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Redox properties of 17-electron thiolate complexes of cyclopentadienyl iron (III)

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Abstract—The redox electrochemistry of iron (III) thiolate complexes of the type [CpFe(dppe)-SR]PF_6, R = CH_3, C_3H_7, C_6H_5, p-C_6H_4Br and thiobenzothiazole has been examined by cyclic voltammetry, coulometry and spectroelectrochemistry methods. Four redox waves were observed in the range −1.5 to +1.5 V (S.C.E) in CH_2Cl_2. Around 0.0 V the metal centered reduction Fe (III)→Fe (II) process was observed, while that around +0.5 V the wave observed was attributed to a ligand centered oxidation. Strongly irreversible waves of oxidation near 1.3 V were assigned to the oxidation of RSSR while a reduction wave also strongly irreversible at very high negative potential was attributed to the reduction of the RSSR free ligand, $RSSR+2e \rightarrow 2RS^-$. The redox wave observed for the disulphides compounds are discussed in terms of a reductive elimination of RSSR. Chemical and electrochemical reduction of the complexes [CpFe(dppe)-SR]PF_6 was accomplished by the color changes blue → red-brown characteristic of the redox change 17e→18e.

Keywords: thiolate; iron complexes; redox properties; phosphine-iron complexes.

INTRODUCTION

The chemistry of transition metal thiolates is currently attracting considerable attention, largely as a result of the possible significance of such complexes in metalloenzyme systems [1–3].

Electron transfer processes on metal complexes containing sulfur ligands are very important for the understanding of redox processes occurring at the thiolate-coordinated metal ions in the active sites of several redox-active enzymes [1–3]. Specifically iron-sulfur thiolate bonds are involved in important metalloproteins [3].

Among the known metal-thiolate compounds, those of iron [3] are relatively more abundant than those of other metals [1, 2]. Although there are now several well-demonstrated methods for synthesizing iron (II)-thiolate compounds [2], few iron (III)-thiolate complexes have been reported [4–6]. We have recently reported a general method of obtaining cyclopentadienyl-iron (III) thiolate complexes in a simple step, starting from the organometallic precursor CpFe(dppe)I and the disulfide RSSR [4, 5].

$$2\mathrm{CpFe(dppe)I} + \mathrm{RSSR} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{NH_4PF_6}} 2[\mathrm{CpFe(dppe)SR}]\mathrm{PF_6} \qquad (1)$$

As previously suggested[6], the formation of the iron (III)-thiolate complexes from the iron (II) precursor involves an intramolecular electron-transfer reaction in the intermediate disulfide complex

$$2\mathrm{CpFe(dppe)I} + 2\mathrm{RSSR} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{NH_4PF_6}} 2[\mathrm{CpFe(dppe)RSSR}]\mathrm{PF_6} \qquad (2)$$

$$2\mathrm{CpFe^{II}(dppe)RSSR} \rightarrow 2\mathrm{CpFe^{III}(dppe)-SR^+} + \mathrm{RSSR} \qquad (3)$$

Fe (III)-thiolate complexes have also recently been obtained by oxidative-addition of thiols to CpFe $(dppe)^+$ -fragment.

$$\mathrm{CpFe(dppe)I} + \mathrm{HSR} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{NH_4PF_6}} [\mathrm{CpFe(dppe)-SR}]\mathrm{PF_6} + [\mathrm{H}] \qquad (4)$$

(In this reaction the unidentified product containing the hydrogen thiol is denoted [H] see ref.[6]). It was

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suggested [4, 6] that this reaction occurs through the intermediate [CpFe(dppe)HSR]PF_6 which after an intramolecular electron transfer leads to the Fe (III)-thiolate product. The oxidative-addition described above for RSSR and RSH has been reported for other organometallic compounds [7].

Because of much of the chemical transformations involved in biological processes involve an electron-transfer process through a bond Fe-S, the redox behaviour of metal-thiolate complexes is essential, for the understanding of the mechanism of such processes.

