(3) H. Sigel, "Metal Ions in Biological Systems", Vol. 2, Marcel Dekker, New York, 1973, p 64; H. Sigel, *Angew. Chem., Int. Ed. Engl.*, **14**, 394 (1975).
(4) P. W. Atkins and M. C. Symons, "The Structure of Inorganic Radicals", Elsevier, New York, 1967, p 20.

Contribution from the Laboratoire de Polarographie Organique,
Faculté des Sciences, F-21100 Dijon, France, and
the Institut für Anorganische Chemie, Universität Würzburg,
D-8700 Würzburg, Federal Republic of Germany

Electrochemistry of Half-Sandwich and Trinuclear Sandwich Complexes Containing Phosphonate Ligands

Nabil El Murr, Annie Chaloyard, and Wolfgang Kläui*

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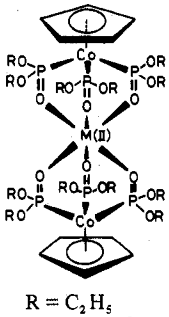
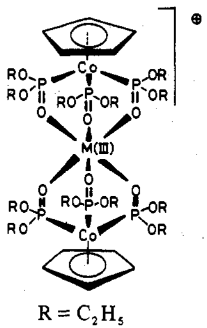
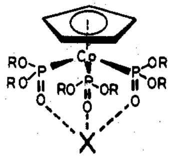
In a broad survey Dessy has reported[1,2] on the redox properties of 130 transition-metal π complexes and complexes with π-acceptor ligands. It is interesting to note that apart from the classical sandwiches ferrocene,[3] cobaltocene,[3] and bis(benzene)chromium[4] only very few *sandwich* or *half-sandwich* compounds are electrochemically oxidized or reduced to yield stable isolable metallocene ions. This has limited the use of electrochemical techniques for synthetic purposes in sandwich chemistry.[5,6] On the other hand much work has been devoted to the study of the electrochemical properties of such organometallic complexes from an analytical point of view.[7-9] To our knowledge only one example of an electrochemical formation of a *triple-decker compound* has been reported, namely, the oxidation of μ-cyclooctatetraene-bis(cyclopentadienylcobalt) by Geiger.[10] We have recently prepared a series of *trinuclear sandwich* complexes,[11,12] and we were interested to learn whether this new and interesting class of compounds shows redox properties comparable to those of the simple sandwiches cobaltocene, ferrocene, etc. or whether they undergo decomposition or ligand rearrangement reactions upon electrochemical oxidation or reduction. In this communication we present the preliminary findings on the trinuclear sandwich compounds **1**–**3**, **5** and **6** and the half-sandwich complex **9**.



R = C_2H_5
1, M(II) = Co
2, M(II) = Fe
3, M(II) = Hg
4, M(II) = Cu



R = C_2H_5
5, M(III) = Co
6, M(III) = Fe
7, M(III) = Ln



R = C_2H_5
8, X = H
9, X = Na

Results and Discussion

$[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Co$ (1). From our investigation of the reactivity of **1** we know that this complex is extremely stable toward oxidation.[13] It can be dissolved, e.g., in concentrated nitric acid, and recovered quantitatively upon dilution with water. It is readily protonated but not oxidized by nitric acid. In fact we have not been able so far to prepare the cation **5** from the corresponding neutral compound **1** by chemical means.

