

Inorganica Chimica Acta 287 (1999) 117-133

Synthesis, X-ray structural determination and Mössbauer characterization of Schiff bases bearing ferrocene groups, their reduced analogues and related complexes[☆]

E. Bullita ^a, U. Casellato ^a, F. Ossola ^a, P. Tomasin ^a, P.A. Vigato ^{a,*}, U. Russo ^b

^a Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, Area della Ricerca Corso Stati Uniti 4, I-35127 Padua, Italy ^b Dipartimento di Chimica Inorganica, Organometallica ed Analitica, Università di Padova Via Loredan 4, I-35100 Padua, Italy

Received 22 July 1998; accepted 9 November 1998

Abstract

[1+1], [1+2], [2+1] or [3+1] acyclic and [1+1] or [2+2] cyclic Schiff bases ($L_A \cdots L_S$), containing ferrocene moieties, have been prepared by reaction of formyl- or 1,1'-diformylferrocene and the appropriate amines. Formyl- and 1,1-diformylferrocene form respectively the acyclic [2+1] L_w and [2+2]_n L_z compounds by reaction with 1,4-diaminomethylbenzene. Similar compounds ($L_T \cdots L_V$) have been obtained by condensation of aminomethylferrocene and 2,6-diformylpyridine, 2,6-diformyl-4chlorophenol and 3-methoxy-2-hydroxybenzaldehyde. By reduction of these compounds with NaBH₄ the corresponding ferrocene-amine derivatives (L') have been synthesized. All these compounds have been characterized by physico-chemical measurements (IR, NMR, Mössbauer spectroscopy and FAB mass spectrometry) and L_H , derived by the condensation of ferrocene-aldehyde and 1,5-diamino-3-oxa-pentane, also by an X-ray structural determination. The X-ray analysis of crystals of L_H , grown from a diethyl ether solution, shows that two independent molecules are present in the asymmetric unit; these two molecules are chemically equivalent with the ferrocenyl groups in the eclipsed form. The coordination ability of these compounds towards d metal ions as copper(II), nickel(II), platinum(II) and rhodium(III) was investigated; while the Schiff bases (L) may suffer hydrolysis, their reduced analogues (L') form stable, well-defined complexes of the type $M(L')(Cl)_n$ (n = 2, 3). The Mössbauer spectra of the prepared compounds show signals with δ at 0.44 and ΔE_Q 2.30 mm s⁻¹ for the Schiff bases $L_A \cdots L_S$, and 0.52 and 2.40 mm s⁻¹ for the reduced analogues and hence may be diagnostic of the presence of Fe-CH=N- or Fe-CH₂-NH- groups. The signals with δ at 0.51-0.55 and ΔE_Q at 2.34-2.38 mm s⁻¹ for the Schiff bases $L_T \cdots L_V$, having Fe-CH₂-N=CH groups, resemble those of the reduced analogues. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ferrocene complexes; Schiff base complexes

1. Introduction

Ferrocene containing compounds have been widely studied owing to their potential in catalysis, material science, molecular devices, hydrometallurgy, etc. [1-4]. Variously substituted ferrocene derivatives, bearing ligating groups with different donor atoms, have been proposed and successfully tested [5,6]. Several efforts have been directed towards the design and synthesis of multielectron redox mediators which could transfer several electrons simultaneously at the same potential [4,5]. Compounds with ferrocene groups attached at the periphery of their coordinating moiety contain redox centers far enough from one another to have the same potential and still close enough to provide all the electrons at the same substrate site [4,5]. Their use as ligands for suitable metal ions makes these receptors quite good candidates as redox-catalytic systems capable of promoting redox reactions on a coordinate substrate.

Macrocyclic and/or macroacyclic ligands containing a redox-active center in close proximity to the coordination binding site are currently studied as molecular

^{*} This article was partially presented at the 5th Meeting on Syntheses and Methodologies in Inorganic Chemistry: New Compounds and Materials, Bressanone, Italy, 2–7 October, 1994.

^{*} Corresponding author. Tel.: + 39-049-829 5962; fax: + 39-049-870 2911.

sensory devices [4-16]. These systems can electrochemically recognize the binding of any charged or neutral inorganic or organic guest molecule, by either interactions or communication via various bond linkages between the receptor site and the redox center [4]. Systems bearing such reactive groups, based on Schiff bases, exhibit appropriate physico-chemical properties and can offer a valid chance to their use as redox catalysts or as binding blocks for the preparation of molecular devices or as switching agents in the cation transport. Selective separation of metal ions from complex mixture is of paramount importance in the treatment of industrial wastes and by products such as electron scrap, ashes of metallurgical processes, effluent streams, etc. Specific extractants as crown-ethers, cryptands, polyaza- or polyethermacrocycles and other related derivatives are currently used for these separations.

More recently macrocyclic and/or macroacyclic switching ligands have been proposed as different, very promising alternative systems for the selective recognition, transport and separation of metal ions [5]. A chemical switching ligand is designed and synthesized in such a way that complexing behaviour and selectivity can be reversibly controlled by changing the pH, by photochemical or redox processes. In the ferrocene-containing compounds, the key design principle is that ferrocene has a readily accessible redox ability such that neutral ferrocene can be easily oxidized into ferrocenium cation. Therefore these systems can act as chemical switches [5].

Over the last few years, several Schiff bases containing ferrocene groups have been prepared and their coordination behaviour studied by means of different physico-chemical measurements such as IR, NMR and electrochemical data and their structure was determined by single crystal X-ray diffractometric investigations. In these studies, Mössbauer spectroscopy was also employed and revealed its important role for a better understanding of the properties of the prepared compounds [4–16].

Recently, we have undertaken studies aimed at the design and synthesis of appropriate systems containing redox active center in close proximity to a host binding site, capable to detect electrochemically the complexation of any charged inorganic and organic guest species, either through space electrostatic interaction, or via various bond linkages [16]. In particular we have prepared Schiff bases containing ferrocene groups and studied their physico-chemical and coordination properties together with their ability to favour ion transfer at the liquid/liquid interface [16].

In the present paper, we refer to the preparation of a variety of cyclic or acyclic ferrocene-containing compounds by condensation of formyl- or diformylferrocene with the appropriate amine in alcohol or acetonitrile solution $(L_A \cdots L_S)$, quite often followed by a reduction of the resulting Schiff base with NaBH₄ (L'_F, L'_G, L'_J, L'_K, L'_M, L'_Q). Similar Schiff bases have been obtained by reaction of aminomethylferrocene with the appropriate formyl- or diformyl-derivatives $(L_T \cdots L_V)$. Finally the acyclic discrete $[2 + 1] (L_w)$ or polymeric $[2 + 2] (L_Z)$ compounds have been prepared by condensation of 1,4-diaminomethyl-benzene respectively with formyl- or 1,1'-diformylferrocene.





These compounds have been designed with the aim to verify their coordination ability towards transition metal ions, with respect to the presence of a progressively increasing number of ferrocene units within the coordination sites, the planar or 3-D geometry of the ligands, the acyclic or cyclic coordinating systems containing different donor atoms or groups, the distance of the ferrocene groups from the coordination moieties, the presence of conjugated systems, etc. Also, the functionalization of these Schiff bases by the insertion of crown–ether moieties was successfully tested.

Attention was devoted also to the chelating properties of these ferrocene derivatives towards transition metal ions such as copper(II), nickel(II), palladium(II), platinum(II) and rhodium(III). Preliminary data on these systems have been presented already [16]. It was verified that the Schiff bases can form unstable complexes which suffer hydrolytic processes, with the consequent formation of non-defined species. Only in some cases the hydrolytic products have been identified. On the contrary, well-defined and stable complexes have been obtained with the reduced ligands (L').

2. Experimental

2.1. Materials

Formylferrocene, the amines H_2NR [$R = (CH_2)_2$ - C_6H_4N ; $(CH_2)_2SC_6H_5$; -benzo-5-crown-5], H_2NRNH_2 [$R = (CH_2)_2$; $(CH_2)_3$; $(CH_3)_2CCH_2$; $CH_2C(CH_3)_2CH_2$; $CH_2CH(OH)CH_2$; $(CH_2)_2X(CH_2)_2$ where X = NH, NCH_3 , $N(CH_2)_{11}CH_3$, O, S; $(CH_2)_2O(CH_2)_2O(CH_2)_2$], tris-(2-aminoethyl)amine, N,N'-bis-(3-aminopropyl)piperazine, 1,3-diaminomethylbenzene, 1,4-diaminomethylbenzene, *n*-BuLi, the salts and the solvents were commercial products (Aldrich) used without further purification. Et₂O and DMF were purified by standard methods [17] and used immediately after distillation. 1,1'-Diformylferrocene [18] and aminomethylferrocene [19] were prepared according to literature. Their purity was checked by elemental analyses, IR and ¹H NMR spectroscopy and FAB mass spectrometry.

In particular, the syntheses of 1,1'-diformylferrocene were carried out in nitrogen-filled glove-boxes with the rigorous exclusion of oxygen and moisture. In the preparation of 1,1'-diformylferrocene, particular attention must be paid to the purity of DMF; in fact, impurities in DMF cause the presence of by-products in the final product (as unreacted ferrocene, formylferrocene, etc.), which make the purification step by crystallization from cyclohexane longer, thus lowering the yield. The best DMF purification procedure turned out to be the use of molecular sieve followed by distillation under reduced pressure.

Also, the [2+2] Schiff base L_H and the reduced analogue L'_N have been prepared following literature procedure [11].

The elemental analyses of the prepared ligands and complexes are reported in Table 1.

The yield is 25-40% for the Schiff bases, 50-55% for the reduced analogues and 70-80% for the complexes. The ligands melt with decomposition at the temperature reported below while the complexes decompose above 300°C. FAB mass spectrometry evidences the parent peak [M + H]⁺ at the appropriate m/z value for all the prepared ligands, accompanied by the [M + Na]⁺ peak especially for the polyamine derivatives. IR and NMR data are reported and discussed in Section 3.