Although the redox behaviour of molybdenum thiolates and other metal-thiolates have been examined [8, 9], few electrochemical studies on iron (II) and iron (III)-thiolate compounds have been reported [10, 11]. In this paper we describe the electrochemical behaviour of a series of iron (III)-thiolate complexes [CpFe(dppe)SR]PF_6, where R = CH_3, 1; C_3H_7, 2; C_6H_5, 3, C_6H_4Br, 4; thiobenzothiazole, 5.

RESULTS AND DISCUSSION

The electrochemical behaviour of the series of thiolates [CpFe(dppe)-SR]PF_6 was studied by cyclic voltammetry in CH_2Cl_2 solution. Almost all the complexes undergo a reversible (irreversible for 1 and 5) reduction in the range 0.1 V to −0.4 V. (see Fig. 1 and Table 1). The electron transfer associated with this redox process can be assigned to the reduction of the Fe (III)-thiolate complex $\text{CpFe(dppe)-SR}^+ + e \rightarrow$ CpFe(dppe)-SR. Thus, the cyclic voltammogram of [CpFe(dppe)-SC_6H_5] exhibits a one electron oxidation wave at −0.25 V corresponding to the Fe (II)→Fe (III) oxidation process [10]. On the other hand, the

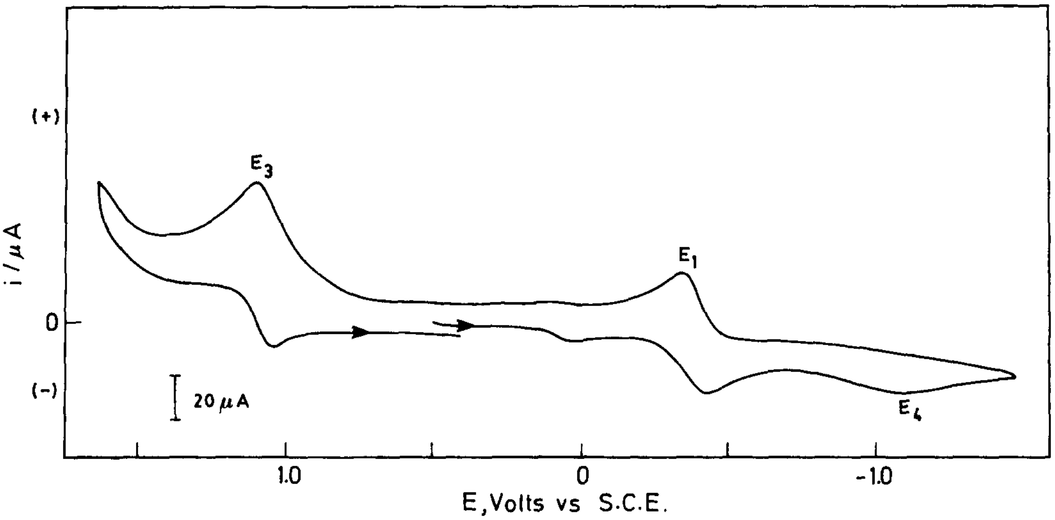


Fig. 1. Cyclic voltammogram for [CpFe(dppe)-S-C_3H_7]PF_6 in CH_2Cl_2 at 25°C and scan rate of 100 mv/s.