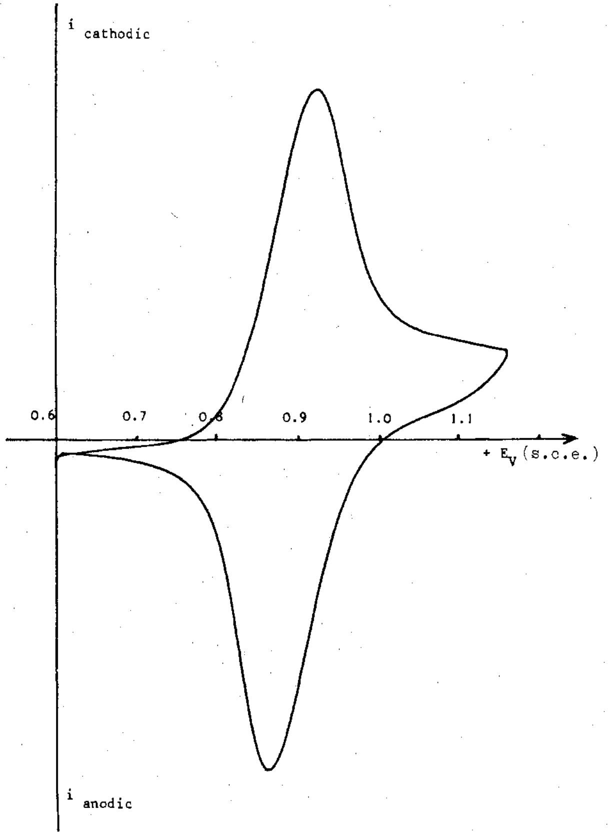


Figure 1. Thin-layer linear potential sweep voltammogram of 0.001 M $[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Co$ (**1**) in CH_2Cl_2; 0.2 M $[Bu_4N]PF_6$, at carbon electrode; scan rate 0.001 V s^{-1}.

A polarographic study of a 0.001 M solution of **1** in methylene chloride with 0.2 M $[Bu_4N]PF_6$ as supporting electrolyte shows that this compound is not reducible and not oxidizable at the dropping mercury electrode (DME) in the accessible potential range of the system (+0.8 to −1.9 V vs. SCE). The cyclic voltammogram of this solution using glassy carbon as the working electrode shows, however, an oxidation peak at +1.02 V. This oxidation is electrochemically reversible even for a sweeping rate of 0.01 V s^{-1}. In thin-layer linear potential sweep voltammetry at a carbon electrode this oxidation process remains reversible even for the very slow scanning rate of 0.001 [V s^{-1}] (see Figure 1). The comparison of the area of the oxidation peak of **1** with that of the monoelectronic reduction of cobalticinium ion to cobaltocene shows that the oxidation of **1** is monoelectronic. By controlled-potential coulometry at +1.3 V we have confirmed that the oxidation is a one-electron process and that the cation is stable in methylene chloride solution. Such solutions remain actually unchanged for several days and the reduction at +1.0 V leads quantitatively back to the starting material.

By electrolysis of **1** on a preparative scale (see Experimental Section) we have been able to isolate **5** as the PF_6 salt. The compound is a dark green solid which dissolves readily in polar organic solvents such as chloroform, methylene chloride, acetone, and nitromethane. The stability of such solutions is remarkable in view of the high oxidation potential. The kinetic stability of **5** is probably due to the difficulty of getting a reducing agent close enough to the central cobalt(III). The X-ray structure determination[14] of the analogous copper compound **4** shows indeed that the 12 OC_2H_5 groups are shielding the central atom very effectively. This is also in line with our observation that the corresponding lanthanide

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*To whom correspondence should be addressed at the Institut für Anorganische Chemie, Universität Würzburg.

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complexes such as **7** are only very weak Lewis acids.[15]

The 60-MHz ^1H NMR spectrum of **5** at room temperature in $CDCl_3$ consists of three slightly broadened signals at δ = 5.05 (Cp, 5 H), δ = 4.40 (OCH_2, 12 H), and δ = 1.55 (CH_3, 18 H). On cooling of the solution, the resolution increases, and below 0 °C the coupling constant $^3J(HCCH)$ = 7 Hz becomes visible.

The room-temperature electronic spectrum of **5** is very similar to the spectrum of the isoelectronic Fe(II) complex **2** (vide infra). It shows two charge-transfer bands at λ = 245 nm ($\epsilon = 5.5 \times 10^4$ L mol^{-1} cm^{-1}) and λ = 328 nm ($\epsilon = 1.0 \times 10^4$ L mol^{-1} cm^{-1}), which are also observed in **9** and all the other trinuclear sandwich complexes, **1**–**7**, plus a very broad absorption at λ = 640 nm (ϵ = 250 L mol^{-1} cm^{-1}).

It is interesting to note that the broad absorption band at 640 nm decreases in intensity at lower temperature whereas the two CT bands show no temperature dependence. The green color of **5** accordingly changes to light yellow on cooling to −100 °C. Magnetic measurements by the NMR method[16] show that the magnetic moment also changes with temperature. We have found μ_{eff} = 2.5 μ_B per molecule at room temperature and 1.3 μ_B at −49 °C in methylene chloride solution. The thermochromism and the temperature dependence of the magnetism are fully reversible. We are currently measuring the magnetic moment of **5** in the solid state at 4.2 K and above room temperature to see whether our observations are compatible with a d^6 spin-crossover situation.