2.2. Schiff bases

2.2.1. Preparation of L_A and L_B

2-Aminomethyl-pyridine (2 mmol) dissolved in CH₃CN or MeOH (25 ml) was added to formylferrocene (2 mmol) dissolved in 25 ml of the same solvent. The red-brown solution was refluxed for 1 h, then stirred at room temperature (r.t.) for a further 2 h and finally reduced in volume. By addition of diethyl ether, L_A was obtained as a red-brown precipitate in a low yield; it was washed with diethyl ether and dried in vacuo (m.p. > 300°C).

 L_B was obtained as an oil by a similar procedure, by reaction of equimolecular amounts of $H_2N(CH_2)_2$ - $S(C_6H_5)$ and formylferrocene. The red-brown reaction solution was refluxed for 1 h and stirred at r.t. for 2 h, then it was evaporated to dryness. The red-brown oil obtained, soluble in almost all the organic solvents, was treated three times with *n*-hexane and dried in vacuo. The final product, obtained as a red-brown oil, was dried in vacuo.

2.2.2. Preparation of $L_C - L_J$

The appropriate polyamine (1 mmol) dissolved in MeOH or CH_3CN (25 ml) was added to a methanolic or acetonitrile solution (25 ml) of ferrocenealdehyde (2 mmol). The red solution was refluxed for 1 h, then

















Lv



Lw

Ň

Ņ

Ėе

Compounds	Cale.			Found				
	C	Н	Ν	S	C	Н	Ν	S
L _A	67.13	5.30	9.21		67.12	5.37	8.87	
L _C	65.03	5.87	5.83		64.57	5.53	5.37	
L _D	65.62	6.11	5.67		65.75	5.83	5.24	
L _E	61.44	5.37	5.97		61.98	5.10	5.39	
$L_F \cdot H_2O$	58.89	5.70	5.28	6.05	58.46	5.22	5.45	6.15
L _G	63.68	6.13	8.25		63.26	6.14	8.12	
L _H	62.94	5.68	5.64		61.91	5.56	5.46	
L	62.25	5.96	5.18		62.29	6.07	5.20	
L	64.89	6.80	9.46		64.46	6.79	9.33	
L _K	63.79	5.76	7.63		64.20	6.10		7.82
$L_{I} \cdot 2H_{2}O$	62.90	5.71	12.22		62.99	5.30	12.46	
$L_{M} \cdot 2.5H_{2}O$	58.76	6.53	3.43		58.61	6.49	3.52	
$L_{N} \cdot 2H_2O$	59.18	5.67	9.86		59.40	5.32		10.36
$L_0 \cdot 3H_2O \cdot CH_2CN$	59.76	6.63	10.25		59.25	7.84	10.69	
$L_{\rm P} \cdot 2H_{\rm 2}O \cdot CH_{\rm 2}CN$	62.35	6.83	10.10		62.00	6.50	10.30	
$L_0 \cdot MeOH$	63.02	7.81	12.78		63.11	8.05	12.43	
$L_{\rm p} \cdot H_{\rm p}O$	65.96	5.53	5.13		66.37	5.79	5.22	
$L_{\rm R} \cdot H_2 O$	68.40	5.45	7.98		68.21	5.66	7.81	
L _s n ₂ o	62.27	4 70	4 48		62.35	4 68	4.55	
$L_{1} \sim 0.5 H_{2}O$	64 72	5.24	7.81		64.65	5 38	7.63	
$I \rightarrow H_0$	62.15	5.24	3.81		62.36	5.85	3.92	
$L_{V} = 11_{20}$	67.07	5 44	5 21		67.28	5 32	5.48	
$L_{z} \cdot 2H_{2}O$	68.40	5.45	7.98		68.38	5.62	7.86	
$L'_{\rm F}$	60.49	6.24	5.43	6.21	60.02	6.46	5.37	6.30
$L'_{G} \cdot H_2O$	61.04	7.01	7.91		61.30	6.95	8.00	
L' _J	64.45	7.43	9.39		64.32	7.52	9.45	
$L'_{M} \cdot H_2O$	60.68	6.18	10.11		60.60	6.75	9.81	
L' _Q	64.39	8.34	13.65		64.42	8.55	13.24	
$Cu(L_H)(ClO_4)_2 \cdot H_2O$	40.21	3.89	3.61		40.49	4.29	4.90	
$Ni(L_H)(ClO_4)_2 \cdot H_2O$	38.74	5.19	6.02		38.90	4.40	5.40	
$Pt(L_F)(Cl)_2 \cdot 3H_2O$	46.62	4.66	4.18		46.65	4.56	4.54	
$Ni(L_K)(ClO_4)_2 \cdot 2.5H_2O$	40.09	4.44	6.68		40.06	4.51	7.02	
$\operatorname{Cu}(L'_G)(\operatorname{Cl})_2 \cdot \operatorname{H}_2O$	49.01	5.02	6.35		49.31	5.63	6.29	
$N_1(L'_G)(Cl)_2$	50.45	5.48	6.54		50.02	5.45	6.42	
$Cu(L'_F)(Cl)_2 \cdot 2H_2O$	45.47	5.28	4.08	4.67	45.34	4.86	3.95	4.32
$Cu(L'_F)(ClO_4) \cdot CHCl_3$	40.61	4.16	3.51	4.01	41.31	4.41	4.07	3.73
$Ni(L'_F)(Cl)_2 \cdot 2H_2O$	46.41	5.24	4.16		46.27	5.16	4.11	
$Pt(L'_F)(Cl)_2 \cdot H_2O$	39.26	4.30	3.52	4.03	39.02	4.98	5.29	3.18
$Cu(L'_K)(Cl_2) \cdot 5H_2O$	48.86	5.46	5.84		48.52	5.15	6.42	
$Ni(L'_K)(Cl_2) \cdot 5H_2O$	48.95	5.79	5.85		48.52	5.15	6.42	
$Cu(L'_J)(Cl_2) \cdot H_2O$	51.33	6.19	7.48		51.51	6.36	7.34	
$Ni(L'_J)(Cl_2) \cdot 2H_2O$	50.44	6.34	7.35		50.65	6.85	7.12	
$Pd(L'_J)(Cl_2) \cdot 1.5H_2O$	48.21	5.94	7.03		48.41	6.63	7.04	
$Pt(L'_J)(Cl_2) \cdot C_6H_5CN$	48.76	5.14	7.29		48.60	4.71	7.09	
$Cu(L'_Q)(Cl_2) \cdot 2H_2O$	45.49	6.59	9.65		45.38	6.80	10.21	
$Rh(L'_Q)(Cl_3) \cdot 2H_2O$	40.42	5.85	8.57		40.37	6.12	8.72	

stirred at r.t. for 2 h, and finally reduced in volume or evaporated to dryness. The solution or the obtained residue was treated with diethyl ether and precipitated with *n*-pentane or *n*-hexane. The orange-red or ochre compound so obtained was filtered, washed with *n*-hexane or *n*-pentane and dried in vacuo. The compounds have been obtained as orange-yellow or red-brown solids (m.p.: $L_C = 105-107^{\circ}C$, $L_D = 105-108^{\circ}C$, $L_E =$ 107–109°C, $L_F = 98-100$ °C, $L_G = 94-95$ °C, $L_H = 110-111$ °C, $L_I = 110-112$ °C, $L_J = 110-112$ °C).

2.2.3. Preparation of L_K

Tris-2(aminoethyl)amine (1 mmol) in methanol (10 ml) was added to a methanolic solution of ferrocenealdehyde (3 mmol). The red solution was stirred for 1 h, then allowed to stand for 1 h. The solution was evaporated to dryness under reduced pressure and the obtained oil was treated with diethyl ether (30 ml). The oil slowly turned into a yellow-ochre solid that was filtered, washed with diethyl ether and dried in vacuo (m.p. = 142-144°C).

2.2.4. Preparation of L_L and L_M

The appropriate amine (2 mmol) in CH₃CN (30 ml) was added dropwise under nitrogen to an acetonitrile solution (30 ml) of 1,1'-diformylferrocene (1 mmol). The dark-red solution was stirred in the dark for 4 h, then evaporated to dryness, the obtained oil was dissolved in CHCl₃. The addition of diethyl ether gave rise to a dark-red precipitate, which was filtered, washed with diethyl ether and dried in vacuo (m.p.: $L_L = 142-144^{\circ}C$, $L_M = 122-125^{\circ}C$).

2.2.5. Preparation of L_0 and L_P

The appropriate diamine (2 mmol) in CH₃CN (30 ml) was added dropwise under nitrogen to a CH₃CN solution (30 ml) of 1,1'-diformylferrocene (2 mmol). The solution was stirred in the dark for 4 h, then reduced in volume ($\cong 5$ ml). The obtained precipitate was collected by filtration and dried in vacuo.

Additional product may be obtained from the mother liquor. This was evaporated to dryness and the residue treated with diethyl ether. The precipitate obtained was filtered, washed with diethyl ether and dried in vacuo (m.p.: $L_0 = 127-129^{\circ}C$, $L_P = 125-126^{\circ}C$).

2.2.6. Preparation of L_o

The tetramine N,N'-bis-(3-aminopropyl)-piperazine (1 mmol) in MeOH (50 ml) was added dropwise to a methanol/chloroform solution (100 ml) of 1,1'-diformylferrocene (1 mmol). The dark-red solution was refluxed for 30 min, then stirred at r.t. for 4 h. The resulting solution was evaporated to dryness and the obtained oil treated with diethyl ether (50 ml). The oil slowly turned into a black-red solid which was filtered, washed with diethyl ether and dried in vacuo (m.p. > 300°C).

