

## Redox behaviour of ferrocene derivatives VIII <sup>☆</sup>. 1,1'-Bis(diphenylphosphino)ferrocenes

Piero Zanello <sup>a,\*</sup>, Giuliana Opromolla <sup>a</sup>, Gianluca Giorgi <sup>b</sup>, Giuseppe Sasso <sup>b</sup>, Antonio Togni <sup>c</sup>

<sup>a</sup> Dipartimento di Chimica dell'Università di Siena, Pian dei Mantellini 44, 53100 Siena, Italy

<sup>b</sup> Centro Interdipartimentale di Analisi e Determinazioni Strutturali dell'Università di Siena, Via P.A. Mattioli 10, 53100 Siena, Italy

<sup>c</sup> Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, Eidgenössische Technische Hochschule Zentrum, CH-8092 Zürich, Switzerland

Received 10 February 1995

### Abstract

A study has been made of the possibility of increasing the stability of the 1,1'-bis(diphenylphosphino)ferrocenium monocation by introduction of appropriate substituents into the cyclopentadienyl ligands. The electrochemical behaviour of a series of 1,1'-bis(diphenylphosphino)ferrocenes bearing substituents with a range of electronic properties has been examined. The results reveal that, the higher the electron-donating ability of the substituents, the longer is the lifetime of the corresponding 1,1'-bis(diphenylphosphino)ferrocenium monocation. However, no stable ferrocenium cation has been obtained; mass spectrometry shows that mixtures of mono- and di-bis(diphenylphosphino)oxides are ultimately formed as products resulting from decomposition of the initially electrogenerated 1,1'-bis(diphenylphosphino)ferrocenium species.

**Keywords:** Iron; Ferrocenes; Electrochemistry; Mass spectrometry

### 1. Introduction

The recently described ability of 1,1'-bis(diphenylphosphino)ferrocene to coordinate to metal centres increases the interest in this redox-active ligand [2]. Its crystal structure [3] and its electrochemical behaviour [4–8] are known. In non-aqueous solutions it undergoes a one-electron oxidation complicated by fast chemical reactions. It has been postulated that the initially electrogenerated bis(phosphine)ferrocenium species is rapidly converted into the bis(phosphinium)ferrocene monocation, which in turn dimerizes to the corresponding dication radical; this dication finally reacts with traces of water to afford bis(diphenylphosphino)ferrocene-protonated and/or bis(diphenylphosphino)ferrocene-oxygenated species [8]. This complicated oxidation path is in sharp contrast with the redox behaviour of the monosubstituted (diphenylphosphino)ferrocene, which undergoes reversible one-electron oxidation [7,9].

In continuation of our interest in the characterization of ferrocenium species [1], we decided to find out whether 1,1'-bis(diphenylphosphino)ferrocenium cations could be stabilized by the introduction of suitable substituents into the cyclopentadienyl rings of 1,1'-bis(diphenylphosphino)ferrocene (Scheme 1).

In view of the well-established applicability of mass spectrometry ionization techniques [10–14] in the study of ferrocene species, we employed the desorption electron ionization (DEI) technique to identify the oxidation products resulting from exhaustive anodic electrolysis processes.

### 2. Results and discussion

#### 2.1. Electrochemistry

Fig. 1 compares the cyclic voltammetric response of 1,1'-bis(diphenylphosphino)ferrocene (1) in dichloromethane solution with those of the substituted complexes 2–4.

<sup>☆</sup> For Part VII, see Ref. [1].

\* Corresponding author.

