Synthesis of μ-$C_2S_4^{4-}$ Cobalt Complexes by Activation of the 1,3,4,6-tetrathiapentalene-2,5-dione, and Electrochemical Study of $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$

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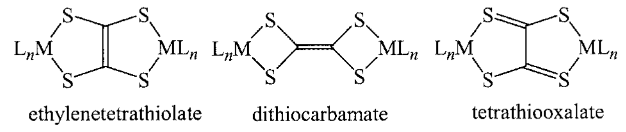
Keywords: Cobalt / S ligands / Cyclopentadienyl ligands / Electrochemistry

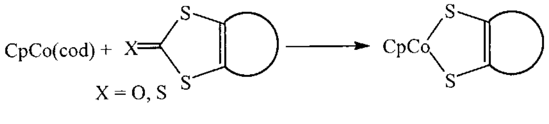
The bimetallic complex $[Cp^{(*)}Co)_2(\mu\text{-}C_2S_4)]$ in which the two metal centres are linked by an ethylenetetrathiolate $C_2S_4^{4-}$ unit, was synthesized in high yield by oxidative addition of 1,3,4,6 tetrathiapentalene-2,5-dione to $[Cp^{(*)}Co(CO)_2]$. The X-ray crystal structure of the intermediate product $Cp^*Co(dmid)$ ($dmid^{2-}$ = 4,5-disulfanyl-1,3-dithiol-2-onate) is presented. The electrochemical behaviour of the $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$ complex was studied in detail in the oxidative range. This study has shown that the nature of the product obtained after oxidation depends on the presence of complexing agent in the solution. The mechanism has been elucidated in a CH_2Cl_2 solution in the presence of $P(OMe)_3$. In addition, chemical oxidation was conducted with several oxidizing agents (Br_2, $TCNQF_4$, and $AgBF_4$). The molecular structure of the tetrathiooxalate bridged complex $[(Cp^*Co\{P(OMe)_3\})_2(\mu\text{-}C_2S_4)](BF_4)_2$ was established by an X-ray diffraction study.

Introduction

Complexes containing the ethylenetetrathiolate $C_2S_4^{4-}$ unit as a bridging ligand between two metal centres are rather rare, despite their potential to form systems with metallic or semiconducting properties.[1] The reason for this is the lack of a general procedure to generate this sulfur-rich ligand. Most of the tetrathiolate transition metal complexes have been synthesised by metal-promoted head-to-head reductive dimerization of CS_2. Representative examples include $[(Cp_2Ti)_2(\mu\text{-}C_2S_4)]$,[2] $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$,[3] $[(Cp^*Ni)_2(\mu\text{-}C_2S_4)]$,[4] and $[\{M(triphosp)\}_2(\mu\text{-}C_2S_4)]$ (M = Rh or Ir).[5] However, we have found in our laboratories that the reaction of $[Cp^*Co(CO)_2]$ with CS_2 leads to the formation of a mixture in which μ-dithiolene and μ-dithiocarbamate $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$ isomers coexist.[6] The same result was observed in the case of the titanium complex $[(Cp_2Ti)_2(\mu\text{-}C_2S_4)]$.[7] Recently, Rauchfuss et al. reported the synthesis of $[(Cp^*Rh)_2(\mu\text{-}C_2S_4)]$ via an efficient reductive dechlorination of the tetrathiooxalate derivative $[(Cp^*RhCl)_2(\mu\text{-}C_2S_4)]$.[8]



The synthesis of metal dimers containing the $C_2S_4^{4-}$ bridging ligand was also explored using the well-known reactivity of dithiocarbonate groups towards strong bases by starting from 1,3,4,6-tetrathiapentalene-2,5-dione (tpd). This method was found unsuccessful, however, or led to the desired product in low yield.[9,10] Another reactivity pattern of dithiocarbonate groups has already been employed for the synthesis of cobaltocene dithiolene complexes, used as model for the molybdenum cofactor.[11] The reaction consists of the oxidative addition of 1,3-dithiol-2-one or 1,3-dithiole-2-thione to [CpCo(cod)] (cod = cyclooctadiene).



With the aim of generating dimetallic complexes, it was tempting to apply this strategy by using bis(1,3-dithiol-2-one) and bis(1,3-dithiole-2-thione) as precursors. In this paper we report on the very efficient formation of $[Cp^{(*)}Co)_2(\mu\text{-}C_2S_4)]$ complexes starting from tpd. The electrochemical properties of the $[Cp^{(*)}Co)_2(\mu\text{-}C_2S_4)]$ complexes have been studied in detail in CH_2Cl_2 and CH_3CN solutions. The molecular structures of the intermediate product

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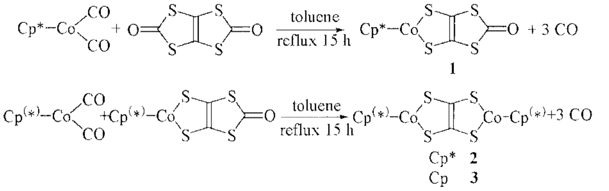
[Cp*Co(dmid)] ($dmid^{2-}$ = 4,5-disulfanyl-1,3-dithiol-2-onate) and of the oxidized species $[(Cp^*CoL)_2(\mu\text{-}C_2S_4)](BF_4)_2$ [L = $P(OMe)_3$] are also described.

