Investigation of the Redox Properties of a Cp*Co(dithiolene) Complex. Evidence of the Formation of a Dimeric Dicationic Species: $[Cp^*Co(dddt)]_2^{2+}$ [†]

F. Guyon,[*,‡] D. Lucas,[§] I. V. Jourdain,[‡] M. Fourmigué,[⊥] Y. Mugnier,[§] and H. Cattey[§]

Laboratoire de Chimie des Matériaux et des Interfaces, 16 Route de Gray, Université de Franche-Comté, 25030 Besançon, France, Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, UMR 5632, Université de Bourgogne, 6 Boulevard Gabriel, 21000 Dijon, France, and Sciences Moléculaires aux Interfaces, FRE 2068 CNRS, 2 Rue de la Houssinière BP32229, 44322 Nantes, France

Received November 27, 2000

*Summary: The synthesis and the electrochemical characterization of $[(\eta^5\text{-}C_5Me_5)Codddt]$ ($dddt^{2-}$ = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) (**1**) are described. The chemical oxidation of **1** by $AgBF_4$ leads to the formation of a bimetallic complex, $[(\eta^5\text{-}C_5Me_5)Codddt]_2^{2+}$ (**2**), which has been characterized by X-ray crystallography. The ^1H NMR study reveals that **2** is diamagnetic, and this has been rationalized by extended Hückel calculations. The addition of trimethyl phosphite on **2** gives the paramagnetic adduct $[Cp^*Co(dddt)\{P(OMe)_3\}]^{\bullet+}$ (**4**). The dissociation of **2** has also been investigated electrochemically.*

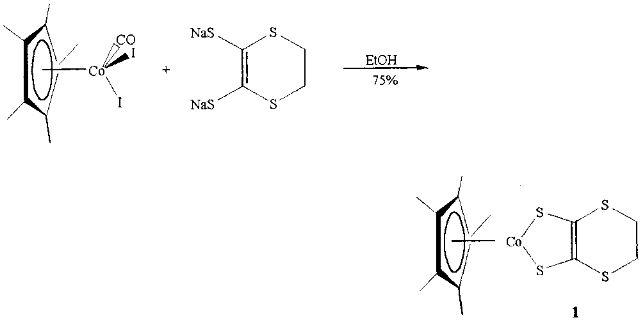
Introduction

Metalladithiolene rings of group 9 metals have received considerable attention because of their unique reactivity due to the coexistence of aromaticity and electronic unsaturation.[1] Our experience in the solid state chemistry of heteroleptic complexes bearing both cyclopentadienyl and dithiolene ligands[2] intrigues us to coordinate sulfur-rich dithiolene ligands such as $dmit^{2-}$ or $dddt^{2-}$ ($dmit^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate; $dddt^{2-}$ = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) on the CpCo fragment for the preparation of precursors of a new class of molecular materials presenting collective electronic properties. Indeed it is expected from these Co^{III} complexes to have a spin density mainly supported by the dithiolene ligand in the oxidized form. Note that this property is a prerequisite for the establishement of interesting electronic properties in the heteroleptic cyclopentadienyl/dithiolene complexes since the intermolecular interactions in the solid state are mainly based on short S···S contacts. Taking into account the work of A. Sugimori and co-workers, who showed that the loss of one electron in the [Cp*Codmit] leads to an unstable species,[3] we turned our effort to the coordination of the more electron-rich $dddt^{2-}$ ligand. We present in this note the synthesis and the redox properties of [Cp*Codddt]. The nature of the product generated after oxidation was investigated by NMR and ESR spectroscopies and by X-ray diffraction to reveal the formation of an unprecedented dimeric dicationic species.

Results and Discussion

Synthesis and Electrochemical Characterization. The complex [Cp*Codddt] (**1**) is readily prepared by stoichiometric reaction between $[Cp^*Co(CO)I_2]$ and Na_2dddt in EtOH solution. This complex is obtained in high yield as a mildly air-sensitive blue solid.