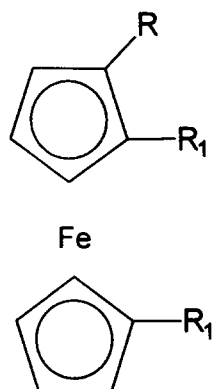
Controlled potential coulometry confirmed that in all cases the anodic step involves the consumption of one-electron per molecule. It can be readily seen that, at a fixed scan rate, the cathodic-to-anodic peak current ratio varies somewhat for the four species; for instance, at the value of  $1.00 \text{ V s}^{-1}$  illustrated in Fig. 1, the cathodic-to-anodic peak-current ratios are 0.7, 0.8, 0.3 and 0.0 for **1**, **2**, **3** and **4** respectively. This suggests that, as in the case for the redox change  $1-[1]^+$  [7], for the substituted species **2–4** the oxidation process is followed by chemical complications [15]. It is evident, however, that  $[2]^+$  is kinetically more stable and  $[3]^+$  more labile than  $[1]^+$ . Quite unexpected was the complete instability of  $[4]^+$ ; we were unable to detect the backward response directly associated with the oxidation of **4** even at a scan rate of  $51.2 \text{ V s}^{-1}$ . This observation is surprising in that vinylferrocene (**8**) undergoes a one-electron oxidation, which is chemically reversible on the cyclic voltammetric time scale [16]. (Macroelectrolysis experiments at room temperature show that about 30% of the green monocation  $[8]^+$  is decomposed.)

Evaluation of the kinetic stability of  $[5]^+$  and  $[6]^+$  was prevented by the presence of an irreversible pre-wave close to the main oxidation potential for **5** and **6**. However,  $[7]^+$  also seems to be slightly more stable than  $[1]^+$  in that, at the reference scan rate of  $1.00 \text{ V s}^{-1}$ , the  $i_{pc}/i_{pa}$  ratio is 0.8. As in the case of vinylferrocene, the precursor **9** exhibits an uncomplicated one-electron oxidation in cyclic voltammetry even if, after

macroelectrolysis experiments at room temperature, about 40% of the green monocation  $[9]^+$  was found to be decomposed. This further confirms the unfavourable effect on the stabilization of ferrocenium species exerted by the concomitant presence of two diphenylphosphino groups.

Table 1 summarizes the redox potentials for the one-electron oxidation of the 1,1'-bis(diphenylphosphino)ferrocene species studied here.

All the complexes oxidize at potentials only slightly different from one another, but significantly higher than that for unsubstituted ferrocene or monosubstituted (diphenylphosphino)ferrocene. This suggests that thermodynamic access to the oxidized species is essentially governed by the electron-withdrawing effect of the two diphenylphosphino substituents. Nevertheless, as indicated by the computed lifetimes of the primarily electro-generated monocations [15], the peripheral substituents may play some role in the kinetic stabilization of the corresponding ferrocenium species. The observed result is that, the higher the electron-donating ability of the substituents, the longer is the lifetime of the corresponding bis(diphenylphosphino)ferrocenium complexes. This seems to support the view that in bis(diphenylphosphino)ferrocene the highest occupied molecular orbital (HOMO) is no longer the non-bonding iron-based  $a'_1$  orbital of ferrocene but is transformed by the strong contribution from the two 1,1'-PPh<sub>2</sub> groups into an antibonding phosphino-based orbital. In this light, the presence of the additional unsaturated vinyl group in **4**



- |  |  |
|--|--|
| 1. R = H R <sub>1</sub> = PPh <sub>2</sub>   | 6. R = CH(CH <sub>3</sub> )N(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> R <sub>1</sub> = PPh <sub>2</sub> |
| 2. R = CH(CH <sub>3</sub> )OH R <sub>1</sub> = PPh <sub>2</sub>  | 7. R = CH(CH <sub>3</sub> )N(CH <sub>3</sub> ) <sub>2</sub> R <sub>1</sub> = PPh <sub>2</sub>  |
| 3. R = CH(CH <sub>3</sub> )SH R <sub>1</sub> = PPh <sub>2</sub>  | 8. R = CH=CH <sub>2</sub> R <sub>1</sub> = H   |
| 4. R = CH=CH <sub>2</sub> R <sub>1</sub> = PPh <sub>2</sub>  | 9. R = CH(CH <sub>3</sub> )N(CH <sub>3</sub> ) <sub>2</sub> R <sub>1</sub> = H   |
| 5. R = CH(CH <sub>3</sub> )SCH(Ph)CH(CH <sub>3</sub> )N(CH <sub>3</sub> ) <sub>2</sub> R <sub>1</sub> = PPh <sub>2</sub> |  |

Scheme 1.

is constant with the complete instability of the  $[4]^+$  cation. However, account must be taken of the fact that in some cases coordination of the two diphenylphosphino groups to metal fragments, which also removes electron density from the bis(diphenylphosphino)ferrocene fragment, leads to stable ferrocenium complexes [18]. This shows how various effects can change the nature of the HOMO level.