Results and Discussions

Synthesis

The reaction of equimolar quantities of 1,3,4,6-tetrathiapentalene-2,5-dione (tpd) and $[Cp^*Co(CO)_2]$ in refluxing toluene afforded the intermediate complex [Cp*Co(dmid)] (**1**), which has already been isolated by the conventional metathesis of Na_2dmid and $[Cp^*Co(CO)I_2]$.[12] Recrystallization from toluene and hexane provided single crystals of **1**. The crystal structure was determined, since it has not been reported previously (see below). This intermediate **1** reacted with a second equiv. of $[Cp^*Co(CO)_2]$ under the same reaction conditions to afford the dimetallic diamagnetic complex $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$ (**2**). This compound was isolated as a green crystalline powder with a yield close to 90%, based on tpd (Scheme 1).



Scheme 1

Of course, this synthesis could also be achieved in one step by the reaction of 2 equiv. of $[Cp^*Co(CO)_2]$ and 1 equiv. of tpd. The isolation of **1** allowed us to deduce the dithiolene nature of the bridge instead of a dithiocarbamate core. Using an analogous procedure, we were able to synthesise the new $[(CpCo)_2(\mu\text{-}C_2S_4)]$ compound **3** in an appreciable yield (58%). In contrast to **2**, the solubility of the complex **3** was very poor in common organic solvents, which prevented any solution NMR characterization. The synthesis of **3** demonstrates the efficiency of this method, since it has not been obtained previously by the action of CS_2 on $[CpCo(CO)_2]$.[3b]

Structural Analysis of 1

The structure shown in Figure 1 is very similar to those of the structurally characterized heteroleptic cyclopentadienyl(dithiolene)cobalt complexes,[13] and particularly that of the [Cp*Co(dmit)] molecule ($dmit^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate).[14] In this compound, the $Co(C_3OS_4)$ moiety is nearly planar and perpendicular to the Cp* moiety [89.3(1)°]. Selected bond lengths and angles are listed in Table 1, and have been compared with those of [Cp*Co(dmit)]. The short length of the C(1)−C(2) bond [1.337(5) Å] of the ligand is in agreement with a dithiolene structure and proves that the reaction between the tpd and the $[Cp^*Co^I(CO)_2]$ compound leads to the coordination of $dmid^{2-}$ on the Cp^*Co^{III} fragment.

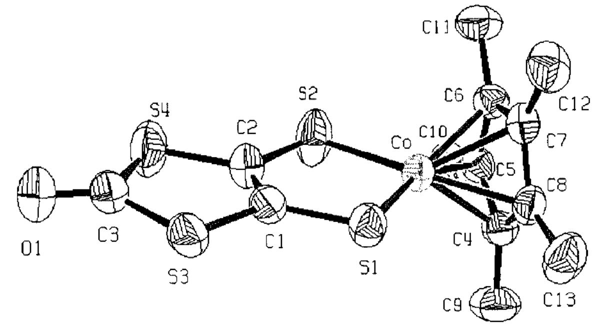


Figure 1. Molecular structure of **1**; hydrogen atoms are omitted for clarity, 50% probability ellipsoids

Table 1. Selected bonds lengths [Å] and angles [°] of **1** and [Cp*Co(dmit)] complexes

	1	[Cp*Co(dmit)][14]
Co-S1	2.1330(10)	2.138(2)
Co-S2	2.1201(10)	2.135(2)
S1−C1	1.722(3)	1.713(6)
S2−C2	1.722(3)	1.725(7)
S3−C1	1.751(3)	1.741(7)
S4−C2	1.750(3)	1.739(6)
S3−C3	1.769(4)	1.719(6)
S4−C3	1.768(4)	1.725(8)
X−C3	1.205(4) (X = O)	1.657(7) (X = S5)
C1−C2	1.337(5)	1.352(9)
Mean Co−C[a]	2.049(11)	2.050(7)
S1−Co−S2	93.16(4)	93.65(7)
C1−S1−Co1	102.54(11)	102.3(2)
C2−S2−Co1	103.08(12)	102.3(2)
S3−C3−S4	112.37(19)	113.3(4)

[a] Estimated errors on averaged Co−C distances are calculated as $\sigma = [\Sigma(d_i - d_{\text{mean}})^2/(n-1)]^{1/2}$, $n = 5$.

Electrochemical Experiments

The electrochemical behaviour of several $C_2S_4^{4-}$ bridged complexes has been studied, but the reported results point out different observations in the oxidation range. Indeed, the cyclic voltammograms of $[(Cp^*Ni)_2(\mu\text{-}C_2S_4)]$[4] and $[(Cp^*Rh)_2(\mu\text{-}C_2S_4)]$[8a] complexes in CH_2Cl_2 show a one-electron process, whereas in the case of $[\{Rh(triphosp)\}_2(\mu\text{-}C_2S_4)]$ a two electron oxidation is observed in CH_2Cl_2 or CH_3CN solutions.[5] Therefore, in order to evaluate the influence of the solvent, the redox behaviour of **2** was studied in CH_2Cl_2 and CH_3CN solutions.