$[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Fe$ (2) and $[[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Fe]BF_4$ (6, BF_4 Salt). We have been able to prepare these two iron complexes directly from aqueous solutions of **8** and $FeSO_4{\cdot}7H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O/[Me_4N]BF_4$, respectively.[11,12] **2** is stable in methylene chloride solution for a few hours but a suspension in H_2O is readily *oxidized* to give the cationic species **6**. Since aqueous solutions of Fe^{2+} inevitably contain traces of Fe^{3+}, the direct preparation of a pure product **2** is difficult. It is worthwhile mentioning that our attempts to *reduce* **6** to the corresponding neutral compound **2** with reducing agents such as $SnCl_2$, $Na_2S_2O_4$, $NaBH_4$, or $LiAlH_4$ have failed.

The polarogram of a tetrahydrofuran solution of **6** containing 0.2 M $[Bu_4N]PF_6$ as supporting electrolyte shows however a cathodic wave at −0.46 V. The study of thin-layer linear potential sweep voltammetry on a carbon electrode clearly demonstrates that this reduction step is monoelectronic and fully reversible at all scan rates. Controlled-potential coulometry at −0.7 V on a mercury pool of a yellow THF solution of **6** leads, after passage of 1 faraday, to a red-violet solution of **2**. This solution shows a polarographic anodic wave at $E_{1/2}$ = −0.48 V. The height of this wave is equal to that of the reduction of **6**. These experiments show that this system is electrochemically reversible in the absence of oxidants. In fact when a small amount of oxygen is introduced into the electrochemical cell, the anodic wave of **2** disappears and the cathodic wave of **6** increases. When the experiment is carried out under an argon atmosphere, compound **2** can be obtained quantitatively after electrochemical reduction of **6** in tetrahydrofuran by evaporation of the solvent and extraction of the solid residue with carbon tetrachloride. The polarogram of a tetrahydrofuran solution of **2** synthesized directly (vide supra) shows at the dropping mercury electrode an anodic monoelectronic wave at $E_{1/2}$ = −0.48 V. This solution exhibits exactly the same properties as the one obtained by electrochemical reduction of **6**.

The electronic spectrum of the Fe(II) complex **2** exhibits two charge-transfer bands at 246 nm ($\epsilon = 5.8 \times 10^4$ L mol^{-1} cm^{-1}) and 339 nm ($\epsilon = 7 \times 10^3$ L mol^{-1} cm^{-1}) plus a very broad absorption at 510 nm (ϵ = 200 L mol^{-1} cm^{-1}). The spectrum resembles the one of the Co(III) complex **5** but is not temperature dependent. The magnetic moment of **2** measured at room temperature in the solid state is μ_{eff} = 5.4 μ_B, a value typical for a high-spin octahedral Fe(II) complex.

The optical and magnetic data are also in accord with the proposed structure for the corresponding Fe(III) complex **6**, BF_4 salt. The two charge-transfer absorptions characteristic for the cyclopentadienylcobalt phosphonate part of the molecule occur at λ = 242 nm ($\epsilon = 5.6 \times 10^4$ L mol^{-1} cm^{-1}) and 336 nm ($\epsilon = 8 \times 10^3$ L mol^{-1} cm^{-1}), and the room-temperature solid-state magnetic moment μ_{eff} = 5.8 μ_B is in the expected range for a high-spin Fe(III) complex.

$Na[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]$ (9). For comparison with the trinuclear cobalt and iron complexes mentioned above we have also looked at the electrochemistry of **9**. This half-sandwich compound can formally be regarded as the sodium salt of the ligand of M in the trinuclear sandwich complexes. It has recently been prepared[17] by the substitution reaction

$$[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Co\ (\mathbf{1}) \xrightarrow{NaCN/O_2} 2Na[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]\ (\mathbf{9}) + Na_3[Co(CN)_6]$$

A polarographic study of **9** in tetrahydrofuran at the DME shows an oxidation wave at $E_{1/2}$ = +0.54 V corresponding to a one-electron and a two-electron reduction wave at $E_{1/2}$ = −1.87 V. Electrochemical oxidation of **9** in the same solvent and 0.2 M $[Bu_4N]PF_6$ leaves a yellow solution after consumption of 1 faraday. Evaporation of the solvent, extraction of the product with diethyl ether, and recrystallization from ether/hexane give a pale yellow solid which was identified by its ^1H NMR and IR spectra[12,18] to be the trinuclear mercury complex **3**. Since the compound can be made directly from aqueous solutions of **8** or **9** and mercuric salts,[12] this electrochemical preparation is not an interesting synthetic route. The method might however be useful for the synthesis of trinuclear sandwich complexes with those central ions M which cannot be handled in aqueous solution.