Table 1. Electrochemical data for [CpFe(dppe)-SR]PF_6 compounds

Compound	Peak potential, [a]V				
	E1 (ΔEp)(ipa/ipc)	E2 (ΔEp)(ipa/ipc)	E3 (ΔEp)(ipa/ipc)	E4 (ΔEp)(ipa/ipc)	Farad/mol[d]
[CpFe(dppe)-SCH_3]PF_6	−0.35(0.1)(i)[b]	54(0.04)(0,83)	1.3(i)(i)	< −2.0(i)(i)	—
[CpFe(dppe)-S-C_3H_7]PF_6	−0.37(0.1)(0.95)	[c]	1.1(i)(0.98)	−1.07(i)(i)	0.90
[CpFe(dppe)-S-C_6H_5]PF_6	−0.293(0.056)(0.82)	—	1.2(0.06)(0.86)	< −2.0(i)(i)	0.89
[CpFe(dppe)-S-C_6H_4-Br]PF_6	−0.22(.12)(0.90)	—	12(i)(i)	< −1.4(i)(i)	0.91
[CpFe(dppe)-S-benzotiazole]PF_6	−0.3(i)(i)	0.54(0.09)(0.81)	1.11(i)(i)	−1,1(i)(i)	—

[a] From cyclic voltammograms in CH_2Cl_2 solution at 100 m V/seg. Values referenced to S.C.E

[b] (i) Indicate a chemical or electrochemical irreversible process electrode.

[c] Wave not observed.

[d] Coulometry data for E1 process at the volt of the bulk electrolysis value indicated in column 1. Data for irreversible processes could be not, measured.

complex $CpFe(PMe_3)_2SC_6H_5$ undergoes an oxidation process at -0.20 V [11]. Furthermore, metal thiolates of the type Ln $M(SR)^{+z}$ with the metal in an accessible higher oxidation state Ln M $(SR)^{+(Z+1)}$ in general, exhibit an initial oxidation metal based with $E_{1/2}$ values near 0 V [9]. Its appears to be that the high polarisable and soft thiolate ligand [1] induces a high electron density on the metal atom, which provokes a low facile oxidation of the thiolate complexes. This can be also due to the electron rich nature of the fragment $CpFe(dppe)^+$ [10, 12].

As expected the controlled potential coulometry confirm that the reduction of the complexes [CpFe(dppe)-SR] PF_6 is a one electron process. Data are shown in Table 1. This was also corroborated by UV-visible spectroscopy. The initial blue solution of the thiolate iron (III) complex turned yellow-brown after total electrochemical reduction. The UV-visible changes for $[CpFe(dppe)\text{-}S\text{-}C_3H_7]PF_6$ are shown in Fig. 2. Similar UV-visible spectral changes are observed in the chemical reduction using Red-Al as reducing agent as is shown in Fig. 3.

The second one electron oxidation wave observed in the cyclic voltammogram of the complexes (which is absent in complexes 2–4), can be assigned to a ligand based oxidation (reaction Eq. (6)) according to previous electrochemistry studies on metal-thiolate compounds [8, 9]. Cyclic voltammogram for complex 5 is shown in Fig. 4.

$$2CpFe(dppe)-SR \xrightarrow{solv} 2CpFe(dppe)Solv^+ + RSSR + e \quad (5)$$

In agreement with this suggestion we have detected in the cyclic voltammograms of the complexes 1–5, the typical oxidation of RSSR [9, 13] (peak E_3) in the range 1.1–1.3 V as well as their reduction at very negative potentials (termed peak E_4). Furthermore we have observed similar oxidation and reduction waves in the cyclic voltammetry of the free RSSR ligands as is shown in Table 2.

All these results are consistent with the scheme shown in Fig. 5, for the redox behaviour of the complexes $[CpFe(dppe)\text{-}SR]PF_6$. The absence of the oxidation peak E_2 for the complexes 2–4 can be due to the high stability of the Fe (II) species CpFe(dppe)-SR, which preclude the oxidation of the thiolate ligand. In fact the ip_a/ip_c ratio parameter value near 1 for these complexes, indicates a high chemical reversibility. In complexes 2–4 however in spite of that the peak 2 is not obseved, the peak corresponding to the