The rotating-disk voltammogram in CH_2Cl_2 displays one anodic and two cathodic waves, all with nearly the same height. These were named O_1', R_1, and R_2, respectively, each associated with a one-electron transfer (Figure 2 and Table 2). In cyclic voltammetry, the first reductive step was found to be reversible, but not the second one, presumably because of the reactivity of the electrogenerated dianion $[(Cp^*Co)(\mu\text{-}C_2S_4)]^{2-}$ with the electrophilic dichloromethane (Scheme 2).[15] This is in contrast to what was observed in acetonitrile (see below). Exploring the oxidation, we observed in CH_2Cl_2 solution a peak O_1' at +0.62 V versus SCE (E_p) coupled on the backward scan with a peak at +0.15 V, which is indicative of a chemical reaction following the one-electron oxidation of the neutral complex. An exhaustive controlled-potential oxidation of **2** consumed nearly 1 F/mol of the initial complex, and left the product reducible at +0.15 V; the electrolysed solution was ESR-silent, which traduces the diamagnetism of this product. We propose that the chemical reaction consists in the dimerization of the intermediate $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]^+$ (Scheme 2). Indeed, this oxidation behaviour has already been observed for the analogous rhodium complex $[(Cp^*Rh)_2(\mu\text{-}C_2S_4)]$[8b] and for a dithiolene cobaltocene complex.[16] With this latter complex, it has also been shown that in the presence of a strong two-electron donor ligand the stabilization occurs via the formation of an adduct.[16] Thus, in order to explain the mechanism of the oxidation of **2** in the presence of a strong Lewis base, electrochemical experiments were conducted in CH_2Cl_2, where an excess of $P(OMe)_3$ was initially added to **2**. The resulting RDE voltammogram is depicted (see b in Figure 3). Reduction wave R_1 is still present, but with a considerably reduced height, attesting to the fact that **2** is still in solution, but in a limited amount (nearly 25% based on the relative value of $i_{d,R1}$). New oxidation waves appear at −0.62, −0.23, and +0.06 V, named $O_1{}^{*\prime}$, $O_1^{\#\prime}$, and $O_2{}^{*\prime}$, respectively. These can be explained by considering that **2** is able to coordinate one or two $P(OMe)_3$ moieties. As $P(OMe)_3$ is a strong σ-donor, the most negative oxidation wave, namely $O_1{}^{*\prime}$, must be assigned to the two-ligand containing complex $[(Cp^*Co\{P(OMe)_3\})_2(\mu\text{-}C_2S_4)]$ (**2b**). Oxidation wave $O_1^{\#\prime}$ is attributed to the mono adduct $[(Cp^*Co)_2\{P(OMe)_3\}(\mu\text{-}C_2S_4)]$ (**2a**), which is predominant since $O_1^{\#\prime}$ is noticeably more intense than R_1 or $O_1{}^{*\prime}$.

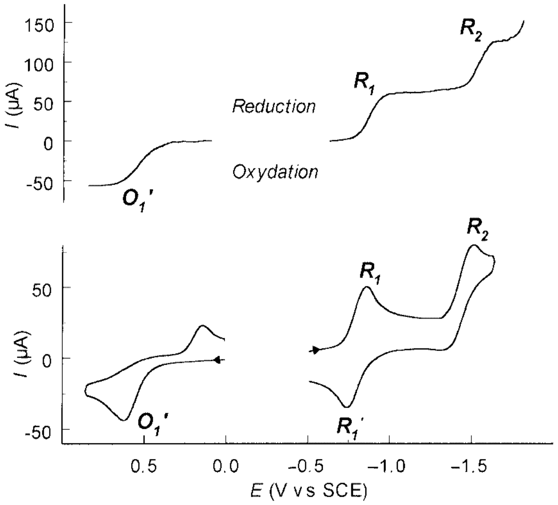
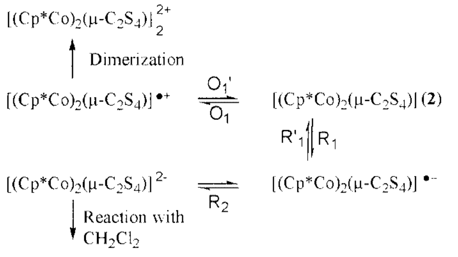


Figure 2. Rotating-disk and cyclic voltammogram of 2.7 mM of **2** in CH_2Cl_2, 0.2 M Bu_4NPF_6; CV: sweep rate = 200 $mV{\cdot}s^{-1}$, initial potential = −0.1 (anodic scan) and −0.65 V (cathodic scan); RDV: rotation speed = 15 rps

Table 2. Voltammetric data of **2** and its $P(OMe)_3$ adducts

Compound	Oxidation		Reduction	
	$E_{1/2,1}$[a][b] [V]	$E_{1/2,2}$ [V]	$E_{1/2,1}$ [V]	$E_{1/2,2}$ [V]
2 in CH_2Cl_2	+0.51		−0.9	−1.56
2 in CH_3CN	+0.25		−0.82	−1.47
2a	−0.23			
2b	−0.62	+0.06		

[a] All potentials are referred to the saturated calomel electrode. [b] Half-wave potentials are taken by RDE voltammetry.



