SYNTHESES, MÖSSBAUER, AND ^{1}H NMR STUDY OF SOME CYCLOPENTADIENYLIRON CARBONYL COMPLEXES WITH POTENTIALLY BIDENTATE AMINE LIGANDS

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Summary

The coordination behaviour of the amines naphthyridine (naph), pyridazine (pyr), pyrazine (pz) and 3,5-dimethylpyrazole (3,5-DMP) towards the iron fragment $[CpFe(CO)_2]^+$ ($Cp = \eta^5\text{-}C_5H_5$) has been studied. The compounds obtained were characterized and their variable temperature (VT) ^{1}H NMR and ^{57}Fe Mössbauer spectra investigated.

Introduction

Several transition metal complexes containing potentially bidentate amine ligands acting in a monodentate mode show a dynamic behaviour which renders both nitrogen atoms equivalent. This dynamic behaviour has been refered to as "metal-shuttling" [1–3]. The major factor in determining both the rate and the mechanism of "metal-shuttling" has been shown to be the relative orientation of the nitrogen lone pairs and the nature of the central atom. This type of study has been carried out either on square-planar complexes of a formally d^8 central atom [2,4–6] or on approximately octahedral complexes of a d^6 transition-metal ion [1,3,7,8]. In an attempt to throw some light on "metal-shuttling" between nitrogen atoms we have prepared pseudooctahedral complexes of a d^6 metal ion of the type $[CpFe(CO)_2L]^+$ ($Cp = \eta^5\text{-}C_5H_5$; L = naph, pyr, pz, 3,5-DMP) and studied their dynamic properties by variable temperature (VT) ^{1}H NMR.

Results and discussion

Preparation and characterization

Several methods for the preparation of cationic complexes of the type $[CpFe(CO)_2L]^+$ have been reported. In the present work we used two of them: (i) displacement of the weakly bound solvent molecule (THF) in $[CpFe(CO)_2(THF)]^+$, prepared by the reaction of $CpFe(CO)_2I$ with $AgClO_4$ in THF, by the incoming

TABLE 1

ANALYTICAL, CONDUCTIVITY, AND IR DATA

Compound	Analytical data (found (calcd.) (%))			IR data [a] (cm^{-1})		Molar conductivity [b] $(ohm^{-1}$ cm^2 $mol^{-1})$	Dec. temp. (°C)
	C	H	N	$\nu(CO)_{sym}$	$\nu(CO)_{antisym}$		
$[CpFe(CO)_2(naph)]ClO_4$ (a)	44.2 (44.31)	2.8 (2.73)	7.3 (7.10)	2060	2015	133	155
$[CpFe(CO)_2(3,5\text{-}DMP)]ClO_4$ (b)	38.5 (38.69)	3.5 (3.52)	7.5 (7.52)	2065	2015	143	160
$[CpFe(CO)_2(pyr)]ClO_4$ (c)	37.0 (37.06)	2.4 (2.50)	7.7 (7.86)	2075	2030	146	150
$\{[CpFe(CO)_2]_2pz\}(ClO_4)_2$ (d)	34.1 (34.16)	2.3 (2.23)	4.4 (4.43)	2090 [c]	2045 [c]	69 [d]	185

[a] In $CHCl_2$ solution unless otherwise indicated. [b] In acetone solution unless otherwise indicated. [c] KBr pellet. [d] In DMSO solution.

ligand [9], and (ii) oxidation of the dimer $[CpFe(CO)_2]_2$ with $AgClO_4$ in the presence of the appropriate ligand [10–12]. When a solution of $[CpFe(CO)_2THF]^+$ in CH_2Cl_2, was treated with two equivalents of the amine, mononuclear complexes of the type $[CpFe(CO)_2L]^+$ were obtained for L = naph (a) and 3,5-DMP (b), while a dinuclear complex $[Cp(CO)_2Fe\text{-}pz\text{-}Fe(CO)_2Cp]^{2+}$ (d) was obtained for L = pyrazine. For L = pyridazine very low yields of the mononuclear complex $[CpFe(CO)_2pyr]^+$ (c) were obtained, and consequently, this product was prepared by method (ii). The preparation of compound (c), has already been reported but in much lower yield [12].

All the compounds are yellow, air-stable solids, which decompose when their solutions are exposed to air. They are soluble in acetone, CH_2Cl_2 and $CHCl_3$, slightly soluble in benzene and toluene, and almost insoluble in saturated hydrocarbons and diethyl ether. Analytical data, decomposition temperatures and conductivity measurements are listed in Table 1.