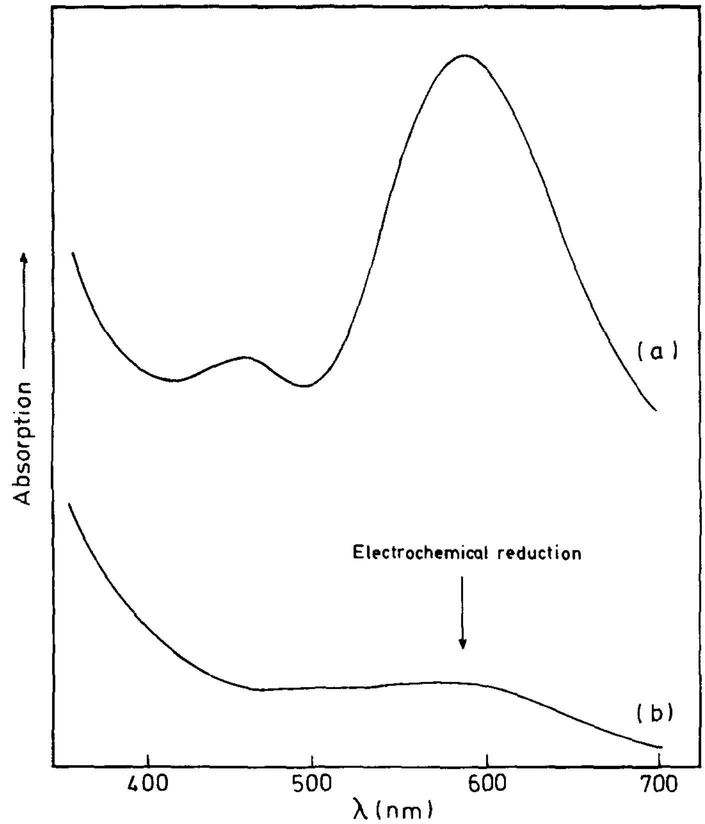


Fig. 2. UV-vis spectra of $[CpFe(dppe)\text{-}S\text{-}C_3H_7]PF_6$ in CH_2Cl_2 solution (a) before the reduction (b) after electrochemical reduction.

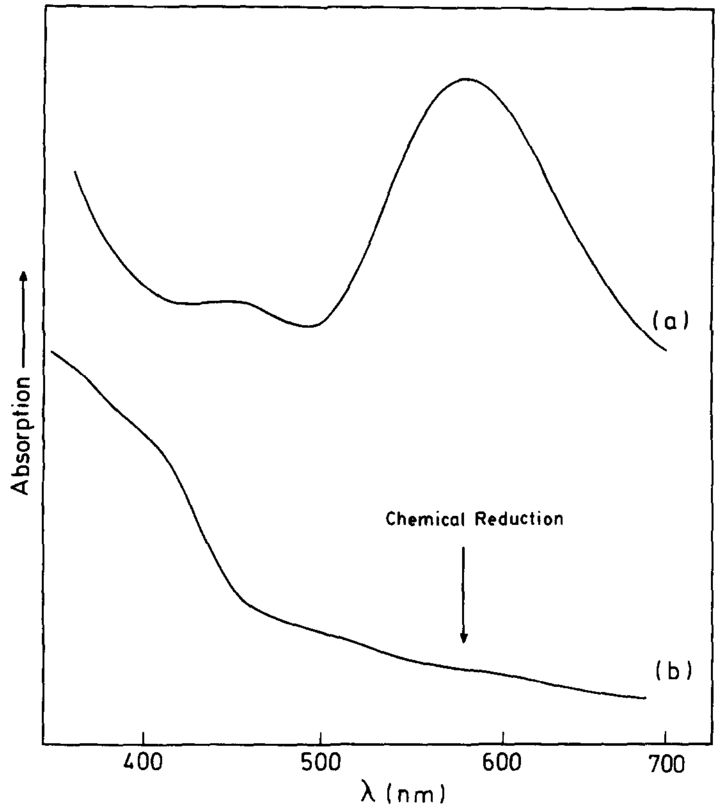


Fig. 3. UV-vis spectra of [CpFe(dppe)-S-C_3H_7]PF_6 in CH_2Cl_2 solution (a) before the reduction (b) after the chemical reduction with Red-Al.