## 2.2. Mass spectrometry

Mass spectrometry investigations were carried out on the 1,1'-bis(diphenylphosphino)ferrocene species 2–4 as well as on their exhaustively electrooxidized solutions. In all cases the mass spectra of the oxidized species reveal the presence of diphenylphosphinoyl derivatives not present in the spectra of their corresponding neutral

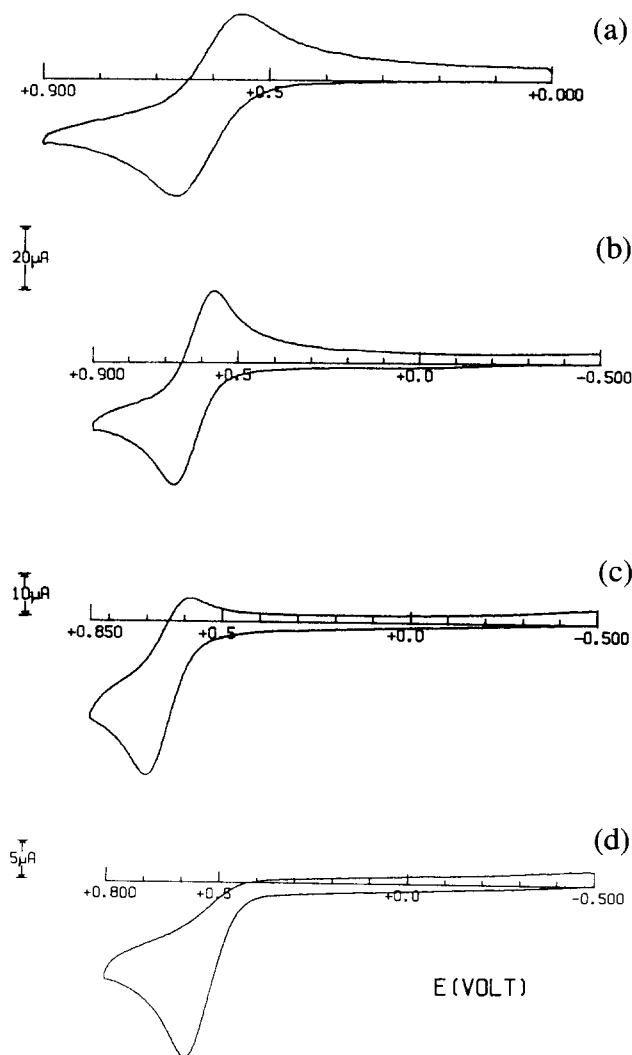


Fig. 1. Cyclic voltammograms recorded at a platinum electrode on  $\text{CH}_2\text{Cl}_2$  solutions containing  $[\text{NBu}_4][\text{ClO}_4]$  ( $0.2 \text{ mol dm}^{-3}$ ) and (a) 1 ( $1.1 \times 10^{-3} \text{ mol dm}^{-3}$ ) (b) 2 ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) (c) 3 ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) and (d) 4 ( $0.7 \times 10^{-3} \text{ mol dm}^{-3}$ ) (scan rate,  $1.00 \text{ V s}^{-1}$ ).

Table 1

Formal electrode potentials (vs. a saturated calomel electrode (SCE)), peak-to-peak separation and monocation lifetimes for the one-electron oxidation of 1,1'-bis(diphenylphosphino)ferrocene and related species in  $\text{CH}_2\text{Cl}_2$  solution