The analytical data are in accord with the proposed formulas, and conductivity measurements show that compounds (a), (b), and (c) are AB electrolytes.

The infrared spectra show the bands due to all the coordinated ligands and to the perchlorate anion. The band maxima for $\nu(CO)$ vibrations are listed in Table 1, and are very similar to those for analogous cationic complexes [10–12]. All the compounds exhibit strong symmetric and antisymmetric stretching vibrations. The higher frequency band is assigned to the symmetric vibration mode and the lower to the antisymmetric, in accord with the fact that the coupling constants for stretching of two CO groups on the same metal atom are positive [13]. Complex (d) is relatively soluble in DMSO, but much less so in most other solvents. The conductivity of a DMSO solution of complex (d) (see Table 1) is twice the value obtained for an AB electrolyte in this same solvent (~ 30 ohm^{-1} cm^2 mol^{-1}). This is taken as an indication of the dinuclear nature of complex (d), which is split into two monomers by reaction with DMSO (see reactions 1 and 2 below).

^{1}H NMR spectra

The ^{1}H NMR parameters for this compounds are listed in Table 2. Complexes (a) (b) and (c) show a sharp resonance for the five protons of the cyclopentadienyl ring.
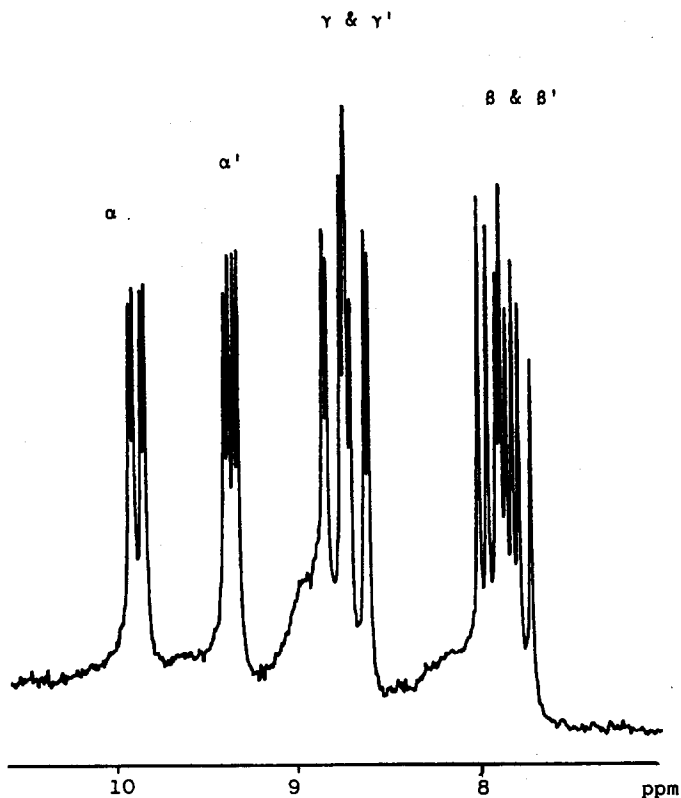
γ & γ'

β & β'

α'

α .

10   9   8   ppm

Fig. 1. 80 MHz ^{1}H NMR spectrum of [CpFe(CO)$_2$(naphthyridine)]ClO$_4$ (a) in acetone-d_6.

[CpFe(CO)$_2$(naph)] $^+$ *(a)*. The ambient-temperature ^{1}H NMR spectrum of the amine ligand of this complex in acetone is shown in Fig. 1. It consists of six double doublets and has the appearance of two superimposed spectra of the free heterocyclic ligand. This spectrum may be interpreted by assuming that the two rings of the naph ligand are chemically inequivalent, and that the inter-ring couplings are small. Thus, the three protons of each ring, α, β, γ and α', β', γ', appear as two AMX spin systems. This supports a formulation in which one nitrogen atom interacts more strogly with the metal than the other (structure I).

(I)
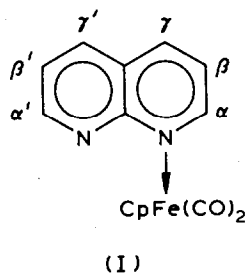
Some degree of interaction with the second nitrogen is possible, especially in the solid state, owing to the relative orientation of the nitrogen lone pairs, but an X-ray

study would be necessary to determine the importance of this interaction. However, it is clear that in solution the two rings are not equivalent, the ligand being bound unsymmetrically.