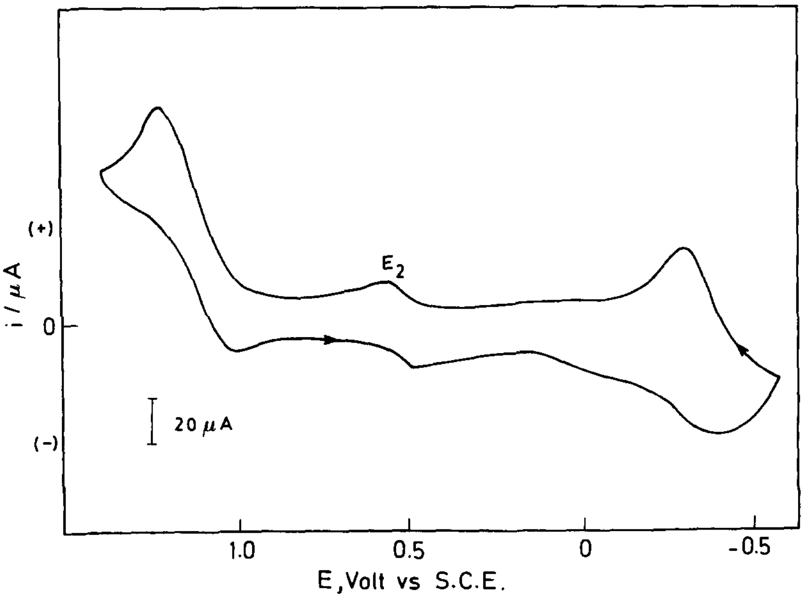
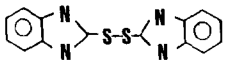
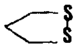


Fig. 4. Cyclic voltammogram for [CpFe(dppe) benzotiazole]PF_6 in CH_2Cl_2 solution at 25°C and scan rate of 100 mv/s.

Table 2. Cyclic Voltammetry Data for Disulfides RSSR[a]

Compound	Epa (V)	Epc (V)	Ref.
Me-S-S-Me	1.62	< -1.8	This work
C_3H_7-S-S-C_3H_7	> 1.8	-0.89	This work
C_6H_5-S-S-C_6H_5	1.4	~ 0	13a
$C_6H_5CH_2$-S-S CH_2-C_6H_5	—	-2.0	9a
CH_3-C_6H_4-S-S-C_6H_4-CH_3	1.3	-2.3	9a
	1.1	-1.05	This work
	$+1.17$	-1.77	

[a] Main peaks. For dithiobenzotiazole an oxidation peak was observed at 0.2 V. For C_3H_7-S-S-C_3H_7 a reduction peak at -0.5 V was also observed See ref [9]. and [13].

oxidation of the dithioether appears at ~ 0.5 V which suggest that the chemical equilibrium Eq. (6) could exist.

$$2\mathrm{CpFe(dppe)-SR}^+ \rightleftarrows 2\mathrm{CpFe(dppe)}^+ + \mathrm{RSSR} \quad (6)$$

Reductive eliminations of RSSR as the shown in eq. (6) have been previously proposed in the formation of thiolate-bridged dimers of group 6B metals [14, 15]. Thus the 16e specie CpFe(dppe)(solvent)$^+$ has been detected by UV-visible spectroscopy [16].