Scheme 1



As already reported for analogous complexes,[4] this 16-electron complex acts as a Lewis acid and forms 1:1 adducts with phosphines or phosphites. This is evidenced by UV−visible spectra since addition of phospine or phosphite on **1** results in a decrease of the absorption of the visible transition near 715 nm. But due to the electron-rich character of this dithiolene and the presence of the pentamethylcyclopentadienyl ligand, the formation constants of the adducts are much weaker than in $[CpCo(S_2C_2R_2)]$ complexes and could not be measured.[4c]

[†] Dedicated to Professor Jacques Amaudrut on the occasion of his 60th birthday.

[*] Corresponding author. E-mail: fabrice.guyon@univ-fcomte.fr.

[‡] Université de Franche-Comté.

[§] Université de Bourgogne.

[⊥] Sciences Moléculaires aux Interfaces, FRE 2068 CNRS.

(1) Sugimori, A.; Akiyama, T.; Kajitani, M.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879−908.

(2) (a) Fourmigué, M. *Coord. Chem. Rev.* **1998**, *178−180*, 823−864. (b) Fourmigué, M.; Domercq, B.; Jourdain, I. V.; Molinié, P.; Guyon, F.; Amaudrut, J. *Chem. Eur. J.* **1998**, *4*, 1714−1723. (c) Jourdain, I. V.; Fourmigué, M.; Guyon, F.; Amaudrut, J. *J. Chem. Soc., Dalton. Trans.* **1998**, 483−488. (d) Jourdain, I. V.; Fourmigué, M.; Guyon, F.; Amaudrut, J. *Organometallics* **1999**, *18*, 1834−1839.

(3) Ushijima, H.; Sudoh, S.; Kajitani, M.; Shimizu, K.; Akiyama, T.; Sugimori, A. *Appl. Organomet. Chem.* **1991**, *5*, 221−228.

(4) (a) Henderson, S.; Stephens, T.; Wharton, E. *J. Organomet. Chem.* **1984**, *179*, 231. (b) Kajitani, M.; Igarashi, A.; Hatano, H.; Akiyama, T.; Sugimori, A.; Matsumoto, S.; Iguchi, Y.; Boennemann, H.; Shimizu, K.; Satô, G. *J. Organomet. Chem.* **1995**, *485*, 31−36. (c) Shimizu, K.; Ikehara, H.; Kajitani, M.; Ushijima, H.; Akiyama, T.; Sugimori, A.; Satô, G. *J. Electroanal. Chem.* **1995**, *396*, 465−471.

10.1021/om001013o CCC: $20.00

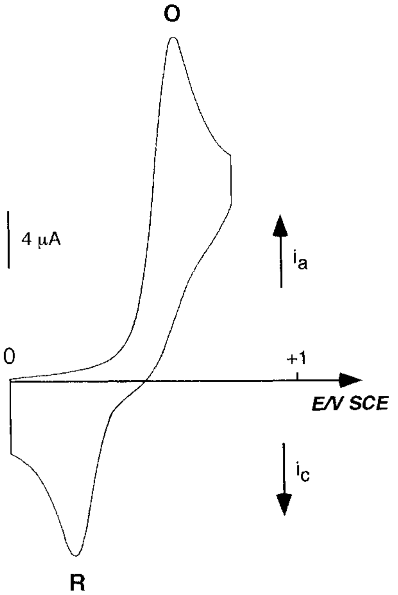


Figure 1. Cyclic voltammogram of 4.8 mM **1** in CH_2Cl_2 with 0.2 M NBu_4PF_6 on a vitreous carbon electrode. Sweep rate: 100 mV s^{-1}. Initial potential: 0 V.