Chemical shifts and coupling constants are listed in Table 2. The coordinate (α, β, and γ,) and non-coordinate (α', β', and γ') ring resonances have been distinguished by use of the observation [4,7] that $J_{\alpha\beta}$ is normally slightly increased on coordination to a metal atom and thus $J_{\alpha\beta} > J_{\alpha'\beta'}$. Once these two coupling constants are assigned, the remaining assignments follow from the results of irradiation experiments and from mutual coupling relationships. All the protons of the amine are deshielded with respect to the free ligand, especially the proton of the coordinated ring.

Warming of the sample to 55°C caused some line broadening accompanied of loss of resolution of the spectrum but no coalescence was observed.

In order to study the behaviour of this complex at higher temperature DMSO-d_6 was used as solvent. The room temperature ^{1}H NMR spectrum in this solvent is essentially similar to that in acetone, except that because of viscosity broadening four broad resonances are observed. Passing from low to high field these resonances are designated as α, α', γ and γ', and β and β'. On warming no change is observed until 75°C, at this temperature the α resonance starts to collapse, but the appearance of new resonances in the C_5H_5 region of the spectrum and the change of the color of the solution from yellow to deep red indicate that decomposition of the compound is taking place.

From these results it appears that for the range of temperature studied the iron atom in this complex does not exchange its coordinated nitrogen atom, and structure I is maintained over the free range of temperature.

[CpFe(CO)$_2$(3,5-DMP)] $^+$ *(b)*. The ambient temperature ^{1}H NMR spectrum of this complex in acetone-d_6 shows two resonances of equal intensity in the methyl region (2.30 and 2.38 ppm). On warming to 60°C the two resonances remain sharp and there is virtually no change of chemical shifts. These results indicate that the two methyl groups of the 3,5-DMP ligand are not equivalent, so that only one nitrogen bound to iron and that no exchange of the ligand takes place over the temperature range studied. The ^{1}H NMR spectrum of this complex in CDCl$_3$ also shows two resonances of equal intensity in the methyl region (2.30 and 2.35 ppm). On warming the low field resonance moves towards the other, and at 45°C only one signal remains (2.30 ppm). ^{13}C {^{1}H} NMR spectra of this complex in CDCl$_3$ at ambient temperature and at 50°C show two sharp singlets in the methyl region at 15.49 and 11.01 ppm, indicating that at this temperature in this solvent the two methyl groups are chemically non-equivalent, since the 3,5-DMP ligand is bound by only one nitrogen atom and is not exchanging.

The coincidence of the signals from the two methyl groups in the acetone ^{1}H NMR spectrum at 45°C must be attributed to a temperature shift and not to an exchange process.

[CpFe(CO)$_2$(pyr)] $^+$ *(c)*. The 80 MHz ambient temperature ^{1}H NMR spectra of this complex in several solvents (CDCl$_3$, acetone-d_6, DMSO-d_6) show only three broad signals in the heterocyclic region. At 200 MHz the signals become three complex multiplets (see Fig. 2). These spectra can be interpreted as arising from ABPX spin systems [19]. The parameters reported in Table 2 were obtained from such an analysis, and the spectrum simulated with these parameters exactly matched
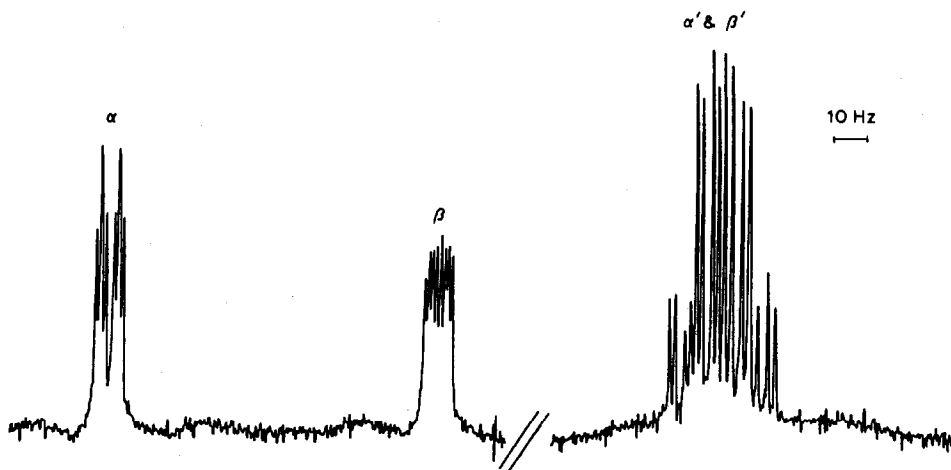
Fig. 2. 200 MHz ^{1}H NMR spectrum of [CpFe(CO)$_2$pyridazine]ClO$_4$ (c) in acetone-d_6.