EXPERIMENTAL

All solution manipulations were carried out under purified argon or dinitrogen. Compounds [CpFe(dppe)-SR]PF_6 where R = CH_3, C_3H_7, C_6H_5 and p'C_6H_4Br were synthesized as described previously [1, 6]. The new complex CpFe(dppe)-S-benzo-thiazol was prepared as follow:**[CpFe(dppe)-S-benzothiazol]PF_6**, CpFe(dppe).I 0.15 g (0.23 mmol) and 2,2'-Dithiobis (benzothiazole) 0.076 g (0.23 mmol) in the presence of NH_4 PF_6 1 g (0.69 mmol) where stirred in CH_3 OH (30 ml) for 24 h. After this time, the solvent was removed under reduced pressure until dryness and the solid extracted with dichloromethane, filtered through celite and the solution concentrated to c.a. 10 ml. Upon addition of a 1:1 n-hexane-diethyl ether mixture the precipitate, a dark-blue solid, was washed twice with the same mixture and the solid residue dried under vacuo. Yield. 0.11 g, 57%. Anal.: Found C 53.5 H 3.8 Calcd. For C_{32} H_{33}N F_6 S_2 P Fe; C 53. 48 H 3.98 Ir (K Br). 1090 δ (C-H) bend in plane vibration of C_5H_5 group (see ref.[4]); 840 ν (PF_6); 700 δ (C-H) bending-out-plane vibration of group C_6H_5 of dppe (see refs.[4–6]).

Electrochemistry

The cyclic voltrammetry experiments were done with a PARC model 370 electrochemistry system in a specially designed three-electrode glass cell [17, 18]. The working electrode was a carbon glassy disk, the counter was a platinum wire, and the reference electrode an aqueous saturated calomel electrode (S.C.E.) connected to the working cell through a Luggin capillary placed ca. 1 mm from the working electrode. A 0.1 M [Bu_4N]PF_6 solution in CH_2Cl_2 was used as supporting electrolyte. Solutions were degassed with nitrogen and a nitrogen atmosphere was maintained

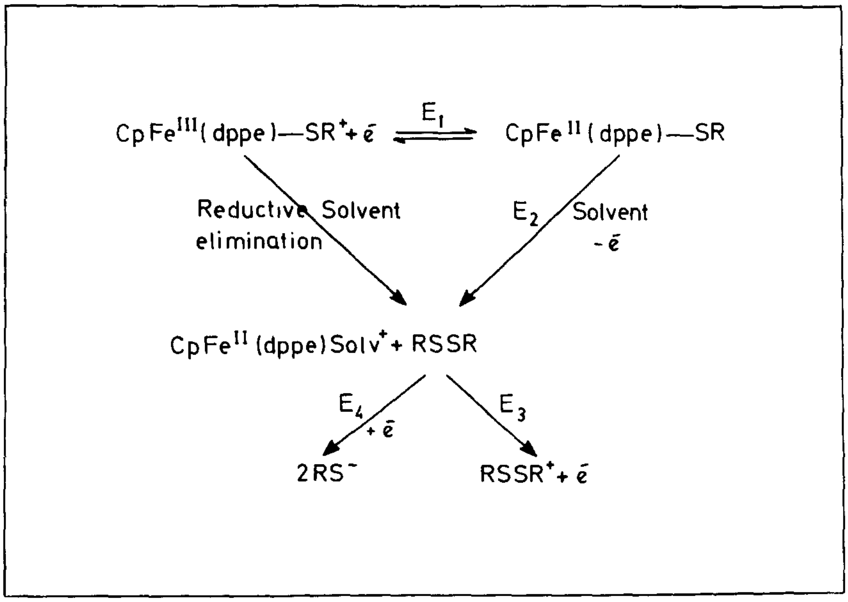


Fig. 5. Redox behavior of [CpFe(dppe)-SR]PF_6 complexes.

over the solution during the experiment. The peak potentials values reported were determined at the first cyclic voltammogram and referenced to the S.C.E.

Controlled potential electrolyses were carried out in the same supporting electrolyte solution using a three electrolysis cell (adapted from Figs 3.14 and 3.16 in ref.[17]) with a platinum gauze as cathode, a platinum wire counter electrode isolated from the working solution by a medium porosity glass frit. The saturated calomel electrode was introduced to the cell through a luggin capillary and placed near the cathode. The charge transfered in the electrolysis was determined with a PARC 179 digital coulometer.