Scheme 2

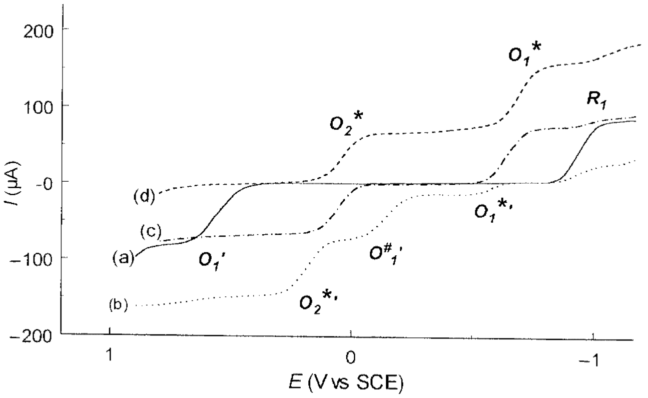


Figure 3. Rotating-disk voltammogram of 4.1 mM of **2** in CH_2Cl_2 0.2 M Bu_4NPF_6, rotation speed = 10 rps; a (——): **2** alone; b (···) after addition of 33 mol-equiv. of $P(OMe)_3$; c (·-·-) after electrolysis at −0.05 V; d (---) after electrolysis at +0.3 V

An exhaustive controlled-potential electrolysis, performed on the plateau of wave $O_1^{\#\prime}$ (E_w = −0.05 V vs. SCE), consumed nearly 1 F/mol of **2**. The resulting RDE voltammogram (see c in Figure 3) displays the anodic wave $O^*{}_2{}'$ together with the cathodic wave $O^*{}_1$, which means that at the monooxidized state, the bis(adduct) $[(Cp^*Co\{P(OMe)_3\})_2(\mu\text{-}C_2S_4)]^{+\cdot}$ (**2e**) is the only stable species. This was confirmed by ESR analysis of the electrolysed solution. The apparently complex morphology of the spectrum (Figure 4) arises from the coupling of the unpaired spin with two phosphorus and two cobalt nuclei (g_{iso} = 2.020; a_{Co} = 3.4 G; a_P = 22.6 G). Particularly, the hyperfine coupling constants are close to those found for similar complexes.[17]

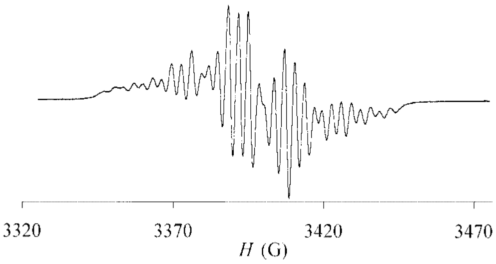


Figure 4. The ESR spectrum (X-band) of **2e**, obtained after the electrolysis (E_w = −0.05 V vs. SCE) of a CH_2Cl_2 solution of **2** in the presence of an excess of $P(OMe)_3$

The second stage of oxidation was also studied. Indeed, starting from **2e**, an electrolysis at 0.3 V (plateau of wave $O^*_2{}'$), consumed nearly 1 equiv. of electrons and quantitatively yielded $[(Cp^*Co\{P(OMe)_3\})_2(\mu\text{-}C_2S_4)]^{2+}$ (**2g**), which is evidenced in RDE voltammetry by the successive cathodic waves O^*_2 and O^*_1 (see d in Figure 3). In contrast with the first oxidation, the electron transfer is not associated herein with any chemical reaction. In summary, the detailed mechanism of the oxidation of **2** in the presence of $P(OMe)_3$ can be formalized according to Scheme 3. The overall process is governed by both electron transfer and $P(OMe)_3$ exchange reaction thermodynamics.

The electrochemical analysis of **2**, performed in acetonitrile, indicates that the dimerization does not occur, like in dichloromethane. Indeed, the rotating-disk voltammogram (Figure 5 and Table 2) exhibits a two-electron charge transfer in the oxidative range, based on the height of the oxidation wave, which is nearly twice compared to that of the reduction ones. In cyclic voltammetry, the oxidation peak O'_1, found at +0.32 V, is associated in the forward scan with a reduction peak located at +0.14V. Moreover, an exhaustive controlled-potential oxidation (E_w = +0.46 V vs. SCE) consumed 2 F/mol of initial complex, ultimately leaving the product reducible at +0.14 V. In addition, the electrolysed solution was found to be ESR-silent. We propose that the final two-electron oxidized complex incorporates two molecules of MeCN, like with $P(OMe)_3$. Within the framework of Scheme 3, the mechanism involves, after the first electron-transfer (**2** → **2c**), the addition of one molecule of solvent (**2c** → **2d**), which prevents the dimerization from occurring. At this stage, there are two possibilities, either the addition of the second molecule of solvent occurs before the second electron step (pathway **2d** → **2e** → **2g**) or after (**2d** → **2f** → **2g**). It must be outlined that this second electrochemical step occurs at the same potential as the oxidation **2** → **2c** due to the basicity of the acetonitrile, which leads to only one wave or peak in the voltammogram of **2**, with a two-electron transfer.