2.2.7. Preparation of L_R and L_S

1,3- or 1,4-diaminomethylbenzene (1 mmol) in chloroform (25 ml) was added to a chloroform solution (50 ml) of formylferrocene (2 mmol) or 1,1'-diformylferrocene (1 mmol), respectively. The resulting orange-red solution was refluxed for 2 h, then evaporated to dryness. The residue was dissolved in CHCl₃ (10 ml) and allowed to stand overnight. The yellow-orange precipitate obtained by addition of diethyl ether was collected by filtration, washed twice with diethyl ether and dried in vacuo (m.p.: $L_R = 115-117^{\circ}C$, $L_S = 117 118^{\circ}C$).

2.2.8. Preparation of L_T , L_U and L_V

Aminomethylferrocene (1 mmol) in methanol (25 ml) was added to 2,6-diformyl-4-chlorophenol (0.5 mmol), 2,6-diformylpyridine (0.5 mmol) or 3-methoxy-2-hydroxybenzaldehyde (1 mmol) in methanol (50 ml), respectively. The resulting orange-red solution was refluxed for 2 h, reduced in volume and treated with diethyl ether. The yellow precipitate obtained was collected by filtration, washed with a methanol/diethyl ether and dried in vacuo (m.p.: $L_T = 165-168^{\circ}C$, $L_U = 124-125^{\circ}C$, $L_V = 106-107^{\circ}C$).

2.2.9. Preparation of L_W and L_Z

1,4-Diaminomethylbenzene (1 mmol) in chloroform (25 ml) was added respectively to a chloroform solution (25 ml) of formylferrocene (2 mmol) or 1,1'-diformylferrocene (1 mmol). The resulting dark red solution was refluxed for 2 h, then reduced in volume and allowed to stand. The obtained red-brown precipitate was collected by filtration, washed with a diethyl ether solution and dried in vacuo (m.p.: $L_W = 110-111^{\circ}C$, $L_Z > 300^{\circ}C$).

2.3. Ferrocene containing amines

2.3.1. Preparation of the reduced polyamines L'_F , L'_G , L'_J , L'_K , L'_M and L'_Q

The appropriate Schiff base (2 mmol) in THF (L_F , L_G , L_J , L_K) or (50 ml) methanol (L_M and L_Q) was treated, under a nitrogen atmosphere, with LiAlH₄ or NaBH₄ (4–5 mmol), respectively. The resulting mixture was refluxed for 30 min (when THF was used, methanol (5 ml) was added). The resulting suspension was clarified twice by filtration. The yellow solution was evaporated to dryness and the obtained oil was dissolved in CH₂Cl₂/isooctane. The yellow solid obtained by slow evaporation of this solution was filtered, washed with isooctane and dried in vacuo.

Using this procedure $L'_{\rm K}$ was obtained as an oil. For $L'_{\rm J}$ and $L'_{\rm M}$, the residue was treated with water (50 ml) and the yellow solid so obtained was filtered, washed with water and dried in vacuo (m.p.: $L'_{\rm F} = 60-62^{\circ}$ C, $L'_{\rm G} = 35-38^{\circ}$ C, $L'_{\rm J} = 50-52^{\circ}$ C).

2.4. Complexes with ferrocene containing polyamine

2.4.1. Preparation of $M(L')(Cl)_n$ $(M = Cu^{2+}, Ni^{2+}, Ni^{2+})$

 Pd^{2+} , Pt^{2+} , Rh^{3+} , $L' = L'_F$, L'_G , L'_J , $L'_K L'_Q$, n = 2, 3) The appropriate metal chloride hydrate (CuCl₂· 4H₂O, NiCl₂·4H₂O or RhCl₃·3H₂O) or complex (Pt(C₆H₅CN)₂Cl₂ or Pd(C₆H₅CN)₂Cl₂) (1 mmol) in methanol (50 ml) was added dropwise to a methanolic solution (50 ml) of the appropriate ferrocene containing

methanol (50 ml) was added dropwise to a methanolic solution (50 ml) of the appropriate ferrocene containing polyamine (L') (1 mmol). The solution was stirred for 4 h, then reduced in volume and allowed to stand. The precipitate obtained by slow evaporation of this solu-

tion or by addition of diethyl ether was collected by filtration, washed with diethyl ether and dried in vacuo.

2.5. X-ray crystallography

Data on crystals of $L_{\rm H}$, grown by slow evaporation of a diethyl ether solution of the compound, were collected at 298 K by a Philips PW 1100 (FEBO System) four-circle diffractometer by using graphitemonochromated Mo K α X-radiation ($\lambda = 0.71069$ Å) and the $\omega/2\theta$ scan method. The structure was solved by using heavy-atom methods with the SHELX86 program [20] and refined by full-matrix least-squares methods using the SHELXL package [21]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in geometric positions. Crystal and intensity data for the compound are reported in Table 2, atomic positional parameters with estimated standard deviations are listed in Table 3, and selected bond distances and angles are reported in Table 4.

2.6. Physico-chemical measurements

IR spectra were recorded as KBr pellets on a Mattson FTIR 3000 spectrometer. ¹H and ¹³C NMR spectra were recorded at 200.132 MHz on a Bruker AC200 spectrometer equipped with an Aspect 3000 computer at r.t. Some of the signals were assigned by

Table 2 Crystal and intensity data for $L_{\rm H}$

Compound	L _H
Formula	$C_{26}H_{28}N_2OFe_2$
Formula weight	496.2
Cell parameters	
a (Å)	10.992(4)
$b(\mathbf{A})$	13.207(6)
$c(\dot{A})$	15.909(6)
α (°)	89.18(4)
β(°)	96.78(4)
γ (°)	102.98(3)
Cell volume (Å ³)	2220(1)
D_{calc} (g cm ⁻³)	1.48
F(000) (e)	1031
System	triclinic
Space group	<i>P</i> 1 (no. 2)
Z	4 (2 independent molecules
	in the asymmetric unit)
Absorption μ (cm ⁻¹)	12.6
(Μο Κα)	
Data collected (2θ limits)	4273 (5–55°)
Data with $I > 3\sigma(I)$	4044
No. of parameters	487 (8.3)
(observed per parameter)	
Discrepancy factor R	0.040
GOF	1.602
Highest shift (e.s.d.)	0.019
Highest map residual (e Å ⁻³)	0.52

Table 3

Fractional coordinates with equivalent isotropic thermal parameters (\mathring{A}^2)

Atom	x	у	Ζ	$U_{ m eq}{}^{ m a}$
Fe(1)	-0.03875(8)	0.67040(6)	0.76155(6)	0.0486(3)
Fe(2)	0.21236(8)	0.85583(6)	0.41820(5)	0.0449(3)
C(1)	-0.0109(7)	0.6183(5)	0.6466(3)	0.095(5)
C(2)	-0.0794(7)	0.5375(5)	0.6938(3)	0.097(4)
C(3)	-0.0030(7)	0.5281(5)	0.7709(3)	0.081(4)
C(4)	0.1128(7)	0.6032(5)	0.7713(3)	0.072(3)
C(5)	0.1079(7)	0.6589(5)	0.6944(3)	0.080(4)
C(6)	-0.1415(4)	0.7770(4)	0.7368(3)	0.067(3)
C(7)	-0.2068(4)	0.6999(4)	0.7887(3)	0.075(3)
C(8)	-0.12/1(4)	0.696/(4)	0.8655(3)	0.071(3)
C(9)	-0.0126(4)	0.7719(4)	0.8611(3)	0.060(3)
C(10)	-0.0215(4)	0.8215(4)	0.7815(3)	0.050(2)
$C(\Pi)$	0.0756(6)	0.9002(4)	0.7493(4)	0.049(2)
N(1)	0.1/56(5)	0.9431(4)	0.7948(3)	0.051(2)
C(12)	0.26/4(6)	1.0232(4)	0.7571(4)	0.053(2)
C(13)	0.3964(6)	1.0001(5)	0.7652(4)	0.058(3)
O(1)	0.3939(4)	0.9119(3)	0.7139(3)	0.055(2)
C(14)	0.5152(6)	0.8898(5)	0.7169(4)	0.058(3)
C(15)	0.5043(6)	0.7909(5)	0.6686(4)	0.061(3)
N(2)	0.4749(5)	0.8038(4)	0.5778(3)	0.054(2)
C(16)	0.3696(6)	0.7516(4)	0.5455(4)	0.050(3)
C(18)	0.3824(3)	0.82/1(3)	0.3955(3)	0.051(2)
C(19)	0.2984(3)	0.812/(3)	0.3191(3)	0.05/(3)
C(20)	0.1890(3)	0.7362(3)	0.3334(3)	0.060(3)
C(21)	0.2053(3)	0.7033(3)	0.4186(3)	0.054(2)
C(17)	0.3248(3)	0.7393(3)	0.4309(3)	0.049(2)
C(22)	0.2023(4) 0.2527(4)	0.9383(4)	0.3240(2) 0.4501(2)	0.039(3)
C(23)	0.2327(4) 0.1604(4)	1.0041(4)	0.4391(2) 0.2870(2)	0.001(3)
C(24)	0.1004(4) 0.0528(4)	0.9893(4)	0.3870(2) 0.4074(2)	0.004(3)
C(25)	0.0328(4) 0.0788(4)	0.9149(4) 0.8834(4)	0.4074(2) 0.4021(2)	0.001(3)
$E_{0}(20)$	0.0700(4)	0.0034(4)	1.37202(5)	0.039(3)
Fe(4)	-0.34236(0) 0.36124(9)	0.67431(7)	0.01102(6)	0.0438(3) 0.0573(4)
C(27)	-0.2409(5)	0.07491(7) 0.7149(3)	0.01102(0) 0.4541(3)	0.0373(4)
C(28)	-0.1611(5)	0.6579(3)	0.4341(3) 0.4210(3)	0.070(3)
C(29)	-0.2016(5)	0.0577(3)	0.4210(3) 0.4431(3)	0.070(3)
C(30)	-0.3065(5)	0.5521(3) 0.5437(3)	0.4897(3)	0.066(3)
C(31)	-0.3308(5)	0.6443(3)	0.4965(3)	0.073(3)
C(32)	-0.4270(4)	0.6728(2)	0.2774(3)	0.051(2)
C(33)	-0.5191(4)	0.6046(2)	0.3199(3)	0.054(2)
C(34)	-0.4974(4)	0.5029(2)	0.3150(3)	0.056(3)
C(35)	-0.3920(4)	0.5082(2)	0.2694(3)	0.053(2)
C(36)	-0.3485(4)	0.6132(2)	0.2461(3)	0.052(3)
C(37)	0.7643(6)	0.6483(5)	0.1974(4)	0.059(3)
N(3)	0.7874(6)	0.7360(5)	0.1651(4)	0.073(3)
C(38)	0.8994(8)	0.7627(6)	0.1174(5)	0.085(4)
C(39)	0.9785(8)	0.8588(6)	0.1462(6)	0.086(4)
O(2)	1.0800(5)	0.8894(4)	0.0956(3)	0.081(2)
C(40)	1.1600(8)	0.9847(6)	0.1222(6)	0.086(4)
C(41)	1.2557(7)	1.0190(5)	0.0614(5)	0.077(3)
N(4)	1.3436(6)	0.9508(5)	0.0617(4)	0.071(3)
C(42)	1.3340(6)	0.9011(5)	-0.0051(5)	0.062(3)
C(44)	0.3973(4)	0.7665(4)	-0.0929(2)	0.064(3)
C(45)	0.4842(4)	0.7005(4)	-0.0825(2)	0.079(4)
C(46)	0.5525(4)	0.7194(4)	-0.0005(2)	0.079(4)
C(47)	0.5079(4)	0.7970(4)	0.0397(2)	0.064(3)
C(43)	0.4120(4)	0.8261(4)	-0.0174(2)	0.058(3)
C(48)	0.1976(6)	0.6564(5)	0.0708(5)	0.095(4)
C(49)	0.2971(6)	0.6294(5)	0.1259(5)	0.083(4)
C(50)	0.3372(6)	0.5488(5)	0.0863(5)	0.095(4)
C(51)	0.2626(6)	0.5261(5)	0.0067(5)	0.111(5)
C(52)	0.1763(6)	0.5925(5)	-0.0029(5)	0.110(4)