Complex	$E^{0'}$ (+/0) <sup>a</sup> (V)	$\Delta E_p$ <sup>b</sup> (mV)	$i_{pc}/i_{pa}$ <sup>c</sup>	$t_{1/2}$ (monocation) (s)
1	+0.61	92	0.7	0.3
2	+0.62	92	0.8	1.0
3	+0.65	104	0.3	0.05
4	+0.53 <sup>d</sup>	—	0.0	< 0.005
5	+0.67	100	<sup>e</sup>	—
6	+0.66	84	<sup>e</sup>	—
7	+0.57	123	0.8	4.0
8	+0.43	162	1.0	Stable
	+0.50 <sup>f</sup>	—	—	—
9	+0.41	120	1.0	Stable
$\text{Fe}(\text{C}_5\text{H}_5)_2$	+0.44	98	1.0	Stable
$(\text{C}_5\text{H}_5)_-$	+0.50 <sup>g</sup>	—	1.0	Stable
$\text{Fe}(\text{C}_5\text{H}_4\text{-PPh}_2)$	+0.58 <sup>h</sup>	—	—	—

<sup>a</sup> Measured at the scan rate in which the  $i_{pa}/i_{pc}$  ratio approaches unity.

<sup>b</sup> Measured at  $0.5 \text{ V s}^{-1}$ .

<sup>c</sup> Measured at  $1 \text{ V s}^{-1}$ .

<sup>d</sup> Peak potential value at  $0.5 \text{ V s}^{-1}$ .

<sup>e</sup> Not computable because the peak-current ratio cannot be reliably measured.

<sup>f</sup> From [17].

<sup>g</sup> From [9].

<sup>h</sup> From [7].

congeners. As an example, Fig. 2 presents a comparison of the mass spectrum of 4 (Fig. 2(a)) with that of the species resulting from its anodic oxidation (Fig. 2(b)).

As a consequence of the electron removal process, new peaks at  $m/z = 596$ , 612 and 630 respectively appear, in addition to the molecular ion of the residual 4 at  $m/z = 580$ . Accurate mass measurements (Table 2) indicate that the first two peaks correspond to the addition of one and two oxygen atoms respectively to the primarily electrogenerated  $[4]^+$  cation. This sequential transformation of the diphenylphosphine moiety into diphenylphosphinoyl derivatives, which is probably promoted by traces of water either present in the nominally anhydrous solvent or adsorbed during the recovery of the sample from the macroelectrolysis process, is constant with previously reported oxidation mechanisms [8]. As illustrated in Scheme 2, one fragmentation path involves the loss of a phenyl group from both  $[4]^+$  and  $[10]^+$  with formation of the ions at  $m/z = 503$  and 519 respectively. The further loss of a  $\text{PPh}_2\text{-P(O)Ph}_2$  radical from the monosubstituted cyclopentadienyl ring affords the ion at  $m/z = 318$ . The direct loss of the same  $\text{PPh}_2\text{-P(O)Ph}_2$  radical from the three ferrocenium species  $[4]^+$ ,  $[10]^+$  and  $[11]^+$  yields the fragment ions at  $m/z = 395$  and 411 respectively. In turn, the  $m/z = 395$  ion may lose either a phenyl radical yielding the ion at  $m/z = 318$ , or  $\text{C}_5\text{H}_6$ , giving the ion at  $m/z = 329$ . The  $\text{C}_5\text{H}_6$  fragment is also lost by the ion at  $m/z = 411$ .

It is evident that the species  $[4]^+$ ,  $[10]^+$  and  $[11]^+$  fragment directly by loss of the pendant group of the monosubstituted cyclopentadienyl ring; this probably indicates that the first diphenylphosphine group to undergo oxidation is that of the substituted diphenylphosphinocyclopentadienyl ring.

Other fragment ions present in the mass spectrum at  $m/z = 347$  and  $321$  are attributable to  $[\text{FeC}_5\text{H}_3(\text{CH}=\text{CH}_2)\text{P}(\text{O})\text{Ph}_2]^+$  and to  $[\text{FeC}_5\text{H}_4\text{P}(\text{O})\text{Ph}_2]^+$  respectively.

Finally, the peak at  $m/z = 630$ , which differs by 18 amu from the ion  $[11]^+$ , can be plausibly attributed to addition of a water molecule to the vinyl group of  $[11]^+$ . The corresponding fragment ion resulting from the loss of  $\text{P}(\text{O})\text{Ph}_2$  is present at  $m/z = 429$ .

