Journal of Organometallic Chemistry, 320 (1987) 317–324
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ELECTROCHEMICAL REDUCTION OF THE DITHIOPHOSPHATE COMPLEXES $Cp^{\star}Fe(CO)_2[\eta^1\text{-}SP(S)(OR)_2]$, ($Cp^{\star} = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$)

M. MORÁN, I. CUADRADO,

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma, Canto Blanco, 28049-Madrid (Spain)

and J. LOSADA

Departamento de Química Inorgánica y Analítica, E.T.S. Ingenieros Industriales, Universidad Politécnica de Madrid, 28006-Madrid (Spain)

(Received April 10th, 1986; in revised form August 28th, 1986)

Summary

The reductive electrochemistry of compounds of the type $Cp^{\star}Fe(CO)_2L$ ($Cp^{\star} = \eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$; $L = SP(S)(OEt)_2$, $SP(S)(O^iPr)_2$) has been examined by polarography, cyclic voltammetry and coulometry. The first one-electron reduction step leads to a bond rupture process with formation of a mercury compound, $[Cp^{\star}Fe(CO)_2]_2Hg$, at a mercury electrode and the corresponding dimer species at a platinum electrode. The second reduction step corresponds to the reduction of the dimer $[Cp^{\star}Fe(CO)_2]_2$, except in the polarographic reduction of pentamethylcyclopentadienyl compounds.

Introduction

The electrochemical reduction of several compounds of the type $(\eta\text{-}C_5H_5)Fe(CO)_2X$ ($X = Cl$, Br, I, $SnCl_3$, $SiPh_3$, $GePh_3$, $SnPh_3$) has been described [1–5]. The results show that the compounds behave differently in respect of the nature of the products of the first reduction step. The mechanisms were found to depend on the structure and stability of the anion X^-.

In this paper we describe and discuss the electrochemical reduction of four new compounds of the type $Cp^{\star}Fe(CO)_2L$ ($Cp^{\star} = \eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, $L = SP(S)(OEt)_2$, $SP(S)(O^iPr)_2$).

Experimental

The electrochemical measurements were carried out under prepurified dinitrogen. Tetrahydrofuran (THF) was purified by the ketyl method. Tetra-n-butylammonium hexafluorophosphate (Fluka) was recrystallised from ethanol and dried in vacuo; it was deoxygenated and dehydrated by melting under vacuum before use. The complexes η-Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$) (R = Et, ^{i}Pr) were made by the published method [6].

The polarography and cyclic voltammetry were carried out respectively with an Amel Model 461 and an Amel Model 4881 A instrument in conjunction with a Hewlett–Packard 7040 A X–Y recorder. The coulometric experiments were carried out with a Beckman Electroscan-30 instrument. Values of potentials are relative to the Ag/AgCl electrode, which was separated from the cell by a KCl bridge. Cyclic voltammetry experiments were made at a platinum working electrode. In the coulometry, the working electrode was a 9 cm^2 platinum plate or mercury pool. The EPR spectra were recorded at room temperature with a Varian-E12, at a microwave frequency of 9 GHz (X-band).

The IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer. The solution spectra (THF) were examined in a liquid cell with KBr windows. In all cases the solvent absorptions were subtracted by use of the software of the spectrophotometer. The UV-Vis spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer.

Results and discussion

The polarographic reduction of the compounds η-Cp*Fe(CO)$_2$[η^1-SP(S)(OR)$_2$] (R = Et, ^{i}Pr) takes place in two waves (Fig. 1) (Table 1). The first wave, is diffusion controlled; the second one, also diffusion controlled, is under normal experimental conditions about 1% smaller than the first reduction step. Both of them correspond to one-electron reduction, as determined by comparison with data for structurally analogous pilot compounds. Complete bulk electrochemical reduction carried out at potentials on the plateau of this wave requires 1 and 2 Faradays per mol, respectively. Both electrode processes are irreversible, as is evident from the shape of the waves. The slopes of the plots of log $i/i_1 - i$ vs. E are 80 and 68 mV, respectively.