 $^{\rm a}$ $U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4								
Selected	bond	lengths	(Å)	and	angles	(°)	for	L

Bond length (Å)			
Fe(1)-C(1)	2.043(6)	Fe(1)-C(2)	2.007(6)
Fe(1)-C(3)	2.003(7)	Fe(1)-C(4)	2.037(8)
Fe(1)-C(5)	2.061(7)	Fe(1)-C(6)	1.997(5)
Fe(1)-C(7)	2.054(5)	Fe(1)-C(8)	2.081(5)
Fe(1)-C(9)	2.041(5)	Fe(1)-C(10)	1.988(5)
Fe(2) - C(18)	2.050(4)	Fe(2)-C(19)	2.076(5)
Fe(2)-C(20)	2.045(4)	Fe(2)-C(21)	1.999(4)
Fe(2) - C(17)	2.002(4)	Fe(2)-C(22)	2.047(5)
Fe(2)-C(23)	2.008(5)	Fe(2)-C(24)	2.011(5)
Fe(2) - C(25)	2.052(5)	Fe(2) - C(26)	2.073(5)
C(1)–C(2)	1.420(8)	C(1)–C(5)	1.420(9)
C(2)–C(3)	1.420(8)	C(3)–C(4)	1.420(9)
C(4)–C(5)	1.420(7)	C(6)–C(7)	1.420(6)
C(6)–C(10)	1.420(6)	C(7)–C(8)	1.420(6)
C(8)–C(9)	1.420(6)	C(9)–C(10)	1.420(6)
C(10)–C(11)	1.444(7)	C(11)–N(1)	1.258(7)
N(1)-C(12)	1.460(8)	C(12)–C(13)	1.50(1)
C(13)–O(1)	1.425(8)	O(1)–C(14)	1.414(8)
C(14)–C(15)	1.50(1)	C(15)–N(2)	1.458(8)
N(2)–C(16)	1.255(7)	C(16)–C(17)	1.447(8)
C(18)–C(19)	1.420(6)	C(18)–C(17)	1.420(6)
C(19)–C(20)	1.420(5)	C(20)–C(21)	1.420(6)
C(21)–C(17)	1.420(5)	C(22)–C(23)	1.420(6)
C(22)–C(26)	1.420(6)	C(23)–C(24)	1.420(5)
C(24)–C(25)	1.420(6)	C(25)–C(26)	1.420(5)
Fe(4)-C(44)	2.062(5)	Fe(4)-C(45)	2.094(5)
Fe(4)-C(46)	2.069(5)	Fe(4)–C(47)	2.021(5)
Fe(4)-C(43)	2.016(5)	Fe(4)–C(48)	2.088(7)
Fe(4)-C(49)	2.066(8)	Fe(4)–C(50)	2.017(7)
Fe(4)-C(51)	2.010(6)	Fe(4)-C(52)	2.054(6)
C(27)–C(28)	1.420(8)	C(27)–C(31)	1.420(7)
C(28)–C(29)	1.420(6)	C(29)–C(30)	1.420(8)
C(30)–C(31)	1.420(6)	C(32)–C(33)	1.420(6)
C(32)–C(36)	1.420(6)	C(33)–C(34)	1.420(5)
C(34)–C(35)	1.420(7)	C(35)–C(36)	1.420(5)
C(37)–N(3)	1.246(9)	N(3)-C(38)	1.49(1)
C(38)–C(39)	1.41(1)	C(39)–O(2)	1.43(1)
O(2)–C(40)	1.401(8)	C(40)–C(41)	1.50(1)
C(41)–N(4)	1.46(1)	N(4)-C(42)	1.24(1)
C(44)-C(45)	1.420(8)	C(44)-C(43)	1.420(6)
C(45)-C(46)	1.420(5)	C(46)-C(47)	1.420(8)
C(47)–C(43)	1.420(7)	C(48)–C(49)	1.420(9)
C(48)–C(52)	1.42(1)	C(49)–C(50)	1.42(1)
C(50)–C(51)	1.42(1)	C(51)–C(52)	1.42(1)
Dand male (9)			
$C(0) = E_2(1) = C(10)$	41.2(2)	$C(0) = E_{0}(1) - C(10)$	(9.7(2))
$C(9) = \Gamma^{2}C(1) = C(10)$	41.2(2)	C(3) - Fe(1) - C(10) C(7) = Fe(1) - C(10)	60.7(2)
C(0) - Fe(1) - C(9) C(7) = Fe(1) - C(9)	40.3(2)	C(7) = Fe(1) = C(10) C(7) = Fe(1) = C(8)	09.2(3)
C(7) = Fe(1) = C(9) C(6) = Fe(1) = C(10)	00.2(2)	C(7) = Fe(1) = C(8) C(6) = Fe(1) = C(8)	40.2(2)
C(0) - Fe(1) - C(10)	41.8(2)	C(0) - Fe(1) - C(9) C(6) = Fe(1) - C(7)	09.4(2)
$C(0) = \Gamma^{2}C(1) = C(0)$	105.0(2)	$C(0) = \Gamma e(1) = C(7)$ $C(5) = E_0(1) = C(0)$	41.0(2) 121.5(2)
C(5) = Fe(1) = C(10)	103.8(3)	C(5) = Fe(1) = C(9)	121.3(3)
C(5) - Fe(1) - C(8)	137.0(2)	C(5) - Fe(1) - C(7)	100.2(2)
C(3) = Fe(1) = C(0)	122.7(2)	C(4) = Fe(1) = C(10) C(4) = Fe(1) = C(10)	122.0(3)
C(4) = Fe(1) = C(9) $C(4) = E_0(1) = C(7)$	107.4(3)	C(4) = Fe(1) = C(8) C(4) = Fe(1) = C(6)	$122.\delta(2)$
C(4) = Fe(1) = C(7)	138.2(2)	C(4) = Fe(1) = C(0)	159.0(3)
C(4) = Fe(1) = C(3) C(3) = Fo(1) = C(0)	40.3(3)	C(3) = Fe(1) = C(10) C(2) = Fo(1) = C(2)	100.1(3) 108.5(2)
$C(3) = \Gamma C(1) = C(3)$ $C(3) = E_0(1) = C(7)$	124.0(2) 122.2(2)	$C(3) = \Gamma C(1) = C(3)$ $C(2) = E_0(1) = C(3)$	100.3(2)
$C(3) = \Gamma^{*}(1) = C(7)$	122.2(3)	C(3) = Fe(1) = C(0) C(2) = Fo(1) = C(4)	137.2(3)
$C(3) = \Gamma^{*}(1) = C(3)$ $C(2) = E_{0}(1) = C(10)$	156 2(2)	C(3) = FC(1) = C(4) C(2) = Fc(1) = C(0)	41.1(3) 161.2(2)
$C(2) = \Gamma c(1) - C(10)$ $C(2) = E_{0}(1) - C(10)$	130.2(2) 124.0(2)	$C(2) = \Gamma C(1) = C(9)$ $C(2) = E_0(1) = C(7)$	101.2(2) 107.6(2)
C(2) = Fc(1) = C(0) C(2) = Fc(1) = C(0)	124.9(3)	C(2) = Fc(1) = C(7) C(2) = Fc(1) = C(5)	68 8(3)
$C(2) = 1^{-1}C(1) = C(0)$	120.3(3)	$C(2) = \Gamma C(1) = C(3)$	(apprimus 1)
			(continued)