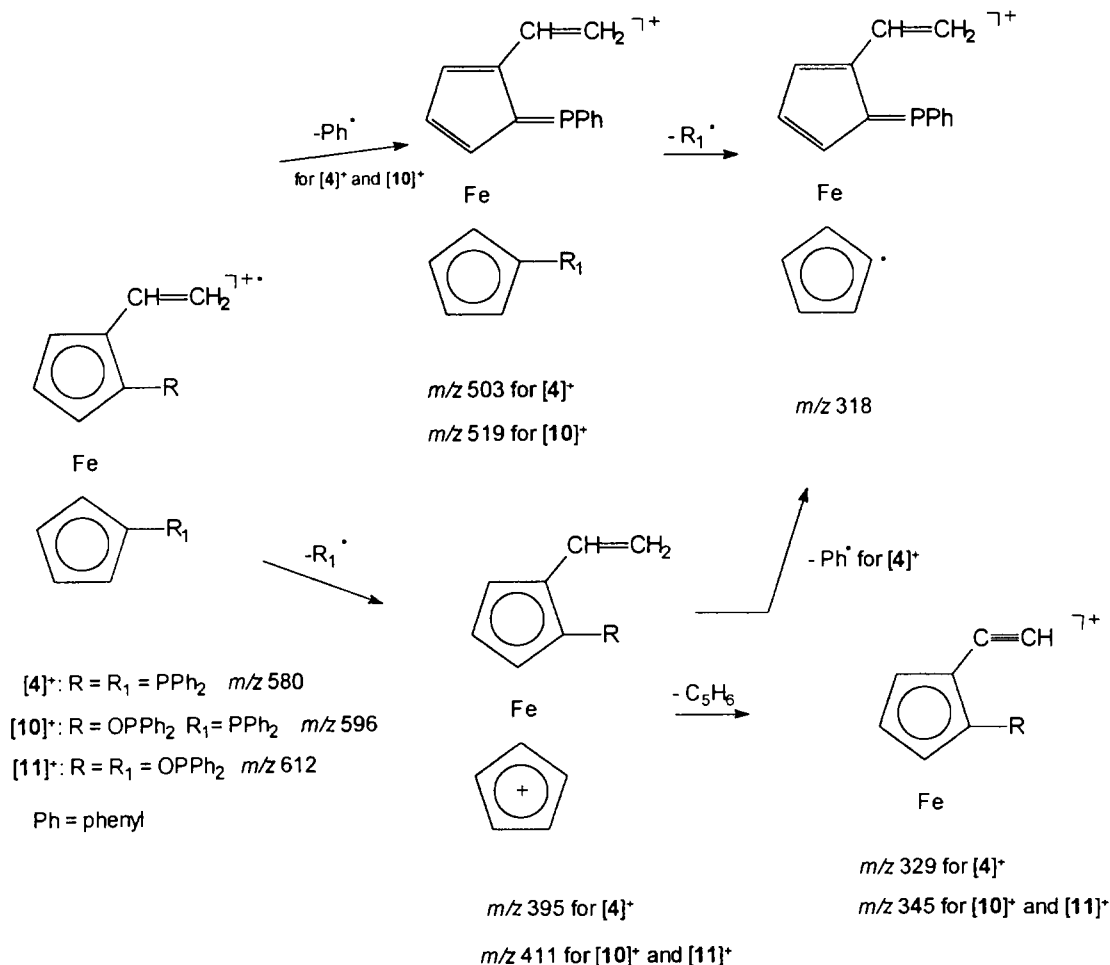
The mass spectrum from the species produced by oxidation of **3** (molecular ion at  $m/z = 614$ ) displays peaks at  $m/z = 612$ ,  $614$ ,  $628$ ,  $630$ ,  $644$  and  $646$  respectively, indicating the formation of a mixture of mono- and di-bis(diphenylphosphine)oxide derivatives differing from each other by 2 amu. It seems reasonable to suppose that during the electrochemical experiment the formation of oxide derivatives is accompanied by

partial dehydrogenation processes, probably centred on the peripheral carbon chain.