Concluding Remarks

The redox properties of the trinuclear sandwich complexes **1**, **2**, **5**, and **6** demonstrate that the iron compound **2** is very easily oxidized to give the cation **6**. The corresponding cobalt complex **1** is very difficult to oxidize, but the product, the trinuclear sandwich **5**, is surprisingly inert despite its high oxidation potential. We think that steric shielding of the central cobalt ion by the phosphonate ligands can account for the kinetic stability of **5**. If this explanation proves correct, one should be able to use the tripod ligand **9** for electrochemical syntheses of complexes with transition-metal ions in unusual oxidation states.

Experimental Section

All potentials reported in this paper are measured vs. the SCE. For the polarographic studies, cyclic voltammetry, and thin-layer linear potential sweep voltammetry we have used a polarograph, Tacussel EPL 2 Tipol. Controlled-potential coulometry and preparative electrolysis were performed with a potentiostat, Tacussel ASA 100-1C. $[Bu_4N]PF_6$ and $[NH_4]PF_6$ used as supporting electrolytes are available from Fluka and Ozark-Mahoning Co. and were used without further purification. Tetrahydrofuran was purified by using the standard benzophenone/sodium procedure and distilled under argon. Methylene chloride was dried with calcium hydride and distilled under argon. The electronic spectra have been measured in CH_2Cl_2 (**5**, **6**) and CCl_4/pentane (**2**) by using a Perkin-Elmer Model 340 spectrophotometer.

Bis[cyclopentadienyltris(diethyl phosphito-*P*,*P*,*P″*)cobalt-*O*,*O′*,*O″*]cobalt(1+) Hexafluorophosphate (5, PF_6 Salt). A solution of 1.0 g (0.89 mmol) of **1** and 2 g of $[NH_4]PF_6$ in 120 mL of methylene chloride was electrolyzed at +1.3 V by using a carbon gauze as the working electrode and a platinum wire as the counterelectrode. After consumption of 1.1 faraday the green solution was washed several times with water to remove the supporting electrolyte. After drying of the mixture with calcium chloride, the solvent was evaporated.

Crystallization of the solid residue from acetone/water and finally from methylene chloride/carbon tetrachloride yields 1.0 g (0.78 mmol) of **5**, PF_6 salt, as dark green crystals (yield 89%, mp 160 °C dec).

Anal. Calcd for $C_{34}H_{70}Co_3F_6O_{18}P_7$: C, 32.04; H, 5.54; Co, 13.87; F, 8.94; P, 17.01. Found: C, 32.15; H, 5.54; Co, 13.28, F, 8.84; P, 16.87.

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Registry No. **1**, 53322-15-9; **2**, 58438-21-4; **3**, 66403-09-6; **5**, PF_6 salt, 70850-85-0; **6**, BF_4 salt, 66245-41-8; **9**, 70850-86-1.

References and Notes

(1) R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 471 (1966).
(2) R. E. Dessy, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 5112 (1966).
(3) J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6149 (1952).
(4) C. Furlani and E. O. Fischer, *Z. Elektrochem.*, **61**, 481 (1957).
(5) N. El Murr and E. Laviron, *Can. J. Chem.*, **54**, 3350, 3357 (1976).
(6) N. El Murr, A. Chaloyard, and E. Laviron, *Nouv. J. Chim.*, **2**, 15 (1977).
(7) N. El Murr, R. Dabard, and E. Laviron, *J. Organomet. Chem.*, **47**, C13 (1973).
(8) W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **96**, 2632 (1974).
(9) J. D. Holloway, W. L Bowden, and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **99**, 7089 (1977).
(10) J. Moraczewski and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **100**, 7429 (1978).
(11) W. Kläui and H. Werner, *Angew. Chem.*, **88**, 187 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 172 (1976).
(12) W. Kläui and K. Dehnicke, *Chem. Ber.*, **111**, 451 (1978).
(13) W. Kläui, H. Neukomm, H. Werner, and G. Huttner, *Chem. Ber.*, **110**, 2283 (1977).
(14) E. Dubler, L. Linowsky, and W. Kläui, *Transition Met. Chem.*, **4**, 191 (1979).
(15) W. Kläui, *Helv. Chim. Acta*, **60**, 1296 (1977).
(16) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(17) W. Kläui, *Z. Naturforsch., B*, in press.
(18) W. Kläui, *J. Organomet. Chem.*, in press.