Table 1. Crystallographic Data of 2

formula	$C_{14}H_{19}CoS_4BF_4$
fw	461.27
color, habit	black, plate
cryst size (mm)	0.44 × 0.28 × 0.02
T (K)	293 (2)
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	21.935 (2)
b (Å)	8.2304 (10)
c (Å)	20.7948 (10)
α (deg)	90.00
β (deg)	105.976(17)
γ (deg)	90.00
V (Å^3)	3609.2(6)
Z	8
ρ_{calc} (g cm^{-3})	1.698
μ (mm^{-1})	1.446
F(000)	1880
λ (Å)	0.71073
2*θ* range, deg	1.93−25.95
index ranges	$-26 \le h \le 26$, $-10 \le k \le 10$, $-25 \le l \le 2$
no. of reflns collected	7050
no. of ind reflns	3473
largest diff peak and hole, e Å^{-3}	−0.437, 0.550
final *R* indices[a]	0.0448
R indices (all data)	0.1266
GOF on F^2	1.023

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

The cyclic voltammogram of complex **1** in CH_2Cl_2 is shown in Figure 1 and consists of an oxidation peak O at +0.6 V versus SCE ($E_{p,O}$) coupled in the forward scan to a reduction peak R ($E_{p,R} = +0.21$ V). The separation of the peak potentials, $E_{p,O} - E_{p,R}$, is higher than 200 mV. Thus a chemical reaction follows the one-electron oxidation of the neutral complex (EC-type behavior). The chemical oxidation of **1** was also investigated in CH_2Cl_2. Treatment with 1 equiv of $AgBF_4$ induces a change of color of the solution from blue to purple. After filtration, addition of diethyl ether afforded dark purple needles of compound **2** which were suitable for X-ray study (Table 1).

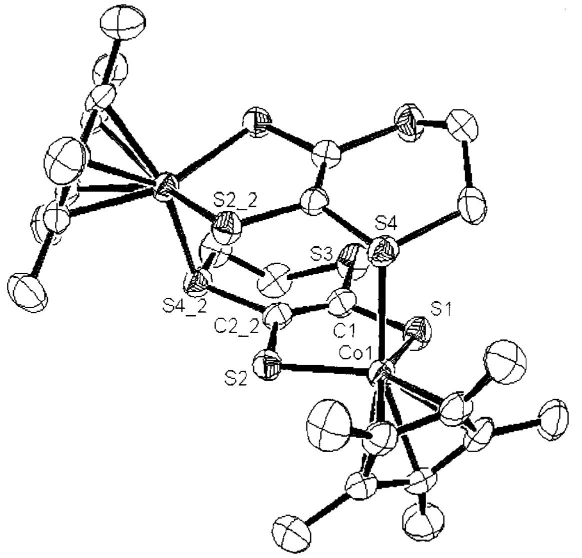


Figure 2. Molecular structure of $[Cp^*Codddt]_2^{2+}$ (**2**). Hydrogen atoms are omitted for clarity, 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Co−S(1) 2.2062(14), Co−S(2) 2.1867(14), Co−S(4) 2.3128(15), S(1)−C(1) 1.703(5), S(2)−C(2) 1.699(5), C(1)−C(2) 1.376(7), S(1)−Co−S(2) 90.94(5), S(1)−Co−S(4) 93.38(6), S(2)−Co−(S4) 93.68(5).

Table 2. Selected Bonds (in Å) and Angles (deg) of dddt Complexes

complex	M−S	C−S	C−C	SMS	ref
$[(Cp)_2Modddt]$	2.435(2)	1.76(1)	1.33(1)	82.41(5)	3
$[(Cp)_2Tidddt]$	2.414(2)	1.739(4)	1.366(10)	82.41(5)	3
2	2.196(14)	1.701(3)	1.376(7)	90.94(5)	this work