In the mass spectrum of the species obtained by exhaustive oxidation of **2** ( $m/z = 598$ ), the molecular ion of the residual **2** or its electrogenerated monocation  $[2]^+$  is present only in very low intensity. On the contrary, peaks at  $m/z = 580$ ,  $596$ ,  $612$  and  $628$  are present with relative intensities higher than 50%. The first three peaks can perhaps be attributed to species produced by a dehydration process preceding the sequential oxidation of the phosphine substituents; this hypothesis is supportive by the fact that the  $B/E$  spectra of the ion at  $m/z = 612$  from  $[2]^+$  and  $[4]^+$  are superimposable, indicating that  $[11]^+$  is formed in all cases. As previously observed for the oxidation of **3**, the ion at  $m/z = 628$  may result from a dioxygenation–dehydrogenation process.

### 3. Experimental details

Materials and apparatus for the electrochemical studies have been described elsewhere [19]. Mass spectrom-



Scheme 2.

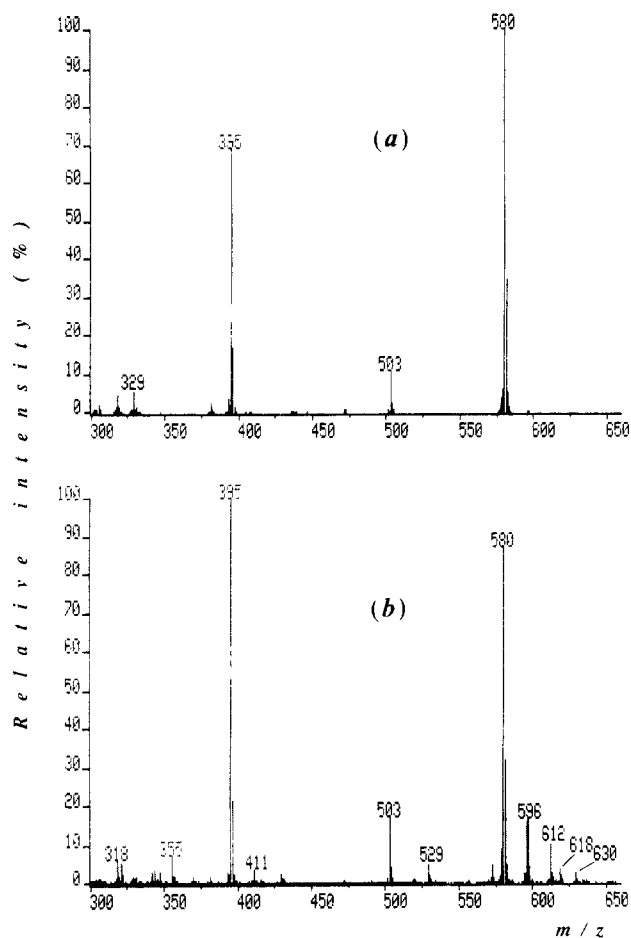


Fig. 2. DEI mass spectra of (a) **4** and (b) the product resulting from its exhaustive anodic oxidation.

etry experiments were carried out on a VG70-250S double-focusing instrument. Experimental conditions were as follows: acceleration voltage, 8 kV; source temperature, 150°C; electron energy, 70 eV; current emission, 100 mA; resolution, 1000M/ΔM (10% of valley). Accurate mass measurements were performed at a resolution of 5000M/ΔM (10% of valley) with perfluorokerosene (Fluka) as the internal standard. A drop of toluene containing the electrochemically oxidized ferrocene species was put on the platinum filament of the desorption probe. The solvent was allowed

Table 2

Accurate mass data and elemental composition for the main ions present in the mass spectrum of the products resulting from electrochemical oxidation of **4**

Composition	Measured mass ( $\mu$ )	Error ( $\mu^{-3}$ )
$[\text{C}_{36}\text{H}_{30}\text{FeP}_2\text{O}_2]^{*+}$	612.1062	0.8
$[\text{C}_{36}\text{H}_{30}\text{FeP}_2\text{O}]^{*+}$	596.1115	0.6
$[\text{C}_{36}\text{H}_{30}\text{FeP}_2]^{*+}$	580.1178	-0.5
$[\text{C}_{30}\text{H}_{25}\text{FeP}_2]^+$	503.0778	0.3
$[\text{C}_{24}\text{H}_{20}\text{FeP}]^+$	395.0653	-0.1

to evaporate, and the wire was introduced into the ion source. The wire heating current ramp was from 0 to 1 A at a rate of 80 mA s<sup>-1</sup>. A scan time of 1 s decade<sup>-1</sup> in the range  $m/z = 800-50$  gave good reproducibility of the experiments.