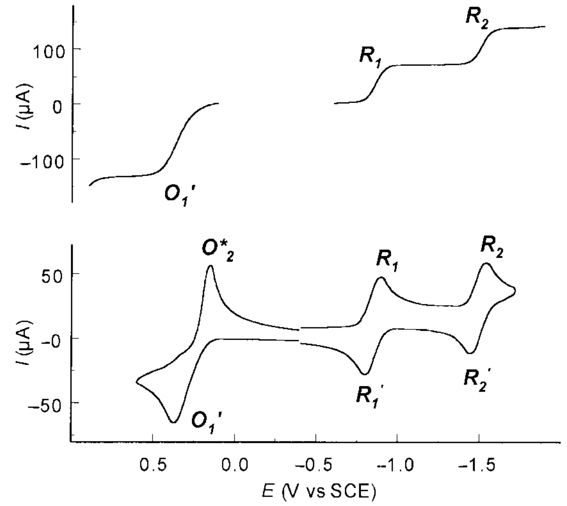
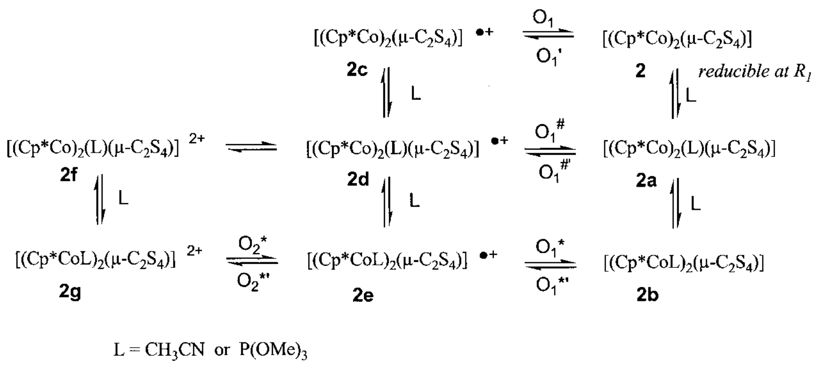


Figure 5. Rotating-disk and cyclic voltammogram of 2.8 mM of **2** in CH_3CN 0.2 M Bu_4NPF_6; CV: sweep rate = 100 mV·s^{-1}, initial potential = −0.4 V (anodic and cathodic scans); RDV: rotation speed = 10 rps

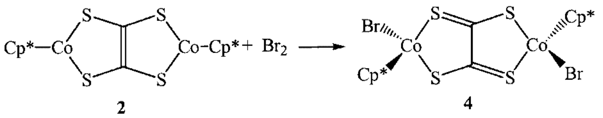
It must be noted from Table 2 that going from CH_2Cl_2 to MeCN causes a strong shift in the oxidation potential (−260 mV against +80 mV in reduction), which may arise from the influence of the kinetics of the chemical reaction following the first electron transfer.[18] In any case, the potential difference between CH_2Cl_2 and MeCN cannot be explained by the complexation of MeCN in the neutral state since we have verified that there is no change at all in the UV/Vis spectra of **2** from one solvent to the other.



Scheme 3

Chemical Oxidation

In agreement with the results of the electrochemical studies, it can be shown that $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$ can be chemically oxidized without destroying its CoC_2S_4Co core. Oxidation of **2** by 1 equiv. of Br_2 gives the diamagnetic neutral complex $[(Cp^*CoBr)_2(\mu\text{-}C_2S_4)]$ (**4**) (Scheme 4).



Scheme 4

The coordination of halides upon oxidation has already been observed for a (dithiolene)cobalt complex,[19] as well as for $[(Cp^*Rh)_2(\mu\text{-}C_2S_4)]$.[8a] The cyclic voltammogram of **4** (Figure 6) shows that the bromine atoms can be reductively decoordinated [Equation (1)]. Indeed, after a first reduction peak located at −0.26 V, the peak R_1 was observed at the second stage.

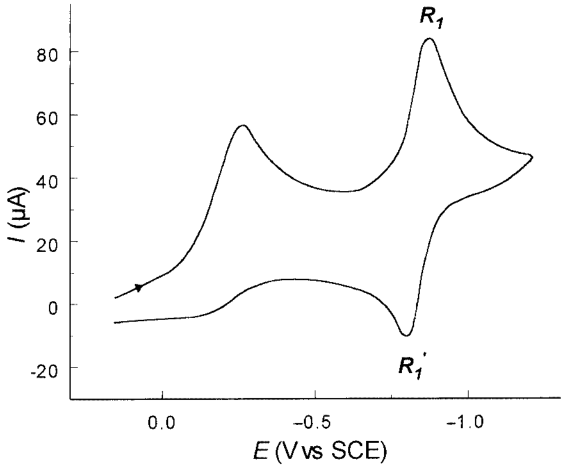
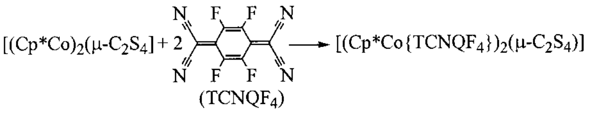


Figure 6. Cyclic voltammogram of 3.2 mM of **4** in CH_2Cl_2 of 0.2 M Bu_4NPF_6 (sweep rate = 100 mV·s^{-1})

$$\underset{\mathbf{4}}{[(Cp^*CoBr)_2(\mu\text{-}C_2S_4)]} + 2\,e^- \rightarrow \underset{\mathbf{2}}{[(Cp^*Co)_2(\mu\text{-}C_2S_4)]} + 2\,Br^- \qquad (1)$$