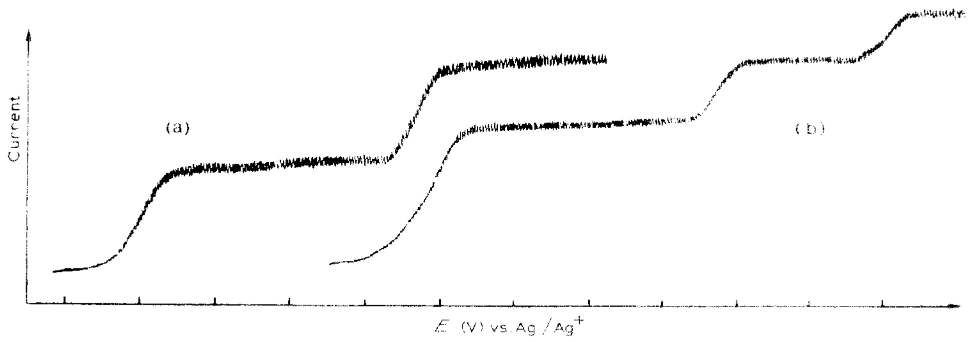


Fig. 1. DC polarograms for η-C$_5$H$_5$Fe(CO)$_2$[η^1-SP(S)(OEt)$_2$] (a) and η-C$_5$Me$_5$Fe(CO)$_2$[η^1-SP(S)(O^{i}Pr)$_2$] (b) at DME in THF containing 0.1 M Bu$_4$NPF$_6$

TABLE 1

HALF-WAVE [a] POTENTIALS OF η-$Cp^{\star}Fe(CO)_2L$ COMPOUNDS (THF, 0.1 M Bu_4NPF_6)

	$_1E_{1/2}$	$_2E_{1/2}$	$_3E_{1/2}$
η-$CpFe(CO)_2[\eta^1$-$SP(S)(OEt)_2]$	−0.81	−1.55	
η-$CpFe(CO)_2[\eta^1$-$SP(S)(O^iPr)_2]$	−0.84	−1.55	
η-$C_5Me_5Fe(CO)_2[\eta^1$-$SP(S)(OEt)_2]$	−1.16	−1.95	−2.39
η-$C_5Me_5Fe(CO)_2[\eta^1$-$SP(S)(O^iPr)_2]$	−1.18	−1.95	−2.39
$[\eta$-$CpFe(CO)_2]_2$		−1.52	
$[\eta$-$C_5Me_5Fe(CO)_2]_2$		−1.91	

[a] V vs. Ag/AgCl

The polarographic reduction of η-$C_5Me_5Fe(CO)_2[\eta^1$-$SP(S)(OR)_2]$ (R = Et, ^{i}Pr) occurs in three waves (Fig. 1) (Table 1). The first limiting current is diffusion controlled. One electron is involved in the process corresponding to this polarographic step, as shown by comparison with model compounds and exhaustive electrolysis carried out at potentials on the plateau of the wave. The overall limiting current of the second and third waves is also diffusion controlled, and about 10% smaller than the first one. However the dependence of the limiting current of second step upon the parameters of the dropping mercury electrode indicates a combination of diffusion and kinetic control of the process. The three electrode processes are irreversible; the slopes of the plots of log $i/i_l - i$ vs. E are 98, 75 and 87 mV, respectively.

The cyclic voltammograms of all compounds at a Pt electrode show two cathodic peaks (A, B) and one anodic peak (B′) (Fig. 2). At sweep rates < 500 mV s^{-1} peak B′ is completely absent in the first run and another new anodic peak B'_1 can be observed at more negative potentials. However at these slow sweep rates multicyclic voltammograms show that on going through repeated cycles peak B'_1 disappears and the appearance of B′ and decrease of A are observed (Fig. 3). If the scan is reversed after peak A, no anodic peak for sweep rates from 10 mV s^{-1} to 1 V s^{-1} is observed. The electrochemical irreversibility of the processes corresponding to peaks A and B is confirmed by the magnitude of the slopes in the plots of E_p vs. log v (v, scan rate) [7], which are significantly larger than those expected for reversible processes.

Complete electrolysis of all compounds, carried out at potentials 100 mV more negative than E_p of the peaks A and B, requires 1 and 2 Faraday/mol respectively.

When the complexes were electrochemically reduced in a cell in the cavity of an EPR spectrometer at the potentials indicated above, after E_p of A and B, no species giving EPR signals were present.

The overall polarographic behaviour of η-Cp $Fe(CO)_2[SP(S)(OR)_2]$ (R = Et, ^{i}Pr) can be described as shown in Scheme 1. This mechanism is similar to that suggested by Vlček et al. [4] for compounds of the type η-$CpFe(CO)_2X$ (X = Cl, Br, I, $SnCl_3$, $GeCl_3$).