1,1'-bis(diphenylphosphino)ferrocene (**1**), (*R*)-*N,N*-Dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]-ethylamine (**7**), vinylferrocene (**8**), (*R*)-(+)-*N,N*-dimethyl-1-ferrocenylethylamine (**9**) and ferrocene were Aldrich products; they were used without further purification. Complexes **2-6** were prepared by established procedures [20].

## References

- [1] P. Zanello, G. Opromolla, M. Herberhold and H.-D. Brendel, *J. Organomet. Chem.*, **484** (1994) 67.
- [2] K.-S. Gan and T.S.A. Hor, in T. Hayashi and A. Togni (eds.), *Ferrocenes. From Homogeneous Catalysis to Material Science*, VCH, Weinheim, 1995, Chapter 1.
- [3] U. Casellato, D. Ajò, G. Valle, B. Corain, B. Longato and R. Graziani, *J. Cryst. Spectrosc. Res.*, **18** (1988) 583; *Chem. Abstr.*, **110** (1989) 48914t.
- [4] D.L. DuBois, C.W. Eigenbrot, Jr., A. Miedaner, J.C. Smart and R.C. Haltiwanger, *Organometallics*, **5** (1986) 1405.
- [5] D.A. Clemente, G. Pilloni, B. Corain, B. Longato and M. Tiripicchio-Camellini, *Inorg. Chim. Acta*, **115** (1986) L9.
- [6] B. Corain, B. Longato, G. Favero, D. Ajò, G. Pilloni, U. Russo and F.R. Kreissl, *Inorg. Chim. Acta*, **157** (1989) 259.
- [7] T.M. Miller, K.J. Ahmed and M.S. Wrighton, *Inorg. Chem.*, **28** (1989) 2347.
- [8] G. Pilloni, B. Longato and B. Corain, *J. Organomet. Chem.*, **420** (1991) 57.
- [9] J.C. Kotz, C.L. Nivert, J.M. Lieber and R.C. Reed, *J. Organomet. Chem.*, **91** (1975) 87.
- [10] L. Friedman, A.P. Irsa and G. Wilkinson, *J. Am. Chem. Soc.*, **77** (1955) 3689.
- [11] D.T. Roberts, W.F. Little, and M.M. Bursley, *J. Am. Chem. Soc.*, **89** (1967) 4917.
- [12] Y.S. Nekrasov and D.V. Zagorevskii, *Org. Mass Spectrom.*, **26** (1991) 733.
- [13] X. Xu, S.P. Nolan and R.B. Cole, *Anal. Chem.*, **66** (1994) 119.
- [14] C.E.C.A. Hop and T.B. McMahon, *J. Am. Soc. Mass Spectrom.*, **5** (1994) 274.
- [15] E.R. Brown and J.R. Sandifer, in B.W. Rossiter and J.F. Hamilton (eds), *Physical Methods of Chemistry. Electrochemical Methods*, Vol. 2, Wiley, New York, 1986, Chapter 4.
- [16] J.B. Flanagan, S. Margel, A.J. Bard and F.C. Anson, *J. Am. Chem. Soc.*, **100** (1978) 4248, and references cited therein.
- [17] A.M. Al-Saeed, E.A. Seddon, K.R. Seddon, A.A. Shimran, S. Tompkins, M.C. Gossel and J.P. Knychala, *J. Organomet. Chem.*, **347** (1988) C25.
- [18] P. Zanello, in T. Hayashi and A. Togni (eds.), *Ferrocenes. From Homogeneous Catalysis to Material Science*, VCH, Weinheim, 1995, Chapter 7.
- [19] P. Zanello, G. Opromolla, M. Casarin, M. Herberhold and P. Leitner, *J. Organomet. Chem.*, **443** (1993) 199.
- [20] T. Hayashi, in T. Hayashi and A. Togni (eds.), *Ferrocenes. From Homogeneous Catalysis to Material Science*, VCH, Weinheim, 1995, Chapter 2, and references cited therein.