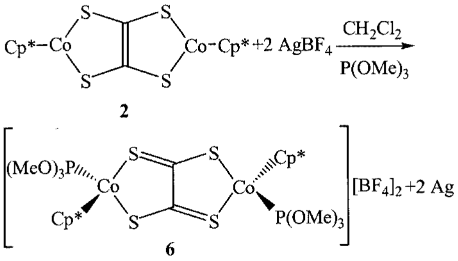
Complex **2** was also oxidized by the strong oxidizer $TCNQF_4$ (perfluoro-7,7,8,8-tetracyano-*p*-quinodimethane). Indeed, treatment of an acetonitrile solution of $TCNQF_4$ with a 0.5 mol-equiv. of **2** was found to afford $[(Cp^*Co\{TCNQF_4\})_2(\mu\text{-}C_2S_4)]$ (**5**) as a blue powder (Scheme 5).



Scheme 5

The stoichiometry of **5** was ascertained from the elemental analysis. Despite the tendency of the $TCNQF_4^{-\cdot}$ to form dimeric dianionic moieties,[20] the elemental analysis suggests that the dication $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]^{2+}$ is stabilized by the coordination of the anionic $TCNQF_4^{-\cdot}$ on both cobalt atoms. Unfortunately, all our attempts to grow crystals of **4** and **5** were unsuccessful.

Information about the structural changes induced by the two-electron oxidation was obtained by chemical oxidation of **2** in the presence of a Lewis base in a CH_2Cl_2 solution. Treatment with 2 equiv. of $AgBF_4$ and an excess of trimethyl phosphite induced a change of colour of the solution from green to brown. After filtration, addition of diethyl ether afforded dark brown needles of compound $[(Cp^*Co\{P(OMe)_3\})_2(\mu\text{-}C_2S_4)](BF_4)_2$ (**6**) (Scheme 6). Note that the cationic part of this salt is equivalent to compound **2g** in Scheme 3.



Scheme 6

The ^1H NMR spectrum of **6** consists of a single sharp signal in the C_5Me_5 region, which is consistent with a symmetric structure and a diamagnetic ground state. Integration of the C_5Me_5 fine peak vs. the $P(OMe)_3$ signal indicates that each centre is coordinated by a molecule of a trimethyl phosphite. The symmetric structure is confirmed by the $^{31}P\{^1H\}$ NMR spectrum since only one signal is observed at δ = 126.8 ppm.

Electrochemical analysis of **6** provided the same RDE voltammogram as that of Figure 3d. In this there is no difference between the chemical and electrochemical approaches to the oxidation of **2**.

Structural Analysis

In addition to the NMR solution study, the solid-state structure of **6** was probed by X-ray crystallography. Crystallographic analysis established the 1:2 stoichiometry, i.e., one organometallic dication for two BF_4^- counterions. Analysis of the bond lengths shows that the C_2S_4 core is better described in **6** as tetrathiooxalate than ethylenetetrathiolate bridge. Especially since the $S_2C{-}CS_2$ distance is 0.1 Å longer in **6** than in reported complexes formulated as $C_2S_4^{4-}$ bridged complexes (Table 3). In addition, the Co−S bond is significantly lengthened in **6** in comparison to the neutral complex. Thus, the oxidation essentially affects the C_2S_4 ligand. Accordingly, with its dicationic nature, complex **6** can be described as two Co^{III} centres linked by a $C_2S_4^{2-}$ bridge. This description is similar to that of the $[(Cp^*RhCl)_2(\mu\text{-}C_2S_4)]$ compound reported by Rauchfuss et

Table 3. Selected bonds [Å] and angles [°] of μ-C_2S_4 bridged complexes

Complex	M−S	C−S	C−C	SMS	Ref.
6	2.1974(11) 2.2101(9)	1.685(4) 1.689(4)	1.460(7)	89.81(4)	this work
$[(RhCp'Cl)_2(\mu\text{-}C_2S_4)]$[a]	2.317(2) 2.334(2)	1.689(6) 1.695(7)	1.447(13)	85.08(6)	[8a]
$[(RhCp^*)_2(\mu\text{-}C_2S_4)]$	2.2432 2.2517	1.744 1.736	1.342(8)	87.33(4)	[8a]
$[(CoCp^*)_2(\mu\text{-}C_2S_4)]$	2.122(2) 2.126(2)	1.725(4) 1.725(4)	1.369(11)	91.6(1)	[3b]
$[(NiCp^*)_2(\mu\text{-}C_2S_4)]$	2.122(1)	1.718(3)	1.360(11)		[4]
$[\{Rh(triphosp)\}_2(\mu\text{-}C_2S_4)]$	2.311(6) 2.296(5)	1.76(2) 1.70(2)	1.37(3)	85.9(2)	[5]

[a] Cp′ = η^5-C_5Me_4Et.

al.[8a] The two $P(OMe)_3$ ligands are complexed in a *trans* manner giving rise to a C_{2h} structure (Figure 7). The Co−P distance [2.1693(11) Å] lies in the range of what is generally observed for this bond.[21] Due to this complexation, the C_2S_4 plane does not lie perpendicular to the Cp* plane, which is in opposition to what was observed in the case of **2**.[3b] The CoS_2 unit makes an angle of 52.1(1)° with the C_5Me_5 ring plane. The Co−C distances [2.080(4)−2.120(4) Å] are appreciably long compared with those of the neutral complex **2** [2.026(6)−2.040(6) Å].