The exhaustive electrolysis at a mercury pool cathode shows that for complete reduction at potentials in the region of the limiting current of the first reduction wave, one electron per particle of depolarizer is consumed. The UV-visible and IR spectrophotometric examination of the reduced solution indicates that the product formed is $[\eta$-$CpFe(CO)_2]_2Hg$ (ν(CO) 1980, 1958, 1921 cm^{-1}, λ 388 nm) [10,12].

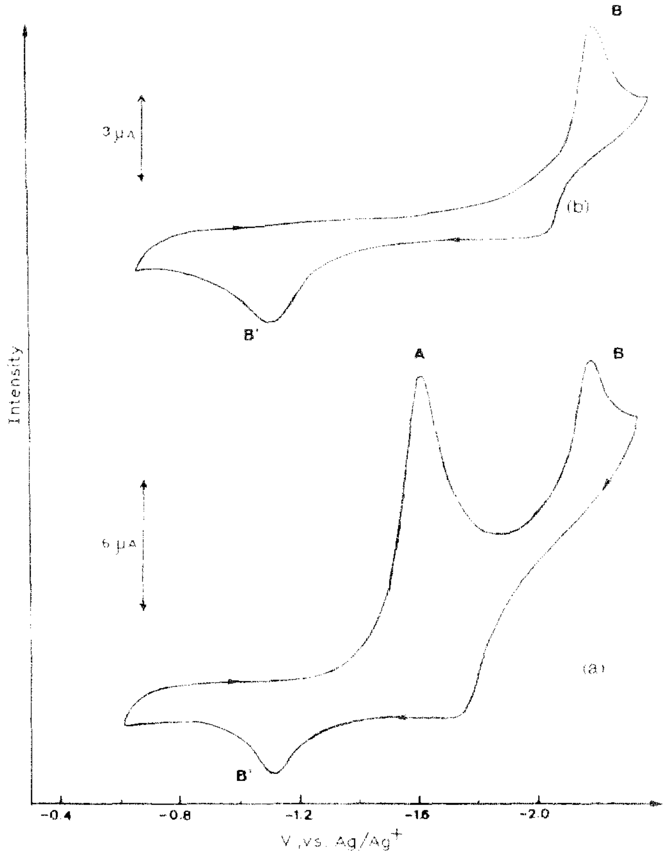
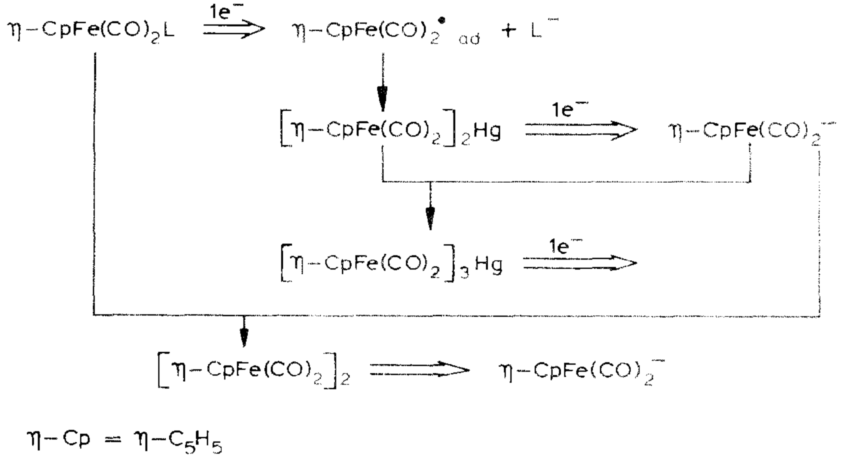


Fig. 2. Cyclic voltammograms for η-$C_5Me_5Fe(CO)_2[\eta^1$-$SP(S)(O^iPr)_2]$ (a), and $[(\eta$-$C_5Me_5)Fe(CO)_2]_2$ (b), in THF containing 0.1 *M* Bu_4NPF_6 at a Pt electrode; scan rate 0.5 V s^{-1}.



