by studying electron transfer processes between differently charged metal fragments (**M**, **M**⁺) connected by a bridge (**B**) of type [**M**–**B**–**M**⁺].

For such intervalence compounds Robin and Day³ suggested a classification scheme which is based on the extent of electron transfer between the metal containing units. Compounds belonging to class I are characterized by complete charge localization, whereas class III comprises compounds with complete charge delocalization. Complexes with detectable electronic interactions belong to class II. Those systems on the interface of class II/class III with low barriers to intramolecular electron transfer have been called ‘almost delocalized’⁴ and are currently of great interest.^{4–12}

We recently studied a series of superphanes with two cobalt centers separated by hydrocarbon bridges of different length (**1**–**3**) by cyclic voltammetry and various spectroscopic techniques.^{12,13}



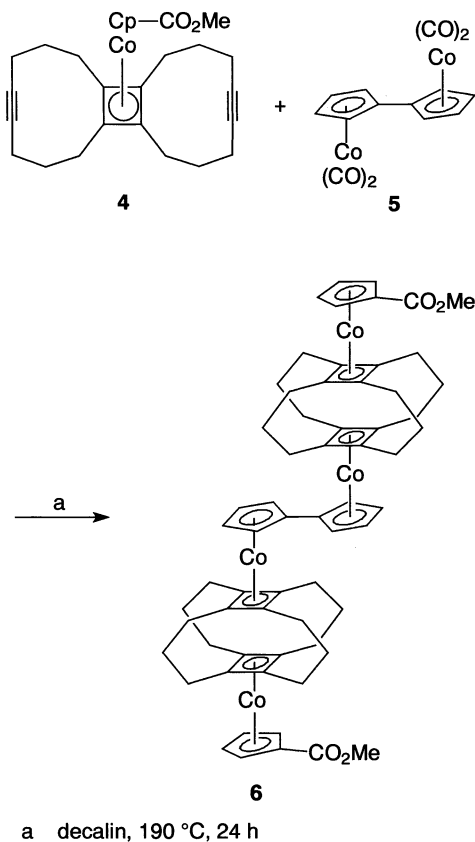
It turned out that on the IR time scale **1**⁺ is valence trapped just like **2**⁺ and **3**⁺. However, the optical spectra show characteristics of both valence-trapped and valence-delocalized behavior.¹²

To contribute further to this topic we have made efforts to prepare substances with two superphane units in one molecule. To achieve this goal we heated the tricyclic butadiene complex **4**¹³ with (η^5 : η^5 -fulvalene)-(tetracarbonyl)dicobalt (**5**)¹⁴ in decalin at 190°C for 24 hours. As a result we could isolate the superphane dimer **6** as a yellow solid.¹⁵ The dimer **6** represents a species with four metal centers in one molecule. Two of them are directly conjugated via the fulvalene ligand, the other two are separated by alkane bridges. Due to the bulky skeletons of the superphane units we expect that both units adopt an *anti* conformation (Scheme 1).

Cyclic voltammetry of **6** in methylene chloride revealed two reversible oxidation events at 460 and 815 mV and two irreversible oxidation steps at 1050 and 1280 mV.¹⁶ To interpret these results we compare them with the oxidation potentials of **7**.¹³ In **7**, we find a reversible one at 510 mV and an irreversible process at 1089 mV. The first oxidation step in **7** was assigned to the Cp*Co

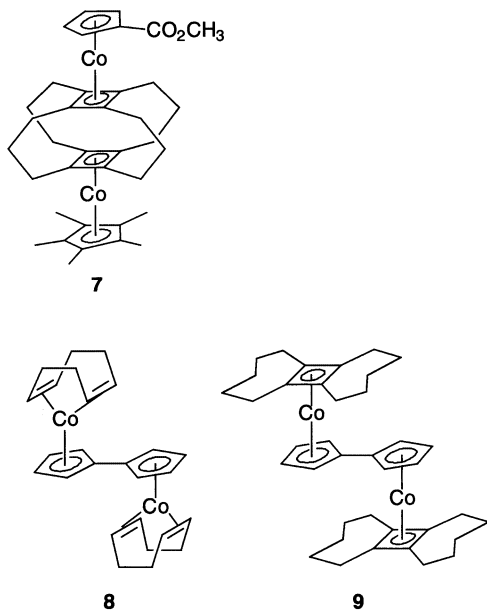
Keywords: metallocenophanes; electron transfer; cyclic alkynes; cyclobutadiene derivatives.

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Scheme 1.

fragment, whereas the second, irreversible oxidation was due to the oxidation of the cobalt associated with the Cp-CO₂CH₃ ligand.



Comparison of the data of **6** and **7** suggests that the two reversible oxidations stem from cobalt centers bound to the fulvalene unit. The large separation of both potentials $\Delta E_{1/2} = 355$ mV we ascribe to a strong

interaction between both cobalt centers on the fulvalene unit. Smaller differences were observed in the fulvalene-cobalt complexes **8** ($\Delta E = 228$ mV)¹⁷ and **9** ($\Delta E = 185$ mV),¹⁸ indicating a moderate interaction between both metal units.¹⁹

Acknowledgements

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- Experimental procedure: 250 mg (0.56 mmol) of **4**¹³ and 200 mg (0.56 mmol) of **5**¹⁴ were refluxed in 75 ml of decalin (190°C) for 24 hours. The reaction mixture was allowed to cool to room temperature, subsequently it was

filtered through alumina (neutral, grade III). With pentane as eluent unreacted **5** could be extracted while the product **6** remained at the top of the column. It could be dissolved with some CH_2Cl_2 and extracted as a yellow band. After removal of the solvent the crude product was purified by column chromatography (alumina neutral, grade III, CH_2Cl_2), yielding **6** as a yellow solid in 15% (95 mg). ^1H NMR (500 MHz, CDCl_3): δ = 4.94 (pt, 2H), 4.57 (pt, 2H), 4.40 (pt, 2H), 4.35 (pt, 2H), 3.72 (s, 3H), 2.09–2.02 (m, 32H), 1.57–1.56 (m, 16H). ^{13}C NMR (125 MHz, CDCl_3): δ = 169.2 (C), 92.9 (C), 84.8 (CH), 83.7 (C), 82.0 (CH), 81.6 (CH), 80.0 (C), 79.2 (CH), 77.5 (C), 51.7 (CH_3), 27.9 (CH_2), 26.4 (CH_2), 26.3 (CH_2). HRMS (FAB): calcd for $\text{C}_{64}\text{H}_{70}\text{O}_4\text{Co}_4$: 1138.2605. Found 1138.2577. IR (KBr) [cm^{-1}]: 3440, 2930, 2847, 1708, 1630, 1463, 1430, 1362, 1346. UV–vis (CH_2Cl_2) [nm ($\log \epsilon$): 284 (4.68), 322 (5.02),

- 382 (4.19).
16. Electrochemistry: Traditional three-electrode, three-compartment cell geometry was employed for voltammetry experiments with a Ag/AgCl reference electrode in CH_2Cl_2 separated from the test solution by a Haber–Luggin capillary. The $E_{1/2}$ values reported for chemically reversible systems were an average of the observed anodic and cathodic peak potentials. A supporting electrolyte concentration of 0.1 M of $[\text{NBu}_4][\text{PF}_6]$ was employed. The working electrode for cyclic voltammetry was a GC disk of 3 mm diameter.
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