Correspondence

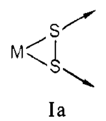
Disulfur Ligands in Transition-Metal Coordination and Cluster Compounds

Sir:

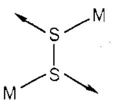
The investigation of complexes with diatomic ligands is of particular interest because of the information regarding basic aspects of homogeneous catalysis[1] (e.g., the type of transition metal–ligand interaction) which may be obtained and because of the bioinorganic relevance of O_2 and N_2 complexes. Despite the fact that several review papers about O_2 and N_2 complexes have been published (in accordance with the large number of original papers concerning this topic), there are only a few papers about S_2 complexes (for notation see ref 2). The nature of the metal–ligand bonding, the different types of metal–disulfur geometries that exist, and preparative methods have not been discussed. In this latter context, it should be pointed out that most of the S_2 complexes have been obtained accidentally.[5,6]

The preparative methods for S_2 complexes can be classified according to the nature of the reagent involved in the reaction. S_2 ligands may be introduced into a complex by (1) a positive S_2 group (agent: $S_2^{\delta+}Cl_2$),[7] (2) a neutral S_2 group (agent: S_8),[8] and (3) a negative S_2^{2-} group (agent: S_2^{2-} in polysulfide solution).[9,10] In the case of (1) and (2), the sulfur species are reduced[7,8] and the central atom is oxidized (assuming that the S_2 ligand in the complex has a negative charge; see below). Dioxygen complexes can only be prepared according to method 2 (with O_2 as reagent in an oxidative addition (oxad) reaction) or 3 (by using H_2O_2).

A further question to be considered is the mode of attachment of the disulfur group to metal ions. A large variety of structural types exists denoted as Ia–d, IIa–c, and III in Table I. The complexes can be categorized according to the number of sulfur atoms in the basic structures Ia (side-on S_2 coordination) and IIa (bridging S_2 ligand) coordinated to other metal centers (the arrows indicate the possibility of further coordination). It is to be noted that Ia and IIa are also important structural types in the case of O_2 complexes. Complexes are known where the S_2 group links two (Ib, IIa), three (Ic, IIb), or four metal atoms (Id, IIc), in the course of which the sulfur atoms are bound to one, two, or even three metal atoms (in Id). There is no other simple ligand which is as versatile as S_2 in its mode of coordination.



Ia



IIa

Whereas S_2 complexes with only end-on bonded S_2 ligands are not known, S_2 groups are side-on and end-on bonded to different metal atoms in the novel complex $[Mo_4(NO)_4(\mu_4\text{-}S)(\mu_3\text{-}S)_2(S\text{-}\mu\text{-}S)_4(S_2)]^{4-}$ which we recently isolated and which contains sulfur in five different valence states (see Figure 1). A novel compound containing *only S_2 ligands* could also be obtained (see Figure 2).

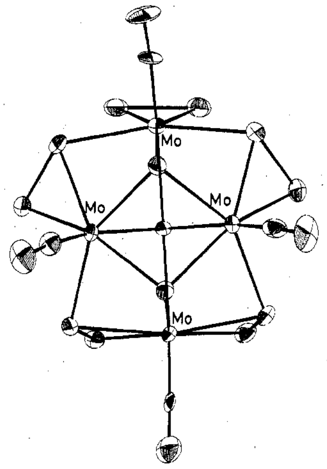


Figure 1. Structure of $[Mo_4(NO)_4S_3(S_2)_5]^{4-}$ (ORTEP plot) in $(NH_4)_4[Mo_4(NO)_4S_{13}]\cdot 2H_2O$ (see Table I).

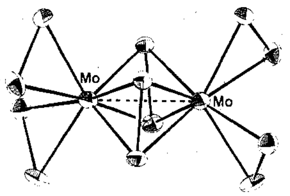


Figure 2. Structure of $[Mo_2(S_2)_6]^{2-}$ (ORTEP plot) in $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ (for details see ref 9 and 17).

Concerning the disulfur complexes, a bridging S_2 group external and roughly perpendicular to a metal–metal bond (type III) is of special importance due to its power of stabilizing metal clusters. This type of coordination occurs in $[Mo_2$-

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