SCHEME 1

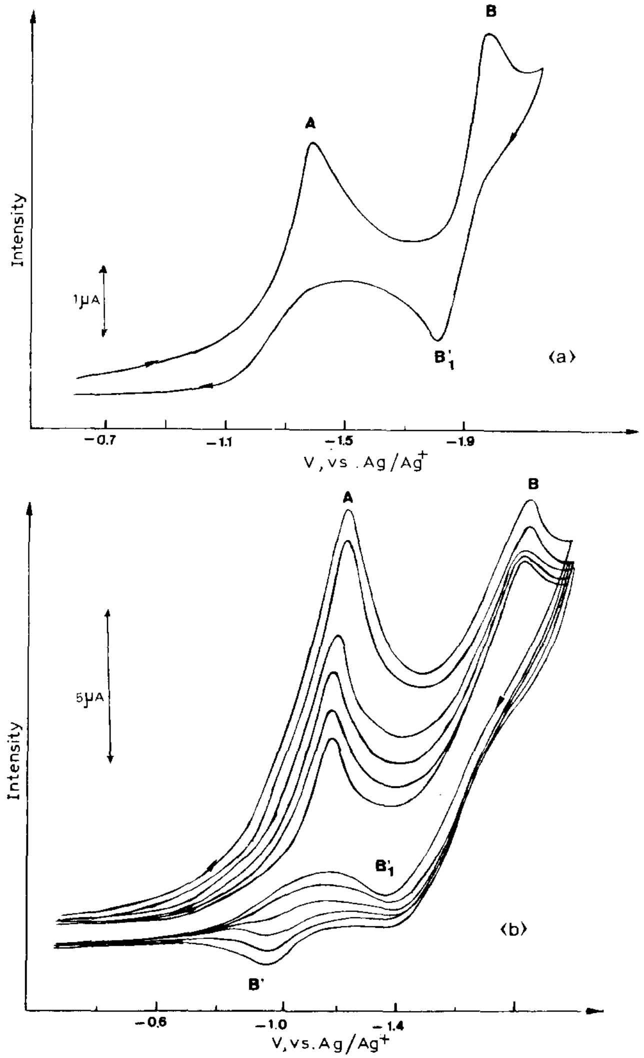


Fig. 3. (a) Cyclic voltammogram for η-$C_5Me_5Fe(CO)_2[\eta^1$-$SP(S)(OEt)_2]$ at Pt electrode in THF containing 0.1 *M* Bu_4NPF_6; scan rate 0.04 V s^{-1}. (b) Multicyclic voltammogram for η-$C_5H_5Fe(CO)_2[\eta^1$-$SP(S)(OEt)_2]$ in THF containing 0.1 *M* Bu_4NPF_6, at a Pt electrode; scan rate 0.1 V s^{-1}.

This compound is polarographically reduced at about −1.2 V to form the anion, $[\eta$-$CpFe(CO)_2]^-$, which upon diffusing into the solution reacts according to eq. 1

$$CpFe(CO)_2L + [CpFe(CO)_2]^- \rightarrow [CpFe(CO)_2]_2 + L \qquad (1)$$

consuming the depolarizer before it reaches the electrode. This is confirmed by a polarographic examination of partly reduced solutions [10].

The second reduction step shows characteristics in respect of the form of the log $i/i_1 - i$ vs E plot and $E_{1/2}$, very close to those for reduction of the dimer. Thus, it is possible to assign the second wave to the reduction of the dimer formed by the chemical reaction 1.

The polarographic behaviour of $\eta\text{-}C_5Me_5Fe(CO)_2[\eta^1\text{-}SP(S)(OR)_2]$ (R = Et, ${}^iPr$) differs from that described above in the nature of the second step, which shows two different waves. This pattern is similar to that exhibited by the mercury compounds $[\eta\text{-}CpFe(CO)_2]_2Hg$ [10]. Attempts to detect the formation of the dimer, $[\eta\text{-}C_5Me_5Fe(CO)_2]_2$, in large scale electrolysis, monitored polarographically and spectrophotometrically, were unsuccessful, even when they were carried out at potentials near to the base of the second wave ($E_{1/2}$ −1.95 V). This wave shows very different properties from those for reduction of the dimer $[\eta\text{-}C_5Me_5Fe(CO)_2]_2$, for which the slope of the log $i/i_1 - i$ vs E plot is 52.5 mV and $E_{1/2}$ is 1.91 V. On the other hand exhaustive electrochemical reduction carried out at potentials on the plateau of the second wave requires for the overall process 1.54 Faradays per mol initially depolarized. However, when the electrolysis takes place in potential regions corresponding to third wave two electrons per particle of depolarizer are consumed, and $[\eta\text{-}C_5Me_5Fe(CO)_2]^-$ (ν(CO) 1869, 1800 cm^{-1}) is identified as the product of the electrode reaction.