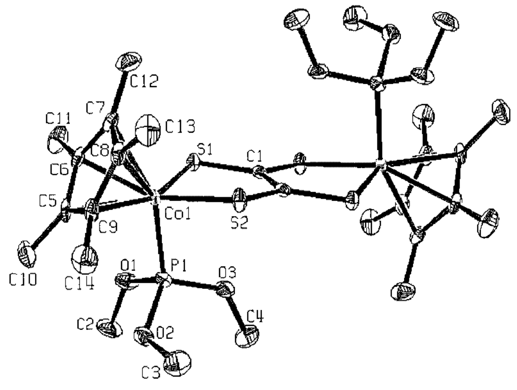


Figure 7. Molecular structure of **6**; hydrogen atoms and BF_4^- are omitted for clarity, 50% probability ellipsoids; selected bond length [Å] and angles [°]: Co(1)−P(1) 2.1693(11), P(1)−O(1) 1.575(3), P(1)−O(2) 1.587(3), P(1)−O(3) 1.575(3), Co(1)−Cp*$^{(vertical)}$ 1.714(2); P(1)−Co−S(2) 94.14(4), P(1)−Co−S(1) 89.04(4), C(1)−S(1)−Co(1) 104.07(12), C(1)−S(2)−Co(1) 104.63(12), O(1)−P(1)−Co(1) 109.62(11), O(2)−P(1)−Co(1) 120.10(12), O(3)−P(1)−Co(1) 110.62(11), C(1)−C(1)−S(1) 119.7(4), C(1)−C(1)−S(2) 118.9(4)

Conclusion

In summary, we have found a new efficient method for the preparation of dimetallic cobalt complexes bridged by the $C_2S_4^{4-}$ unit starting from 1,3,4,6-tetrathiapentalene-2,5-dione. Electrochemical and chemical oxidations of $[(Cp^*Co)_2(\mu\text{-}C_2S_4)]$ have shown that the loss of electrons involves mainly the bridging ligand without breaking the link between the two metal centres. The stabilization of the oxidized species results from coordination, complexation, or dimerization according to the nature of the solution in which the oxidation is conducted.

Further studies will concentrate on the formation of the first heterobimetallic complexes bridged by the $C_2S_4^{4-}$ ligand.

Experimental Section

General Comments: All reactions were carried out under dry argon using standard Schlenk techniques. Solvents were purified by standard methods and freshly distilled under nitrogen. The NMR spectra were recorded with a Bruker AC and a Bruker Avance 300 MHz spectrometer. Electron spin resonance spectra were recorded at room temperature with a Bruker ESP 300 spectrophotometer. Field calibrations were made with dpph (g = 2.0034). Elemental analyses were performed at the Université de Bourgogne with an EA 1108 Fisons instrument. The 1,3,4,6-tetrathiapentalene-2,5-dione[22] and $Cp^*Co(CO)_2$ [23] were prepared according to published literature methods and $CpCo(CO)_2$ was purchased from Aldrich. The method described by Wheland and Martin was employed for the synthesis of $TCNQF_4$.[24]

Electrochemical Experiments: Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The electrolyte consisted of 0.2 M nBu_4NPF_6 solution in CH_2Cl_2 or in MeCN. The reference electrode was a saturated calomel electrode (SCE) separated from the analysed 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 couple (+0.46 V in CH_2Cl_2 and +0.4 V in MeCN).

Synthesis of $[Cp^*Co(C_3OS_4)]$ (1): Equimolar quantities (1 mmol) of $[Cp^*Co(CO)_2]$ and 1,3,4,6-tetrathiapentalene-2,5-dione were heated under reflux in toluene (30 mL) overnight under argon. After filtration, the green solution was removed under reduced pressure. Washing the residue by a small quantity of pentane (5 mL) afforded the complex **1** as a green powder (0.36 g, 96% yield). A single crystal of **1** was obtained by recrystallization from toluene and hexane. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.97 (s, Me_5C_5) ppm. IR (KBr): ṽ = 1626 and 1670 (C=O), 1340 (C=C) cm^{-1}.

Synthesis of [(Cp*Co)$_2$(μ-C_2S_4)] (2): Equimolar quantities (1 mmol) of [Cp*Co(CO)$_2$] and **1** were heated under reflux in toluene (30 mL) overnight under argon. Cooling the solution in an ice bath resulted in the precipitation of complex **2** as green needles, which were collected by filtration. Yield: 0.485 g (90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (s, Me_5C_5) ppm. IR (KBr): ṽ = 1375 (C=C) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 322, 809 nm. MS: *m/z* = 540 [M$^+$]. $C_{22}H_{30}Co_2S_4$: calcd. C 48.89, H 5.56, S 23.70; found C 48.52, H 5.65, S 23.15.