X-ray Structural Analysis of 2. The structural determination reveals that the oxidized complex **2** consists of dicationic dimers of $[Cp^*Codddt]_2^{2+}$ and BF_4^- anions. Within each $[Cp^*Codddt]^{\bullet+}$ fragment, the Co−S bond distances amount to 2.1867(14) and 2.2062(14) Å for S1 and S2, while the Co−S4 distance is almost as short, 2.3128(15) Å (Figure 2). The metallacycle is slightly folded along the S1- - -S2 axis by 15.1(1)°, while it makes an angle of 52.8(1)° with the C_5Me_5 ring plane. This is in sharp contrast with the geometry of similar unimolecular neutral complexes ([CpCodmit]; [Cp*Codmit]) in which the dithiolene plane lies mostly perpendicular to the Cp plane with shorter Co−S distances around 2.10 Å.[5] Furthermore, the shortening of the C−S and concurrent lengthening of the C=C bonds within the dddt moiety, when compared with analogous dddt^{2-} complexes such as [CpTidddt][6] or [CpModddt][7] (Table 2), clearly indicate that the oxidation essentially affects the dithiolene ligand together with a weakening of the Co−S bonds. This has also been observed in the paramagnetic [Cp*Co(dmit)Br] complex described by Matsubayashi,[8] in which the Br^- counteranion was reported to enter in the coordination sphere of the cobalt center. In our case, each fragment acts as a Lewis base for the

---

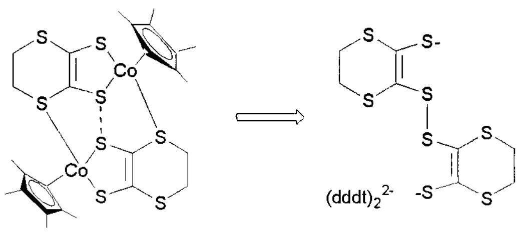
(5) Fourmigué, M.; Perrocheau, V. *Acta Crystallogr. C* **1997**, 1213−1215.

(6) Guyon, F.; Lenoir, C.; Fourmigué, M.; Larsen, J.; Amaudrut, J. *Bull. Soc. Chim. Fr.* **1994**, *131*, 217−226.

(7) Fourmigué, M.; Lenoir, C.; Coulon, C.; Guyon, F.; Amaudrut, J. *Inorg. Chem.* **1995**, *34*, 4979−4985.

(8) Mori, H.; Nakano, M.; Tamura, H.; Matsubayashi, G. *J. Organomet. Chem.* **1999**, *574*, 77−85.

other one via one sulfur atom (S4) of the outer dithiine ring, giving a pseudo-tetrahedral environment for the cobalt atom, as already observed in the solid state for neutral [CpCobdt] (bdt^{2-} = *o*-benzenedithiolate)[9] and [CpRhmnt] (mnt^{2-} = maleonitriledithiolate),[10] where one of the dithiolene sulfur atoms enters the coordination sphere of the cobalt center. Dimerization is also a common feature in the bis dithiolene cobalt complexes but gives rise to a square pyramidal stereochemistry around the metal.[11] But the radical nature of the $[Cp^*Codddt]^{\bullet+}$ moiety (**3**) leads to another strong interaction between the two almost parallel dithiolene moieties, as revealed by the extremely short $S2\cdots S2^i$ (*i*: $1-x$, y, $^1/_2-z$) distance of 2.776(5) Å. In that respect, the $[Cp^*Codddt]^{\bullet+}$ moiety can be formally described as a Co^{III} 16-electron complex coordinated to a radical $dddt^{\bullet 1-}$ ligand. Accordingly, it undergoes two different interactions related to its dual character: (i) the coordination sphere expansion of the coordinatively unsaturated Co atom via the $Co\cdots S4$ bond, and (ii) the setting of a weak covalent bond between the open-shell $dddt^{\bullet 1-}$ ligands, giving rise formally to a novel dianionic hexadentate ligand, $(dddt)_2^{2-}$.