From the above described results it follows that in the case of the compounds $\eta\text{-}C_5Me_5Fe(CO)_2[\eta^1\text{-}SP(S)(OR)_2]$ (R = Et, ${}^iPr$), reaction 1 does not take place in the second step of the polarographic reduction. Thus the wave at −1.95 V corresponds to the direct reduction of $[\eta\text{-}C_5Me_5Fe(CO)_2]_2Hg$ to generate the corresponding anion, which deactivates further portions of the depolarizer as follows:

$$[\eta\text{-}C_5Me_5Fe(CO)_2]_2Hg + x[\eta\text{-}C_5Me_5Fe(CO)_2]^- \rightarrow [\eta\text{-}C_5Me_5Fe(CO)_2]_{2+x}Hg^{x-} \quad (2)$$

This reaction prevents the reduction wave of $[\eta\text{-}C_5Me_5Fe(CO)_2]_2Hg$ reaching the overall diffusion controlled limit.

The direct microscopic observation of mercuric drop surface during electrolysis shows the formation of a red colour in the vicinity of the drop surface, which is consistent with the formation of the mercury-containing anion.

This different behaviour of pentamethylcyclopentadienyl compounds may be related to the difference between the peralkylcyclopentadienylmetal complexes compared with the corresponding unsubstituted cyclopentadienyl compound in respect of reactivity in carbonyl substitution reactions [8] and in catalytic activity [9].

The first peak A of the cyclic voltammograms can be ascribed to the formation of the corresponding dimer:

$$Cp^\star Fe(CO)_2L \xrightarrow{+e} Cp^\star Fe(CO)_2^{\cdot} + L^-$$

$$2\ Cp^\star Fe(CO)_2^{\cdot} \rightarrow [Cp^\star Fe(CO)_2]_2$$

$$(Cp^\star = \eta\text{-}C_5H_5 \text{ or } \eta\text{-}C_5Me_5)$$

This is in accord with the one-electron reduction obtained in the exhaustive electrolysis on a Pt electrode at potentials 100 mV more negative than E_{PA} and with the polarographic and spectrophotometric examination of the resulting solution ($[\eta\text{-}C_5H_5Fe(CO)_2]_2$, ν(CO) 1992, 1950, 1784 cm^{-1}; $[\eta\text{-}C_5Me_5Fe(CO)_2]_2$, ν(CO) 1921, 1758 cm^{-1}). Furthermore the potential peaks of B and B′ are identical with the cathodic and anodic peaks of the corresponding dimers (Fig. 2) (Table 2).

TABLE 2

CYCLIC VOLTAMMETRY OF η-Cp*Fe(CO)$_2$L COMPOUNDS AT A SWEEP RATE OF 0.1 V s^{-1} (THF, 0.1 *M* Bu$_4$NPF$_6$)

	E_p(A)	E_p(B)	E_p(B′)	E_p(B′$_1$)
η-CpFe(CO)$_2$[η^1-SP(S)(OEt)$_2$]	−1.175	−1.76	−0.94	−1.38
η-CpFe(CO)$_2$[η^1-SP(S)(O^{i}Pr)$_2$]	−1.28	−1.75	−0.94	−1.40
[η-CpFe(CO)$_2$]$_2$		−1.76	−0.94	
η-C$_5$Me$_5$Fe(CO)$_2$[η^1-SP(S)(OEt)$_2$]	−1.475	−2.12	−1.13	−1.80
η-C$_5$Me$_5$Fe(CO)$_2$[η^1-SP(S)(O^{I}Pr)$_2$]	−1.50	−2.11	−1.14	−1.79
[η-C$_5$Me$_5$Fe(CO)$_2$]$_2$		−2.13	−1.13	

It has been reported [11] than in the steady state cyclic voltammogram of [η-C$_5$H$_5$Fe(CO)$_2$]$_2$ in acetonitrile, cathodic and anodic peaks are observed. The process corresponds to the reduction of iron dimer at cathodic peak (B) and the oxidation of a reaction product, presumably [η-C$_5$H$_5$Fe(CO)$_2$]$^-$, (B′). Scheme 2 was proposed to account for the results.