Table 4 (continued)
-----------	------------

C(2)-Fe(1)-C(4)	69.2(3)	C(2)-Fe(1)-C(3)	41.5(3)
C(1)-Fe(1)-C(10)	120.0(3)	C(1)-Fe(1)-C(9)	156.5(3)
C(1)-Fe(1)-C(8)	161.2(3)	C(1)-Fe(1)-C(7)	124.1(3)
C(1)-Fe(1)-C(6)	105.9(2)	C(1)-Fe(1)-C(5)	40.5(3)
C(1)-Fe(1)-C(4)	68.5(3)	C(1)-Fe(1)-C(3)	69.2(3)
C(1)-Fe(1)-C(2)	41.0(3)	C(25)-Fe(2)-C(26)	40.3(2)
C(24)-Fe(2)-C(26)	68.4(2)	C(24)-Fe(2)-C(25)	40.9(2)
C(23)-Fe(2)-C(26)	68.5(2)	C(23)-Fe(2)-C(25)	68.9(3)
C(23)-Fe(2)-C(24)	41.4(2)	C(22)-Fe(2)-C(26)	40.3(2)
C(22)-Fe(2)-C(25)	68.2(2)	C(22)-Fe(2)-C(24)	69.0(2)
C(22)-Fe(2)-C(23)	41.0(2)	C(17)-Fe(2)-C(26)	120.9(2)
C(17)-Fe(2)-C(25)	157.3(2)	C(17)-Fe(2)-C(24)	159.1(3)
C(17)-Fe(2)-C(23)	121.2(2)	C(17)-Fe(2)-C(22)	105.2(2)
C(21)-Fe(2)-C(26)	108.1(3)	C(21)-Fe(2)-C(25)	122.6(3)
C(21)-Fe(2)-C(24)	158.2(2)	C(21)-Fe(2)-C(23)	159.3(2)
C(21)-Fe(2)-C(22)	123.3(2)	C(21)-Fe(2)-C(17)	41.6(2)
C(20)-Fe(2)-C(26)	126.4(3)	C(20)-Fe(2)-C(25)	109.8(2)
C(20)-Fe(2)-C(24)	122.4(2)	C(20)-Fe(2)-C(23)	157.0(2)
C(20)-Fe(2)-C(22)	161.6(3)	C(20)-Fe(2)-C(17)	69.2(2)
C(20)-Fe(2)-C(21)	41.1(2)	C(19)-Fe(2)-C(26)	163.0(2)
C(19)-Fe(2)-C(25)	126.3(2)	C(19)-Fe(2)-C(24)	108.0(2)
C(19)-Fe(2)-C(23)	120.6(2)	C(19)-Fe(2)-C(22)	155.6(3)
C(19)-Fe(2)-C(17)	68.6(2)	C(19)-Fe(2)-C(21)	68.6(2)
C(19)-Fe(2)-C(20)	40.3(2)	C(18)-Fe(2)-C(26)	155.8(2)
C(18)-Fe(2)-C(25)	161.2(2)	C(18)-Fe(2)-C(24)	123.1(3)
C(18)-Fe(2)-C(23)	105.1(3)	C(18)-Fe(2)-C(22)	119.7(3)
C(18)-Fe(2)-C(17)	41.0(2)	C(18)-Fe(2)-C(21)	69.1(2)
C(18)-Fe(2)-C(20)	68.3(2)	C(18)-Fe(2)-C(19)	40.3(2)
Fe(1)-C(1)-C(5)	70.4(3)	Fe(1)-C(1)-C(2)	68.1(3)
C(2)–C(1)–C(5)	108.0(5)	Fe(1)-C(2)-C(1)	70.8(4)
C(1)–C(2)–C(3)	108.0(6)	Fe(1)-C(2)-C(3)	69.1(4)
Fe(1)-C(3)-C(2)	69.4(4)	C(2)-C(3)-C(4)	108.0(5)
Fe(1)-C(3)-C(4)	70.7(5)	Fe(1)-C(4)-C(3)	68.2(5)
C(3)–C(4)–C(5)	108.0(6)	Fe(1)-C(4)-C(5)	70.6(4)
C(1)-C(5)-C(4)	108.0(6)	Fe(1)-C(5)-C(4)	68.8(4)
Fe(1)-C(5)-C(1)	69.1(4)	Fe(1)-C(6)-C(10)	68.8(3)
Fe(1)-C(6)-C(7)	71.7(4)	C(7)-C(6)-C(10)	108.0(4)

the spin decoupling technique. All the examined samples were dissolved in CDCl_3 that was used also as an internal reference.

The homogeneity of the ligands containing iron and sulfur or of the complexes was checked by using a Philips XL40 model scanning electron microscope equipped with an EDAX PV99 X-ray energy dispersive spectrometer. Metal or iron:sulfur ratios were determined by energy dispersive X-ray spectrometry (EDX) [22].

The solvent content (H₂O or MeOH) was evaluated by thermal analysis curves by using a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml min⁻¹; heating rate 5°C min⁻¹) and in air under the same conditions. Neutral alumina (Carlo Erba product) was used as reference material.

All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG Analytical Ltd.) operating in electron impact (EI) (70 eV, 200 mA,



Scheme 1.

ion source temperature 200°C) and fast atom bombardment (FAB) (8 KeV Xe atom bombarding a thioglycerol/acetic acid solution of the sample) conditions [23].

Mössbauer spectra were obtained at 80 K on a conventional constant-acceleration spectrometer, which utilizes a room-temperature rhodium matrix cobalt-57 source. The spectra were fitted to Lorentzian line shapes by using a standard least-squares computer minimization technique [24].

3. Results and discussion

3.1. Schiff bases bearing ferrocene groups

Formylferrocene and 1,1'-diformylferrocene are excellent precursors in the preparation of acyclic and cyclic Schiff bases containing redox active groups in close proximity to the coordinating moieties. While formylferrocene is commercially available, 1,1'-diformylferrocene must be prepared, following literature procedure [18], by reaction of ferrocene with *n*-BuLi in the presence of *N*,*N*-tetramethylethylenediamine and converting the resulting 1,1'-dilithiumferrocene compound into the diformyl-derivatives with dimethylfor-

mamide. As reported in Section 2, particular care must be devoted to the purity of dimethylformamide to avoid the formation of by-products. Formyl- and diformylferrocene are respectively yellow and dark red solids, very soluble in the common organic solvents that can be recrystallized from hydrocarbons.

The acyclic Schiff bases $L_A \cdots L_K$ bearing a progressively increasing number of ferrocene groups have been prepared by condensation in acetonitrile or methanol of the appropriate amine and formylferrocene according to Scheme 1.

The synthetic pathways in Scheme 1 show that formylferrocene forms, with amines bearing only one NH₂ group (as 2-aminomethyl-pyridine or 2-aminoethylthiophenol), the [1 + 1] condensation products L_A and L_B while a [2 + 1] condensation reaction takes place when formylferrocene is reacted with the diamines H₂N-R-NH₂ in a 2:1 molar ratio. By this procedure L_C-L_J have been obtained. Finally a [3 + 1] condensation, with the formation of L_K , occurs when the amine precursor tris-(2-aminoethyl)amine is condensed with formylferrocene in a 1:3 molar ratio. By a similar synthetic procedure the macroacyclic (L_L and L_M) or macrocyclic compounds (L_O , L_P , L_Q and L_S) of Scheme 2 have been obtained by condensation of 1,1'-



Scheme 2.

diformylferrocene and the appropriate amine in a 1:2 and 1:1 molar ratio, respectively. While for the acyclic complexes only a [1 + 2] condensation occurs, a [2 + 2]or [1 + 1] cyclization may take place when polyamines of the type $H_2N-R-NH_2$ are used, the type of cyclization strongly depending on the nature of R. In fact it was already reported that, when 1,1'-diformylferrocene is reacted with diamines as 1,2-diaminoethane (or 1,3-diaminopropane), [2+2] cyclic compounds as L_N are obtained [11], while with amines containing longer aliphatic chains the [1 + 1] cyclic compounds are formed [25]. Thus, using the tetramine N,N'-bis-(3-aminopropyl)-piperazine, the [1 + 1] cyclic compound L_Q was found while, when 1,2-diamino-2-methylpropane or 1,3diamino-2,2-dimethylpropane or 1,3-diamino-methylbenzene are the diamine precursors, respectively, the [2+2] macroacycles L_O, L_P and L_S are formed.

In these Schiff bases ($L_A \cdots L_S$) the ferrocene groups are in close proximity to the coordinating site; this can cause hydrolysis when reacted with metal ions. In order to avoid this behaviour and maintain the coordinating ability of the Schiff base, aminomethylferrocene was prepared [18] and reacted with the appropriate formylor diformyl-precursors. In this amine precursor and hence in the related Schiff base derivatives a CH₂ spacer was inserted between the amine or imine and the ferrocene groups. Aminomethylferrocene was prepared by reaction of {[tris-(methylammonium)methyl]ferrocene}. iodide with sodium azide followed by the reduction of the resulting ferrocene azide by means of NaBH₄ [19]. Very recently it has been conveniently prepared by initially converting formylferrocene into its oxime by condensation with hydroxylamine followed by the reduction of the resulting product with LiAlH₄ in THF [26]. Aminomethylferrocene is very soluble in the common organic solvents; its IR spectrum shows the characteristic (NH₂ at 3290 and 3250 cm⁻¹). The condensation reaction of aminomethylferrocene respectively with 2,6diformylpyridine, 2,6-diformyl-4-chlorophenol in a 2:1 molar ratio and with 3-methoxy-2-hydroxybenzaldehyde in a 1:1 molar ratio produces the acyclic compounds $L_T \cdots L_V$ as shown in Scheme 3.