Synthesis of [(CpCo)$_2$(μ-C_2S_4)] (3): A mixture of CpCo(CO)$_2$ (0.5 mL, 3.47 mmol) and 1,3,4,6-tetrathiapentalene-2,5-dione (360 mg, 1.73 mmol) were heated under reflux in toluene overnight under argon. After cooling to room temperature, the blue reaction mixture was filtered. The collected solid afforded complex **3** as a dark blue powder. Yield: 0.400 g (58%). MS: *m/z* = 400 [M$^+$]. $C_{12}H_{10}Co_2S_4$: calcd. C 36.01, H 2.50, S 32.04; found C 36.25, H 2.39, S 31.67.

Synthesis of [(Cp*CoBr)$_2$(μ-C_2S_4)] (4): To a solution of MeCN (30 mL), containing 60 mg of **2** (0.111 mmol), was added 6 μL (0.117 mmol) of Br_2.The colour of the solution turned slowly from green to blue. After 12 h of stirring, the precipitate was filtered off and washed with diethyl ether to afford the complex **4** as a blue powder. Yield: 62 mg (80%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.50 (s, Me_5C_5) ppm. $C_{22}H_{30}Br_2Co_2S_4$ (700): calcd. C 37.71, H 4.29, S 18.32; found C 37.42, H 4.19, S 17.66.

Synthesis of [(Cp*Co{$TCNQF_4$})$_2$(μ-C_2S_4)] (5): An MeCN solution (10 mL) of $TCNQF_4$ (60 mg, 0.214 mmol) was added to an MeCN solution (20 mL), containing 58 mg of **2** (0.107 mmol). The resulting solution was stirred overnight at ambient temperature. The complex **5** was obtained as a blue powder after filtration and washing with CH_2Cl_2. Yield: 89 mg (76%). IR (KBr): ṽ = 2216 and 2198 (C≡N) cm^{-1}. $C_{46}H_{30}Co_2F_8S_4N_8$ (1092): calcd. C 50.55, H 2.75, N 10.26; found C 49.90, H 2.79, N 9.65.

Synthesis of [(Cp*Co{P(OMe)$_3$})$_2$(μ-C_2S_4)](BF$_4$)$_2$ (6): Complex **2** (0.070 g, 0.130 mmol) was dissolved in 20 mL of CH_2Cl_2 in the presence of P(OMe)$_3$ (0.12 mL, 1 mmol). This solution was added to a suspension of $AgBF_4$ (0.051 g, 0.260 mmol) in 5 mL of CH_2Cl_2. After 1 h of stirring, the brown solution was filtered. Addition of 10 mL of ether afforded dark brown crystalline solid of **6**, which was washed with 2 × 10 mL of ether. Yield: 0.095 g (85%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.66 (s, 15 H), 3.8 (m, 9 H) ppm. ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 11.8 (C_5*Me_5*), 58.59 [P(OMe)$_3$], 105.3 (*C_5*Me_5), 115 (C=C) ppm. ^{31}P{H} NMR (300 MHz, CD_2Cl_2): δ = 126.8 [P(OMe)$_3$].

Crystallographic Data Collection and Structure Determination for 1 and 6: A single crystal of each compound was mounted in a glass capillary using Araldite glue. Data were collected with a Stoe-IPDS diffractometer, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Details are given in Table 4. 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.[25] CCDC-77465 for [Cp*Co(dmid)] and -177466 for [(Cp*Co{P(OMe)$_3$})$_2$(μ-C_2S_4)](BF$_4$)$_2$ contain the supplementary crystallographic data for this paper. These data can

Table 4. Crystallographic data

Compound	1	6
Empirical formula	$C_{13}H_{15}CoOS_4$	$C_{28}H_{48}B_2Co_2F_8O_6P_2S_4$
Formula mass	374.42	962.32
Cryst size [mm]	0.2 × 0.2 × 0.15	0.16 × 0.16 × 0.08
T [K]	293(2)	293(2)
Cryst system	monoclinic	monoclinic
Space group	*P*2$_1$/*n*	*P*2$_1$/*c*
a [Å]	8.0269(16)	11.0910(11)
b [Å]	14.067(3)	14.1973(13)
c [Å]	14.386(3)	13.1834(14)
α [°]	90	90
β [°]	98.43(3)	104.303(12)
γ [°]	90	90
V [Å^3]	1606.8(6)	2011.5(3)
Z	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.548	1.589
μ [mm^{-1}]	1.576	1.187
F(000)	768	988
λ [Å]	0.71073	0.71073
θ range [°]	2.04−25.90	1.89−25.97
Index ranges	$-9 \le h \le 9, 0 \le k \le 17, 0 \le l \le 17$	$-13 \le h \le 13, 0 \le k \le 17, 0 \le l \le 16$
No. of reflections collected	3100	3872
No. of ind reflections	2243	2483
Largest diff peak and hole [e/Å^3]	−0.284/0.280	−0.409/0.517
Final *R* indices[a]	0.0349	0.0401
R indices (all data)	0.0546	0.0757
GOF on F^2	0.926	0.906

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

be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank Dr. Hélène Cattey (LSEO, Dijon, France) and Dr. Chikako Takayama (Sophia University, Tokyo, Japan) for fruitful discussions on the EPR spectrum. Financial support from the Ministère de la Recherche et de la Technologie is gratefully acknowledged.

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Received January 15, 2002
[I02024]