$$[\mathrm{CpFe(CO)_2}]_2 + e^- \rightleftharpoons [\mathrm{CpFe(CO)_2}]_2^{\dot{-}}$$

$$[\mathrm{CpFe(CO)_2}]_2^{\dot{-}} \xrightarrow{K} \mathrm{CpFe(CO)_2}^{\cdot} + \mathrm{CpFe(CO)_2}^{-}$$

$$\mathrm{CpFe(CO)_2}^{\cdot} + [\mathrm{CpFe(CO)_2}]^{\dot{-}} \xrightarrow{\text{fast}} \mathrm{CpFe(CO)_2}^{-} + [\mathrm{CpFe(CO)_2}]_2$$

(Cp = η-C$_5$H$_5$)

SCHEME 2

Upon going to either lower temperatures or higher sweep rates the oxidation of the anion radical regenerating [CpFe(CO)$_2$]$_2$ could be observed on the reverse scan.

In our case this peak (B′$_1$) also appears at low sweep rates, as a consequence of a reaction which involves the initial depolarizer, presumably:

$$\mathrm{Cp^\star Fe(CO)_2}^{\cdot} + \mathrm{Cp^\star Fe(CO)_2L} \rightarrow [\mathrm{Cp^\star Fe(CO)_2}]^{\dot{-}} + \mathrm{L}^-$$

(Cp* = η-C$_5$H$_5$ or η-C$_5$Me$_5$; L = SP(S)(OR)$_2$, R = Et, ^{i}Pr)

From this observation it follows that in all cases the first reduction step of Cp*Fe(CO)$_2$L compounds results in the rupture of the Fe–L bond and formation of the radical and L anion. The radical, Cp*Fe(CO)$_2^{\cdot}$ is strongly attached to the electrode surface and it gives rise to the corresponding dimer or mercury compound. Therefore, the reduction is a concerted electron transfer and bond rupture process, a type EC electrode reaction inherently irreversible electrochemically. The increase of electron density by one unit in the redox orbital, the σ-antibonding orbital of the Fe–L bond, cannot be compensated by any electron drift to the space outside the bond and gives rise to instability of the Fe–L bond.

Analogous arguments were used by Vlček et al. [4] in the interpretation of the behaviour of the CpFe(CO)$_2$X (X = Cl, Br, I, GeCl$_3$, SnCl$_3$) compounds. However those authors observed different behaviour for the compounds CpFe(CO)$_2$MPh$_3$ (M = Si, Ge, Sn), which give rise to the stable anion radicals CpFe(CO)$_2$MPh$_2^{\dot{-}}$ [5]. The existence of these radicals is accounted for in terms of the possibility of interaction of the unpaired electron with the π-system of the phenyl groups.

Finally, the more negative reduction potential observed for the η-$C_5Me_5Fe(CO)_2L$ compounds are due to the greater electron donor ability of pentamethylcyclopentadienyl ligands, which leads to a higher electron density around the metal atom.

References

1 R.E. Dessy and P.M. Weissman, J. Am. Chem. Soc., 88 (1966) 5124.
2 R.E. Dessy and P.M. Weissman, J. Am. Chem. Soc., 88 (1966) 5129.
3 S.P. Gubin, Pure Appl. Chem., 23 (1970) 463.
4 D. Miholova and A.A. Vlček, Inorg. Chim. Acta, 43 (1980) 43.
5 D. Miholova and A.A. Vlček, Inorg. Chim. Acta, 73 (1983) 249.
6 M. Morán and I. Cuadrado, J. Organomet. Chem., 295 (1985) 353.
7 R.J. Klinger and J.K. Kochi, J. Am. Chem. Soc., 102 (1980) 4790.
8 K. Tabatabaian and C. White, Inorg. Chem., 20 (1981) 2020.
9 A. Fusi, E. Cesarotti and R. Ugo, J. Mol. Catal., 10 (1981) 213.
10 D. Miholova and A.A. Vlček, Inorg. Chim. Acta, 41 (1980) 119.
11 S.G. Davies, S.J. Simpson and V.D. Parker, J. Chem. Soc. Chem. Commun., (1984) 352.
12 J.M. Burlitch and A. Ferrari, Inorg. Chem., 9 (1970) 563.