Finally, 1,4-diaminomethylbenzene was used as amine precursor in the condensation reaction with formylferrocene and 1,1'-diformylferrocene to yield respectively the [2 + 1] condensation product (L_W) and the $[2 + 2]_n$ oligomeric or polymeric species (L_Z) (Scheme 4a). It must be noted that 1,3-diaminoxylylbenzene reacts with the 1,1'-diformylferrocene to form the cyclic $[2 + 2]_n$ compound L_s and not the polymeric $[2 + 2]_n$. This was confirmed by mass spectra where the parent peak due to the cyclic species has been obtained. Of course, formylferrocene, by reaction with 1,3-diaminoxylylbenzene, forms the [2 + 1] acyclic compound L_R (Scheme 4b).





The prepared compounds L_A…L_Z are orange-red solids (only L_B is a red-brown oil), very soluble in the most common organic solvents including hydrocarbons. In the compounds containing sulfur, the homogeneity and the correct 2:1 ($L_{\rm E}$) or 1:1 ($L_{\rm B}$) Fe:S ratio was ascertained by SEM and EDX analyses. In addition, ¹H NMR, IR and mass spectrometry agree with the formulation proposed. In particular in the ¹H NMR spectra in CDCl₃ a characteristic peak at 8.15-8.07 ppm due to the CH=N iminic protons can be detected; it must be noted that the peaks due to the formyl protons CH=O lie at 9.93 and 9.91 ppm, respectively, in the formyland diformylferrocene derivatives. However, they completely disappear in the Schiff base derivatives, suggesting that the designed condensation takes place. As significant examples of the prepared Schiff bases, the ¹H NMR spectra of L_F , L_G and L_J are discussed in detail. The ¹H NMR spectrum of L_F shows the iminic protons at 8.12 ppm, the cyclopentadienyl protons at 4.60, 4.34 and 4.18 ppm and the ethylenic protons as coupled triplets at 3.66 and 2.84 ppm. For L_G the iminic protons lie at 8.11 ppm, the cyclopentadienyl protons at 4.60, 4.33 and 4.15 ppm, the ethylenic protons at 3.58 and 2.71 ppm, and the methylenic protons at 2.38 ppm. Similarly in the ¹H NMR spectrum of L_J, the peaks due to the iminic protons occur at 8.08 ppm, the cyclopentadienyl protons at 4.60, 4.32 and 4.14 ppm and the ethylenic protons at 3.40, 2.49, 2.39 and 1.81 ppm, respectively.

Furthermore, the absence in the IR spectra of the Schiff bases of the ν C=O, which lies in the formylferrocene at $\cong 1680$ cm⁻¹, and the simultaneous presence of a strong peak at 1650–1635 cm⁻¹ due to ν C=N add further evidences that the condensation reaction was successful. Moreover, additional IR peaks, due to specific groups present in the Schiff bases, are easily detectable; for example, in the compounds containing etheric or crown–ether moieties (L_H, L_J and L_N), strong absorptions at 1310 cm⁻¹ due to ν C–O–C group have been observed and in those containing pyridine (L_A and L_M) characteristic peaks at 1600 and 735 cm⁻¹ have been detected.

Mass spectrometry has proved to be a particularly valid analytical tool for the characterization of these systems. In the FAB mass spectra of almost all the prepared compounds, the parent peak $[M + H]^+$ was detected at the appropriate m/z value; moreover, the fragmentation patterns are consistent with the proposed structure. A specific and detailed mass spectrometry investigation on some of the prepared compounds was carried out and published elsewhere [16].

The coordination properties of these compounds have also been studied; when reacted with transition metal salts (i.e. copper(II), or nickel(II) chloride, nitrate, acetate or perchlorate), they form complexes that, according to elemental analyses, IR, SEM and EDX investigations, may be formulated as $M(L)(X)_2$ (L = $L_D \cdots L_K$) (X = Cl⁻, ClO₄⁻). For instance, the com-





plexes $Pd(L_F)(Cl)_2$, $Cu(L_H)(H_2O)(ClO_4)_2$, $Ni(L_I)-(ClO_4)_2 \cdot 4H_2O$ and $Ni(L_K)(ClO_4)_2$ have been isolated: a correct elemental analysis and a metal:iron:chloride ratio of 1:2:2 for the first three complexes and 1:3:2 for the fourth complex was ascertained by SEM and EDX investigations, respectively. When dissolved for crystallization, they quite often suffer additional reactions. These complexes are not very stable in solution and easily give rise to hydrolytic products with the consequent formation of complexes apparently of the type $M(L-NH_2)X_2$ or $M(L_KNH_2)X_2$. Quite often the hydrolytic process occurs before the isolation of the Schiff

base complex; this may explain why we were only able to isolate a few complexes with the prepared Schiff bases. The formulation of these hydrolytic compounds is proposed on the basis of their elemental analyses, SEM and EDX investigations and IR spectroscopy.

Thus, during the experimental procedure to obtain purify or recrystallize the di- or tri-imine complexes, the monoimine $Cu(L_F-NH_2)_2(CH_3COO)_2H_2O$, $Ni(L_G-NH_2)_2(CH_3COO)_2 \cdot 2H_2O$, $Ni(L_H-NH_2)_2(ClO_4)_2 \cdot 2H_2O$ and the diamine derivatives $Ni(L_K-NH_2)(ClO_4)_2 \cdot 4.5H_2O$ and $Pt(L_K-NH_2)(Cl)_2$ have been isolated. Again the atomic ratios and the homogeneity of the complexes as determined by SEM and EDX investigations support the proposed formulations.



The presence in the IR spectra of these complexes of bands at about $3300-3200 \text{ cm}^{-1}$ due to $v \text{ NH}_2$, suggests that the ligand has suffered hydrolytic process while the strong IR band at 1650–1640 cm⁻¹, due to v C=N, confirms the presence of iminic bonds. Finally, the absorptions due to the presence of the counteranions are clearly detectable; these groups seem to be coordinated in the case of the chloride, v M-Cl at about 330–315 cm⁻¹, and ionic in the case of the prechlorate (a band centered at 1150 cm⁻¹ due to $v \text{ ClO}_4^-$).

3.2. The structure of L_H

In order to confirm that the condensation reactions proposed above really occur, an X-ray structural determination of L_F was carried out. Yellow–ochre crystals of the Schiff base, suitable for diffractometric investigation, were obtained by slow evaporation of a diethyl ether solution of the compound.

Two molecules are present in the asymmetric unit and are reported in Fig. 1 together with the numbering scheme. The two molecules are chemically equivalent and the most relevant difference is the spatial develop-



Fig. 1. ORTEP plots at the 50% probability ellipsoid for the two molecules (a and b) present in the asymmetric unit together with the numbering scheme.

ment of the etheric-iminic chain that connects the ferrocenyl groups. In molecule B (containing Fe(3) and Fe(4)), the chain is more elongated than that in molecule A (containing Fe(1) and Fe(2)). The Fe(1)...Fe(2) distance is, in fact, 6.592(2) Å while the Fe(3)...Fe(4) distance is 10.008(2) Å. The N-C-C-O torsion angles are very similar (around $\pm 68-69^{\circ}$) apart from the case of the N(3)-C(38)-C(39)-O(2) chain that presents a torsion angle of -174.8° .

All the distances and angles are normal. The iminic C=N distances range between 1.27 and 1.28 Å, while the etheric C–O bond distances are in the 1.40–1.43 Å range. The ferrocenyl groups are in the eclipsed form and no relevant intra- or intermolecular interactions are present.

The crystal packing (Fig. 2) shows a columnar arrangement of the molecules along the *a*-direction.

3.3. Ferrocene containing amines

In order to overcome the hydrolytic problems encountered especially during the complexation reactions, the Schiff bases have been reduced to the corresponding acyclic or cyclic polyamines by reaction with NaBH₄ in THF; the same reactions have also been successfully carried out in methanol and water (Schemes 1 and 2). The obtained compounds are generally yellow solids stable both in air and solution. They do not suffer hydrolysis and give rise, when treated with a variety of transition metal salts such as copper(II), nickel(II), palladium(II) and rhodium(III), to stable, well-defined complexes.

Again, IR and NMR are diagnostic that the reaction does occur. In the IR spectra of these polyamines the strong peak at $\simeq 1640-1635$ cm⁻¹ (v C=N), present in the related Schiff bases, disappears and bands at 3312-3257 cm⁻¹, due to v NH, can be detected. The NMR spectra in CDCl₃ show the peaks due to the methylenic protons of the NH- CH_2 -Cp groups at 3.50-3.45 ppm, while the peaks due to the CH=N iminic protons, clearly detectable in the corresponding Schiff bases, are completely absent. As a significant example of the prepared amine derivatives, the ¹H NMR spectra of L'_{F} , L_{G}^{\prime} and L_{J}^{\prime} are discussed in detail and compared with those related to L_F , L_G and L_H reported earlier in this report. For L'_F , the cyclopentadienyl protons lie at 4.15, 4.11 and 4.08 ppm, the methylenic HN-CH₂-Cp protons at 3.49 ppm and the ethylenic protons at 2.80 and 2.65 ppm. For L'_G , the cyclopentadienyl protons occur at 4.16, 4.08 and 4.07 ppm, the methylenic protons HN-CH₂-Cp at 3.49 ppm, the ethylenic -CH₂CH₂protons at 2.68 and 2.46 ppm and the methylic proton (CH₃) at 2.14 ppm. Finally in L'_J, the ¹H NMR spectrum reveals peaks at 4.14, 4.08 and 4.07 ppm (cyclopentadienyl protons), at 3.47 ppm (methylenic protons), and at 2.63, 2.43, 2.35 and 1.68 ppm



Fig. 2. Crystal packing along the *a*-direction.

(ethylenic and propylenic protons). In all the prepared compounds there is a shift towards lower ppm for the same protons on going from the Schiff bases to the corresponding reduced amine derivatives as a consequence of the different deshielding ability of the iminic -CH=N- and the aminic $-CH_2-NH-$ groups.