The ^1H NMR study demonstrates that the dimeric form exists not only in the solid state but also in solution and reveals its diamagnetic character. Indeed the ^1H NMR spectrum in CD_2Cl_2 at room temperature consists of a sharp peak for the hydrogen atoms of the methyl groups and in a multiplet centered at 3.55 ppm due to the AA′BB′ spin system of the CH_2-CH_2 fragment.

Extended-Hückel Calculations. An extended-Hückel fragment analysis (Figure 3) shows indeed that the SOMO and LUMO frontier orbitals of each $[Cp^*Codddt]^{\bullet+}$ fragment, both π orbitals centered on the dithiolene moiety with a small d_{yz} Co contribution, strongly interact in the dimerization process. The two remaining electrons are stabilized in the bonding combination of the fragment's LUMOs, explaining the diamagnetic character of the dimer.

Solution Studies on the Dissociation of 2. Surprisingly ESR analysis of the solution of **2** in CH_2Cl_2 provided an eight-line spectrum resulting from the coupling of the unpaired electron with the cobalt nucleus (g = 2.0124; a_{Co} = 14.4 G). The poor signal-to-noise ratio is indicative of a very low concentration of the paramagnetic species, showing that **2** is dissociated to a small extent into its two monomeric components $[Cp^*Codddt]^{\bullet+}$ (**3**), while the small a_{Co} value confirms that most of the spin density is centered on the dithiolene ligand. Lowering the temperature to 100 K (frozen solution) results in complete disappearance of the ESR signals, demonstrating that in the solid state **2** is the only form present.

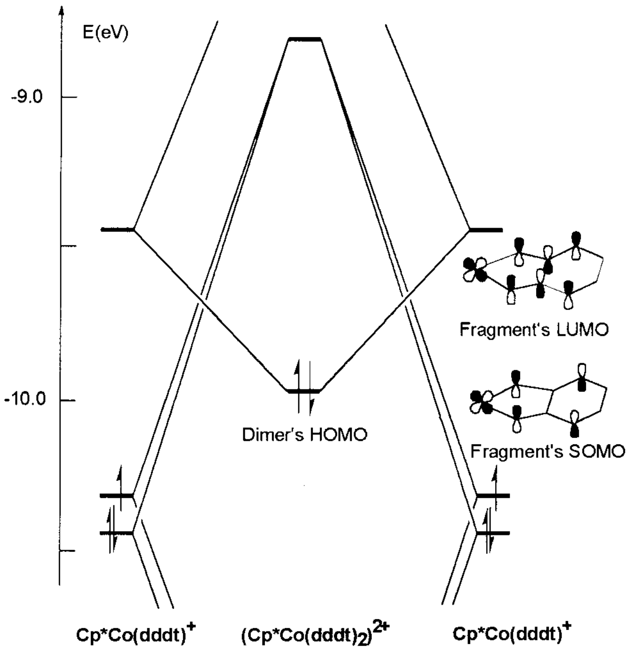


Figure 3. Extended Hückel fragment orbital interactions of the dimeric complex **2**.

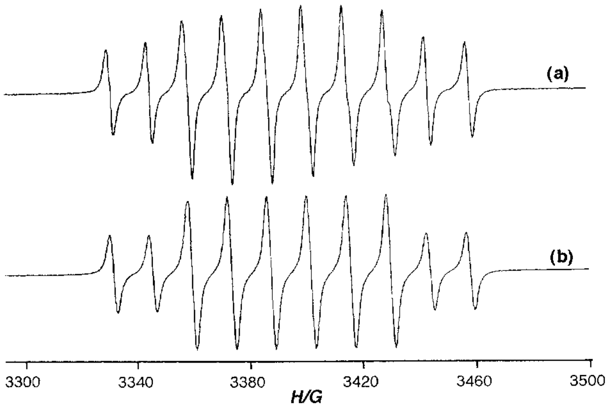


Figure 4. ESR spectrum (X-band) of **2** in CH_2Cl_2 after addition of $P(OMe)_3$: (a) experimental; (b) simulated.