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REFERENCES

1. Kuehn, Ch.T. and Isied, S., *Prog. Inorg Chem.*, 1990, **27**, 153.
2. Dance, I. G. *Polyhedron*, 1986, **5**, 1037; Blower, P. J. and Dilworth, J. R., *Coord. Chem. Rev.*, 1989, **76**, 121.
3. Beinert, H., Hohn, R. H. and Münck, E., *Science*, 1977, **277**, 653 and reference therein. Evans, D. J., Hughes, D. L. and Silver, J., *Inorg. Chem.*, 1977, **36**, 747. Butt, J. N., Armstrong, F. A., Breton, J., George, S. J., Thomson, A. J. and Hatchikion, E., *J. Am. Chem. Soc.*, 1991, **113**, 6663. Butt, J. N., Sucheta, A., Armstrong, F. A., Breton, J., Thomson, A. J. and Hatchikion, E. C., *J. Am. Chem. Soc.*, 1993, **115**, 1413. Dawson, J. H. and Sono, M., *Chem. Rev.*, 1987, **87**, 1255.
4. Díaz, C., Leal, C. and Yutronic, N., *J. Organomet. Chem.*, 1996, **516**, 59 and references cited therein.
5. Díaz, C., Leal, C. and Yutronic, N., *Bol. Soc. Chil. Quim.*, 1996, **41**, 99.
6. Díaz, C., *Polyhedron*, 1997, **16**, 999.
7. Ju, T. D., Capps, K. B., Lang, R. F. and Hoff, C.D., *Inorg. Chem.*, 1997, **36**, 614.
8. Katz, J. C., Vining, W., Coco, W., Rosen, R., Romao Dias, A. and García, M.H., *Organometallics*, 1983, **2**, 68.

9a. Bradbury, J. R., Masters, A. F., McDonell, A. C., Brunette, A. A., Bond, A. M. and Wedd, A. G., *J. Amer. Chem. Soc.*, 1981, **103**, 1959. Sawyer, D. T., Susan Srivatsa, G., Bodini, M. E., Schaefer, W. P. and Wing, R. M., *J. Am. Chem. Soc.*, 1986, **108**, 93. Barnard, K. R., Bruck, M., Huber, S., Grittini, C., Enemark, J. H., Gable, R. W. and Wedd, A. G., *Inorg. Chem.*, 1997, **36**, 637. .

10. Treichel, P. M., Molzahn, D. C., and Wagner, K. P., *J. Organomet. Chem.*, 1979, **179**, 191. Treichel, P. M. and Komar, D. A., *J. Organomet. Chem.*, 1981, **206**, 77.
11. Roth, E. K. and Jordanov, J., *Inorg. Chem.*, 1992, **31**, 240.
12. Legzdins, P., McNeil, W. S., Rettig, S. J. and Smith, K.M., *J. Am. Chem. Soc.*, 1997, **119**, 3513.

13a. Magno, F., Bontempelli, G. and Pilloni, G., *Electroanal. Chem. and Interf. Electrochem.*, 1971, **30**, 375.

13b. Wowie, J. K., Houts, J. and Sawyer, D. T., *J. Am. Chem. Soc.*, 1977, **99**, 6323.

14. Boorman, P. R., Chivers, T., Mahadev, K. N. and O'Dell, B. D., *Inorg. Chin. Acta*, 1976, **19**, L35.
15. Boorman, P. M., Patel, V. D., Kerr, K. A., Codding, P. W. and Van Rocy, P., *Inorg. Chem.*, 1980, **19**, 3508.
16. Díaz, C. and Yutronic, N., *Polyhedron*, 1996, **15**, 1001.
17. Sawyer, D. T. and Roberts, J. L. Experimental Electrochemistry for Chemists, John Wiley; New York, 1974, p. 147 and 151.
18. González, G., Santa Ana, M. A. and Chadwick, I. *J. Chem. Soc. Perkin Trans. II*, 1983, 1803.