Moreover, in the Schiff bases and in the reduced homologues derived from ferrocenedialdehyde, only one peak at 4.10-4.14 ppm due to the protons of the non-substituted cyclopentadienyl groups is observed. This peak lies at 4.25 ppm for formylferrocene; thus the reduction does not cause any significant shift on this signal. On the contrary, significative shifts are observed for the protons in the 2-, 5- and 4-positions of the cyclopentadienyl rings bearing the imine or amine groups. The peaks due to these protons, at 4.77 and 4.58 ppm in the formylferrocene, lie at 4.60 ppm and 4.34– 4.32 ppm in the Schiff bases, and are located at 4.15– 4.07 ppm in the reduced analogues.

The FAB mass spectra give further useful information on their structure. They show the parent peaks at the appropriate m/z value accompanied by the $[M + Na]^+$ cations; in particular, for the cyclic compounds, they further support the [2 + 2] nature of L'_O and L'_P and the [1 + 1] nature of L'_R .

These reduced ferrocene–amines do not suffer hydrolysis as a consequence of the reaction with the appropriate metal salts and easily form the related complexes in which the metal:ligand ratio depends on the shape of the ligand and also on the experimental conditions; for instance it was found that bidentate ligands favour the formation of $[M(L)_2]^{2+}$ complexes [5].

The potentially tridentate L'_F and L'_G or tetradentate L'_J ligands react with the appropriate metal salts (copper(II), nickel(II), and rhodium(III) chloride) to form the 1:1 complexes $M(L')(Cl)_n$ (n = 2 or 3) (Scheme 1). SEM and EDX analyses evidence the homogeneity of the prepared samples, the iron:metal:chloride:sulfur ratio 2:1:2:1 for $Ni(L'_F)(Cl)_2$ or $Cu(L'_F)(Cl)_2$ and the iron:metal:chloride ratio 2:1:2 for Cu(L'_G)(Cl)₂. Moreover, [Cu(CH₃CH₄)]ClO₄ reacts in CHCl₃/CH₃CN with $L'_{\rm F}$ to give the brown complex $[Cu(L'_{\rm F})]ClO_4$; for this complex, an iron:copper:chloride:sulfur ratio of 2:1:1:1 was deduced. The tripodal ligand L'_K also forms with copper(II) and nickel(II) chloride the complexes $M(L'_{K})(Cl)_{2}$ and with nickel(II) perchlorate Ni(L'_{K})- $(ClO_4)_2$; moreover L'_O , when treated with rhodium(III) chloride, gives rise to Rh(L'_O)(Cl)₃. SEM and EDX investigations give atomic ratios which fully agree with these formulations. The prepared complexes are solids, stable in air and in solution, moderately soluble in the most common organic solvents. Their IR spectra show peaks at 3275 - 3130 cm⁻¹ due to v NH; these absorption peaks are ca. 100 cm⁻¹ lower than those observed in the corresponding reduced ligands.

3.4. Mössbauer spectra

The Mössbauer spectra at 80 K (Table 5) of all the complexes present a single quadrupole split doublet with a narrow linewidth that indicates the presence of a single iron site deriving from the electronic and structural identity of the iron atoms in the two or three ferrocene groups present in the same compound. The

 Table 5

 Mössbauer effect parameters collected at 80 K

Compound	$\delta^{a} (\mathrm{mm} \ \mathrm{s}^{-1})$	$\Delta E_{\rm Q} \ ({\rm mm} \ {\rm s}^{-1})$	$\Gamma \text{ (mm s}^{-1}\text{)}$
L _A	0.444	2.294	0.282
L'_A	0.522	2.411	0.270
$Cu(L'_F)(ClO)_4$	0.518	2.349	0.286
$Cu(L'_A)Cl_2$	0.519	2.352	0.252
$Ni(L'_A)Cl_2$	0.522	2.369	0.259
L _B	0.439	2.288	0.343
L'_{B}	0.520	2.410	0.280
$Cu(L'_B)Cl_2$	0.523	2.392	0.277
$Ni(L'_B)Cl_2$	0.518	2.385	0.254
L _C	0.439	2.288	0.302
L _E	0.438	2.292	0.296
L' _E	0.512	2.360	0.264
$Cu(L'_E)Cl_2$	0.518	2.387	0.357
$Pd(L'_E)Cl_2$	0.513	2.380	0.340
$Ni(L'_E)Cl_2$	0.517	2.383	0.264
L _F	0.435	2.308	0.323
L'_F	0.538	2.387	0.291
$Cu(L'_F)Cl_2$	0.520	2.281	0.408
$Ni(L'_F)(ClO)_4$	0.512	2.246	0.363
L _H	0.431	2.218	0.328
$L'_{\rm H}$	0.511	2.361	0.331
$Ni(L'_H)Cl_2$	0.509	2.343	0.262
L' _G	0.509	2.214	0.423
Fe-am ^b	0.555	2.375	0.372
L	0.507	2.348	0.340
L _M	0.508	2.335	0.445
Fe-az ^b	0.514	2.35	0.42

^a δ is referred to r.t. α -Fe.

^b Fe-am, ferrocene-methylamine; Fe-az, ferrocene-azide.

parameters are typical for ferrocene derivatives containing low spin iron(II)¹. It is usually assumed that compounds of this type present isomer shift values virtually independent from the presence of ring substituents and close to that of FeCp₂ and quadrupole splittings, depending slightly on their electron-donor abilities [27-29]. In partial disagreement with these statements, the present compounds can be easily divided into two groups according to the respective values of the isomer shift. The first group with δ around 0.44 mm s⁻¹, is formed by the Schiff bases (L), while the second, with δ around 0.52 mm s⁻¹, contains the reduced analogues (L') and the related complexes. Within each group, δ is rather constant i.e. 0.438 + 0.004 and 0.517 + 0.007 mm s⁻¹, respectively. It is evident that the Mössbauer parameters for these compounds are mainly governed by the ferrocene-imine function and that virtually no role is played by the nature of the central atom, N, O, or S, or by the

eventual presence of a second metal in the molecule. The isomer shift values for the Schiff base compounds are smaller than that of the parent FeCp₂ (0.52 mm s⁻¹), meaning that the s electron density at the iron nucleus is affected by the presence of the imine function, while the reduction of that function increases the isomer shift towards values comparable with FeCp₂. The reason for this may be found in the electron withdrawing capability of the C=N moiety that enhances the metal-to-ligand charge transfer and indirectly increases the s electron density at the iron nucleus.

As already observed, the imine function of the Schiff base behaves as an electron buffer that completely isolates the cyclopentadienyl ring from the influence of any other group eventually bonded to the nitrogen atoms. In fact, the Mössbauer parameters of L_Q-L_T , in which the C=N double bond is on the opposite side with respect to the nitrogen atom, corroborate this statement: the isomer shift values are in full agreement with those of the reduced compounds. Finally, the reduction of the double bond of the Schiff base gives the ferrocene moiety the same electronic structure of a normal FeCp₂ derivative, as proved by the values of the isomer shift.

The behaviour of the quadrupole splitting can be explained in a similar way; compared to the $FeCp_2$ compound, the presence of the Schiff base on the Cp rings causes a small but significant decrease, while the reduction of the C=N double bond increases its value toward that of $FeCp_2$. The rigidity imposed to the structure by the iminic function compared to the aminic one can cause the loss of the parallelism between the two Cp rings and so to an imbalance of the iron to Cp bonds that affect the quadrupole splitting in an opposite way giving rise to an overall decrease in its value. In general the coordination of a metal causes a slight decrease in the quadrupole splitting that may be due to very small variations in the crystal structure of these compounds.

Some compounds display unexpected parameters: L_I , L_L and L_O present values perfectly in line with those of the reduced compounds. It is possible that reduction takes place during the many and long operations required to obtain a suitable purity for these compounds. This reduction process has been observed already for the [2 + 2] cyclic Schiff base obtained by condensation of 2,6-diformyl-4-chlorophenol and 1,2-diaminobenzene ascertained also by single crystal X-ray diffractometric data [30]. However, it must be noted that Mössbauer parameters comparable with those found for the reduced species, have been reported in the recent literatures [27–29] for mono- or bis-aldimine derivatives of the following type:

¹ The Mössbauer spectrum of $L_{\rm H}$ collected at 298 K, gives the same parameters as those at 80 K, as expected for ferrocene derivatives containing low spin iron(II).



Also, for these compounds, which closely resemble, respectively, L_A or L_B and L_L or L'_M ; X-ray structural investigations demonstrate the occurrence of the designed imine derivatives. Further studies are currently in progress over a variety of substituted Schiff bases bearing ferrocene groups to completely evaluate the electronic contribution of the different groups on the Mössbauer parameters.

Finally, it may be interesting to note that formylferrocene and 1,1'-diformylferrocene give Mössbauer parameters in line with those of the reduced ferrocene amine compounds but not with those of the related imine derivatives. These results may be ascribed to the differences in electronegativity between the iminic and formyl groups (i.e. the iminic nitrogen or the formylic oxygen).

4. Conclusions

In conclusion, a synthetic route is described to obtain Schiff bases bearing up to three ferrocene moieties, their reduction by $NaBH_4$ to the corresponding amine derivatives and the related complexes. The amine compounds form stable, well-defined complexes, while the corresponding imine derivatives easily suffer hydrolytic processes.

The Mössbauer spectra of the prepared ligands and complexes show the presence of a single iron site deriving from the electronic and structural identity of the two or three ferrocene groups in the same compound and may be diagnostic of the presence of Fc-HC=NR, Fc-CH₂-N=CHR or Fc-CH₂-NHR groups. Moreover, the complexation of different metal salts to the aminic groups induces only minor effects on the Mössbauer parameters. These results indicate that the presence of a CH₂ spacer between ferrocene and iminic or aminic moieties seems to be the crucial reason for the significant variation of the Mössbauer parameters with respect to the imine derivatives containing Fe-CH=N-R groups.