At this stage, by adding $P(OMe)_3$ (5 equiv) to **2** in CH_2Cl_2, the intensity of the ESR signal is multiplied by 1000. The resultant spectrum (Figure 4) consists of 10 lines arising from the coupling with both cobalt and phosphorus nuclei (g = 2.0116; a_{Co} = 14.2 G and a_P = 28.4 G) Thus complexation of $P(OMe)_3$ stabilizes strongly the monomeric form with formation of an adduct that can be formulated as $[Cp^*Co(dddt)\{P(OMe)_3\}]^{\bullet+}$ (**4**).

Coming back to the first electrochemical observations, voltammetric analysis of a chemically prepared sample of **2** demonstrates that it is reducible at peak R. Accordingly, the exhaustive controlled-potential oxidation of **1** in CH_2Cl_2 (E_w = 0.6 V vs SCE) consumes one faraday per mole of **1** and gives **2** as the main product in solution. In view of these results, the overall oxidative process can be summarized in terms of Scheme 2.

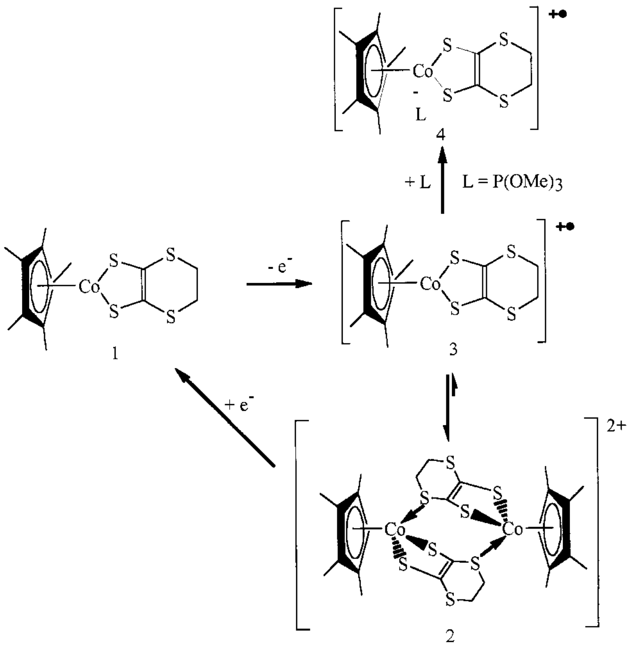
---

(9) Miller, E.; Brill, T.; Rheingold, A.; Fultz, W. *J. Am. Chem. Soc.* **1983**, *105*, 7580−7584.

(10) Don, M. J.; Yang, K.; Bott, S. G.; Richmond, M. G. *J. Organomet. Chem.* **1997**, *544*, 15−21.

(11) (a) Baker-Hawkes, M. J.; Dori, Z.; Eisenberg, R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4253−4259. (b) Enemark, J. H.; Lipscomb, W. N. *Inorg. Chem.* **1965**, *4*, 1729−1734. Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253−6277.

Scheme 2



The oxidation of **1** leads to the monocationic species **3**. In CH_2Cl_2, the open-shell complex dimerizes, giving rise to a diamagnetic bimetallic complex (**2**) with a strong S···S interaction. In the presence of $P(OMe)_3$, which is a strong two-electron-donor ligand, the stabilization occurs via the formation of the adduct **4**. Further investigations are in progress to determine the influence of either the ligands (dithiolene and cyclopentadienyl) or the operating solvent in the establishment of the original dimeric structure.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were purified by standard methods and freshly distilled under nitrogen. The NMR spectra were recorded on a 300 MHz Bruker spectrometer in CD_2Cl_2 with $SiMe_4$ as internal references. Electron spin resonance spectra were carried out at the X-band frequency on a Bruker ESP 300 spectrometer. The spectrometer was calibrated with DPPH ($g = 2.0037$). ESR spectra simulations and fittings were performed with Win EPR Simfonia also available from Bruker. Elemental analyses were performed at the Université de Bourgogne on a EA 1108 Fisons instrument.