Parallel studies [16] show that these systems can facilitate the transfer of Cu^{2+} , Cd^{2+} , Ni^{2+} and Zn^{2+} across the water/1,2-DCE interface when the aqueous phase is at appropriate pH. These ligands can be readily oxidized and reduced at a metallic electrode. The ligands in their reduced form show coordination ability

towards a few transition metal ions and the complexes formed between them exhibited intermediate stability, which is important for the stripping processes when the ligand is oxidized to release the metal ion.

The results so far obtained are very promising and further studies are currently in progress on the possibility of setting up new separation technologies or new molecular devices based on ferrocene derivatives.

5. Supplementary material

Atomic coordinates, bond distances and angles, and thermal parameters are available upon request from the authors.

Acknowledgements

The authors would like to thank A. Aguiari, O. Biolo, A. Moresco and C. Everti for their technical assistance and the Progetto Strategico-CNR 'Tecnologie Chimiche Innovative' and the EEC (contract no. BRPR-CT95-0010) for financial support.

References

- (a) T. Hayashi, Pure Appl. Chem. 60 (1988) 7. (b) A. Hayashi, M. Konishi, Y. Kobon, M. Kudoa, T. Haguchi, K. Hinsu, J. Am. Chem. Soc. 106 (1984) 138. (c) A. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, J. Am. Chem. Soc. 111 (1989) 6301. (d) A. Hayashi, A. Yamamoto, Y. Ito, J. Chem. Soc., Chem. Commun. (1986) 1090.
- [2] (a) C.P. Andrieux, C. Blooman, J.M. Dumas-Bouchiat, F. M'Halla, J.M. Saveaat, J. Am. Chem. Soc. 102 (1980) 3806. (b) C.P. Andrieux, C. Blooman, J.M. Dumas-Bouchiat, F. M'Halla, J.M. Saveaat, J. Am. Chem. Soc. 101 (1979) 431. (c) V. Guerchais, E. Roman, D. Astnic, Organometallics 39 (1986) 2505.
- [3] J.A. Epstein, J.S. Miller, in: D. Gattesci, O. Kahn, J.S. Miller, F. Palacio (Eds.), Magnetic Molecular Materials, NATO ASI Ser. No. 198, Kluwer, Dordrecht, Netherlands, 1990, pp. 151, 159.
- [4] (a) P.D. Beer, Adv. Inorg. Chem. 39 (1993) 79. (b) P.D. Beer, in: L. Fabbrizzi, A. Poggi (Eds.), Transition Metals in Supramolecular Chemistry, vol. 448, Nato ASM Ser. C, Kluwer, Dordrecht, Netherlands, 1994, p. 33 and references therein. (c) C.S. Slone, C.A. Mirkin, G.P.A. Yap, I.A. Guzei, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 10743. (d) P.D. Beer, F. Szemes, V. Balzani, C.M. Salà, M.G.B. Drew, S.W. Dent, M. Maestri, J. Am. Chem. Soc. 119 (1997) 11864.
- [5] (a) A. Benito, J. Camo, R. Martinez-Manez, J. Soto, J. Paya, F. Lloret, M. Julve, J. Faus, M.D. Maroos, Inorg. Chem. 32 (1993) 1197. (b) M.J.L. Tendero, A. Benito, R. Martinez-Manez, J. Soto, J. Chem. Soc., Dalton Trans. (1996) 4121. (c) M.J.L. Tendero, A. Benito, R. Martinez-Manez, J. Soto, E. Garcia-Espana, J.A. Ramirez, M.J. Burguete, S.V. Luis, J. Chem. Soc., Dalton Trans. (1996) 2923.
- [6] (a) P.D. Beer, Chem. Soc. Rev. 18 (1989) 409. (b) P.D. Beer, Adv. Inorg. Chem. 39 (1992) 79. (c) E.C. Constable, Angew. Chem., Int. Ed. Engl. 30 (1991) 407 and references therein. (d) M.C. Grossel, M.R. Goldspink, J.A. Hriljac, S.C. Weston,

Organometallics 10 (1991) 851 and references therein. (e) J.C. Medina, T.T. Goodnow, M.T. Rojas, J.L. Atwood, B.C. Lynn, A.E. Kaifer, G.W. Gokel, J. Am. Chem. Soc. 114 (1992) 10583.

- [7] (a) B. Delavaux-Nicot, Y. Guary, B. Douziech, R. Mathieu, J. Chem. Soc., Chem. Commun. (1995) 585. (b) B. Delavaux-Nicot, N. Lugan, R. Mathieu, J.-P. Majoral, Inorg. Chem. 31 (1992) 334. (c) B. Delavaux-Nicot, R. Mathieu, Phosphorous, Sulfur, Silicon Relat. Elem., 77 (1993) 323. (d) B. Delavaux-Nicot, R. Mathieu, D. de Montauzon, G. Lavigne, J.-P. Majoral, Inorg. Chem. 33 (1994) 334. (e) B. Delavaux-Nicot, B. Douziech, R. Mathieu, G. Lavigne, Inorg. Chem. 34 (1995) 4256. (f) B. Delavaux-Nicot, Y. Guary, R. Mathieu, J. Organomet. Chem. 489 (1995) C87. (g) B. Delavaux-Nicot, A. Begeard, A. Banssekson, B. Donnadien, G. Commenges, Inorg. Chem. 36 (1997) 4789
- [8] C.M. Asseling, G.C. Fraser, H.K. Halljr, W.E. Lindsell, A.B. Padias, P.M. Preston, J. Chem. Soc., Dalton Trans. (1997) 3765.
- [9] (a) C. Lopez, J. Sales, X. Solans, Z. Zquiak, J. Chem. Soc., Dalton Trans. (1992) 2321. (b) R. Bosque, C. Lopez, J. Sales, X. Solans, M. Font-Bardia, J. Chem. Soc., Dalton Trans. (1994) 735. (c) R. Bosque, M. Font Bardia, C. Lopez, J. Sales, J. Silver, X. Solans, J. Chem. Soc., Dalton Trans. (1994) 747.
- [10] (a) A. Houlton, N. Jasim, R.M.G. Roberts, J. Silver, D. Cunningh, P. Mc Ardle, T. Higgins, J. Chem. Soc., Dalton Trans. (1992) 2235. (b) M. Bracci, C. Ercolani, B. Floris, M. Bassetti, A. Chesi-Villa, C. Guastini, J. Chem. Soc., Dalton Trans. (1990) 1357.
- [11] P.D. Beer, Z. Chen, M.G.B. Drew, A.O.M. Johnson, D.K. Suite, P. Spencer, Inorg. Chem. Acta 246 (1996) 143.
- [12] A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, Germany, 1995.
- [13] G. Lopez, R. Bosque, X. Solans, M. Font-Bardia. J. Silver, J. Fern, J. Chem. Soc., Dalton Trans. (1995) 4053.
- [14] R.E. Blumer, F. Lianza, P.S. Pregosin, H. Ruegger, A. Togni, Inorg. Chem. 32 (1993) 2663.
- [15] P. Guerriero, S. Tamburini, P.A. Vigato, Coord. Chem. Rev. 139 (1995) 17.

- [16] (a) E. Bullita, S. Tamburini, P.A. Vigato, M. Carbini, S. Catinella, P. Traldi, Rapid Commun. Mass Spectrom. 10 (1996) 490. (b) T. Cheng, D.J. Schiffrin, E. Bullita, P. Guerriero, P.A. Vigato, in: S. Daolio, E. Tondello, P.A. Vigato (Eds.), Syntheses and Methodologies in Inorganic Chemistry, vol. 5, La Photograph, Padua, Italy, 1995, p. 464. (c) A. Aguiari, E. Bullita, P.A. Vigato, U. Russo, in: S. Daolio, E. Tondello, P.A. Vigato (Eds.), Syntheses and Methodologies in Inorganic Chemistry, vol. 6, La Photograph, Padua, Italy, 1996, p. 288.
- [17] D.D. Perrin, W.L. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, 2nd ed., Pergamon, Oxford, UK, 1982.
- [18] G.G.A. Balavoine, G. Doisneau, T. Fillebeen-Khan, J. Organomet. Chem. 412 (1991) 381.
- [19] D.E. Bublitz, J. Organomet. Chem. 23 (1970) 225.
- [20] G.M. Sheldrick, SHELX86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1985.
- [21] G.M. Sheldrick, SHELXL, Program for the Crystal Structure Refinement, University of Göttingen, Germany, 1993.
- [22] P. Guerriero, P.A. Vigato, B. Burtet-Fabris, Inorg. Chim. Acta 16 (1989) 155.
- [23] P.P. Morgan, J.M. Beynon, R.M. Bateman, B.M. Green, Int. J. Mass Spectrom. Ion Phys. 28 (1978) 171.
- [24] W.M. Reiff, in: G.J. Long, F. Grandjean (Eds.), Mössbauer Spectroscopy Applied to Magnetism and Materials Science, vol. 1, Plenum Press, New York, 1993, Ch. 6.
- [25] P.D. Beer, Z. Chen, M.G.B. Drew, J. Kingston, M. Ogden, P. Spencer, J. Chem. Soc., Chem. Commun. (1993) 1046.
- [26] P.D. Beer, D.K. Smith, J. Chem. Soc., Dalton Trans. (1990) 2181.
- [27] A. Houlton, J.R. Miller, R.M.G. Roberts, J. Silver, J. Chem. Soc., Dalton Trans. (1998) 417.
- [28] R. Bosque, M. Font-Bardia, C. Lòpez, J. Sales, J. Silver, X. Solans, J. Chem. Soc., Dalton Trans. (1994) 747.
- [29] J. Silver, J.R. Miller, A. Houlton, M.T. Ahmet, J. Chem. Soc., Dalton Trans. (1994) 3355.
- [30] A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato, Inorg. Chim. Acta 202 (1992) 157.