Electrochemical Experiments. Voltammetric analysis were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The electrolyte consisted of 0.2 M $N^nBu_4PF_6$ solution in CH_2Cl_2. The reference electrode was a saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk; the auxiliary electrode was a platinum wire. For all voltammetric measurements the working electrode was a carbon disk electrode initially polished with alumina. The controlled potential electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 771 integrator. A carbon gauze was used at the anode, a platinum plate as the cathode, and an SCE as the reference electrode, each electrode being separated from the others by sintered glass disks. After each measurement the reference electrode was checked against the ferrocene–ferricinium (+0.46 V).

Synthesis of [Cp*Codddt], 1. Equimolar quantities (1 mmol) of $[Cp^*Co(CO)I_2]$[12] and Na_2dddt[6] were reacted in EtOH (20 cm^3) for 1 h at room temperature. The blue solution was then removed under reduced pressure, and the residue was extracted with $CHCl_3$ (2 × 30 cm^3). After filtration on alumina, the chloroform was evaporated under vacuum to afford the complex [Cp*Codddt] as a blue powder (0.280 g, 75%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.94 (s, 15H, C_5Me_5), 3.08 (s, 4H, CH_2-CH_2). Anal. Calcd for $C_{14}H_{19}CoS_4$: C, 44.93; H, 5.08; S, 34.23. Found: C, 43.56; H, 4.83; S, 32.54. Despite several attempts no more satisfactorily analyses were obtained probably due to the lability of the compound.

Synthesis of $[Cp^*Codddt]_2[BF_4]_2$, 2. A solution of **1** (0.3 mmol) in CH_2Cl_2 (10 cm^3) was added to a suspension of $AgBF_4$ (0.3 mmol) in CH_2Cl_2 (10 cm^3). The color of the solution turned immediately from blue to purple. The reaction mixture was stirred for 1 h at room temperature. After filtration, diethyl ether (~5 cm^3) was added and the resulting solution was cooled to −20 °C to give a purple needlelike crystalline solid. The supernatant was then decanted, and the solid was dried in a vacuum (0.125 g, 90%). Anal. Calcd for $C_{14}H_{19}CoS_4BF_4$: C, 36.45; H, 4.16; S, 27.80. Found: C, 37.05; H, 4.35; S, 27.12.

Crystallographic Data Collection and Structure Determination for 2. A crystal was mounted in glass capillaries using Araldite glue. Data were collected on a Stoe-IPDS diffractometer, with graphite-monochromated Mo Kα radiation (λ 0.710 73 Å). Details are given in Table 1. A numerical absorption correction was applied (FACEIT, Stoe). The structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-H atoms. H atoms were introduced at calculated positions and constrained to ride on the parent C atoms. All calculations were performed with the SHELTX package: Sheldrick G. M. SHELXS-97 and SHELXL-97; University of Göttingen, Göttingen, Germany.

Extended Hückel Calculations. Extended-Hückel type calculations[13] were performed with double-ξ quality orbitals[14] for C, Co, and S. Single-ξ orbitals were used for H. The geometry of the two monomers was taken from the X-ray structure.

Acknowledgment. We are grateful to Teresa Monzon for her technical assistance.

Supporting Information Available: Complete tables of atomic coordinates, H atom parameters, bond distances, bond angles, and isotropic thermal parameters; a packing diagram for complex **2**; and ^1H NMR spectra for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM001013O

---

(12) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 273–274.

(13) Hoffmann, R. J. *Chem. Phys.* **1963**, *39*, 1397.

(14) (a) Whangbo, M.-H.; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H.; Carlson, K. D.; Crabtree, G. W. *J. Am. Chem. Soc.* **1985**, *105*, 5815. (b) Clementi, E.; Roetti, C. *At. Nucl. Data Tables* **1974**, *14*, 177.