the experimental one. These results indicate that the α and α' as well as the β and β' positions are chemically inequivalent, and the complex is static with only one nitrogen bound to iron (structure II).
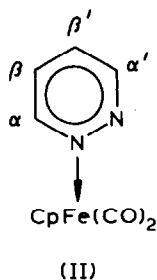

(II)

TABLE 2

^{1}H NMR SPECTRA

Compound	solvent	δ(C$_5$H$_5$) (ppm)	Spectrum of heterocycle [a]							
			Chemical shifts (ppm)			Coupling constants (Hz)				
			α α'	β β'	γ γ'	$\alpha\beta$ $\alpha'\beta'$	$\alpha\gamma$ $\alpha'\gamma'$	$\beta\gamma$ $\beta'\gamma'$	$\alpha\alpha'$ $\beta\beta'$	$\alpha\beta'$ $\alpha'\beta$
(a)	acetone-d_6	5.61	9.89 9.37	7.79 7.92	8.80 8.67	5.3 4.2	1.7 1.8	8.1 8.3		
(b)	acetone-d_6	5.63								
(c)	acetone-d_6	5.65	9.65 7.95	9.14 7.88		-1.48 8.22			1.74 2.48	5.57 4.85
	CDCl$_3$	5.42	9.64 7.70	8.91 7.82		-1.37 8.27			1.56 2.43	5.68 4.95
(d)	DMSO-d_6	5.59	8.82							
(e)	DMSO-d_6	5.59	~ 8.84	~ 8.65		[b]				

[a] α, β, and γ positions denote locations relative to nitrogen atoms. Primes denote positions adjacent to the noncoordinated ring. [b] Not resolved.

The assignment α, β (nearer to the coordinated nitrogen) and α', β' (nearer to the non-coordinated nitrogen) was made on the basis of the larger deshielding which can be expected (and has been observed [4]) for the proton *ortho* to the coordinated nitrogen (α proton), and of the mutual coupling constants and the results of irradiation experiments.

No change of the 80 MHz spectrum was observed when $CDCl_3$ or acetone-d_6 solutions of this complex were warmed to the boiling point of the solvent. No change is observed with DMSO-d_6 as solvent up to ca. 80°C, at which extensive decomposition takes place.

These results show that in this complex the amine ligand is coordinated through only one nitrogen atom as in structure II, and that structure II is maintained over the full range of temperatures.

[Cp(CO)$_2$Fe-pz-Fe(CO)$_2$Cp]$^{2+}$ (d). This complex is only very slightly soluble in most solvents, but it proved possible to obtain resonable spectra in DMSO-d_6, even though reaction with this solvent takes place at ambient temperature. The ambient temperature ^{1}H NMR spectrum of a DMSO-d_6 solution of this complex, and its change with time is shown in Fig. 3. Figure 3(A) shows the spectrum of the freshly prepared solution. It consist of two singlets in the C_5H_5 region (5.60 and 5.78 ppm), and two other singlets (8.69 and 8.82 ppm) in the aromatic region, each partially overlapping one broad resonance (~ 8.65 and ~ 8.84 ppm). Figure 3(B) shows the spectrum of the same solution after 1 h; it is essentially identical to the first as far as chemical shifts are concerned, but some interesting intensity changes have taken place without the appearance of any new resonance. Thus the singlets at 5.78 and 8.69 ppm have gained in intensity while the singlets at 5.60 and 8.82 ppm have weakened.

The spectrum run 24 h later shows only two singlets, at 5.78 and 8.70 ppm, this latter resonance coincides with that for the free ligand in this solvent. The resonances in the heterocyclic region are taken as indicative of the presence of three chemically different pyrazines. The two singlets are assigned to the free ligand (8.69 ppm) and to complex (**d**) (8.82 ppm) respectively.

The two broad resonances are assigned to a monocoordinated pyrazine complex [CpFe(CO)$_2$pz]$^+$ (**e**) (structure III). The four protons of a monocoordinated pyrazine form an AA'BB' spin system which should give rise to a complex spectrum. The spectrum of a pyrazine coordinated in this manner has been reported to show a pseudo-doublet of doublets [20]. The resonances at ~ 8.84 ppm and at ~ 8.65 ppm are tentatively assigned to the α and β protons, respectively, on the basis of (a) the larger deshielding that could be expected for the former, and (b) the similarities in the chemical shift for the complex and the free and bridging ligands. Eventually, all the coordinated pyrazine becomes free ligand.
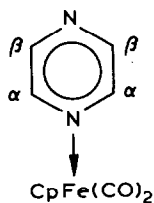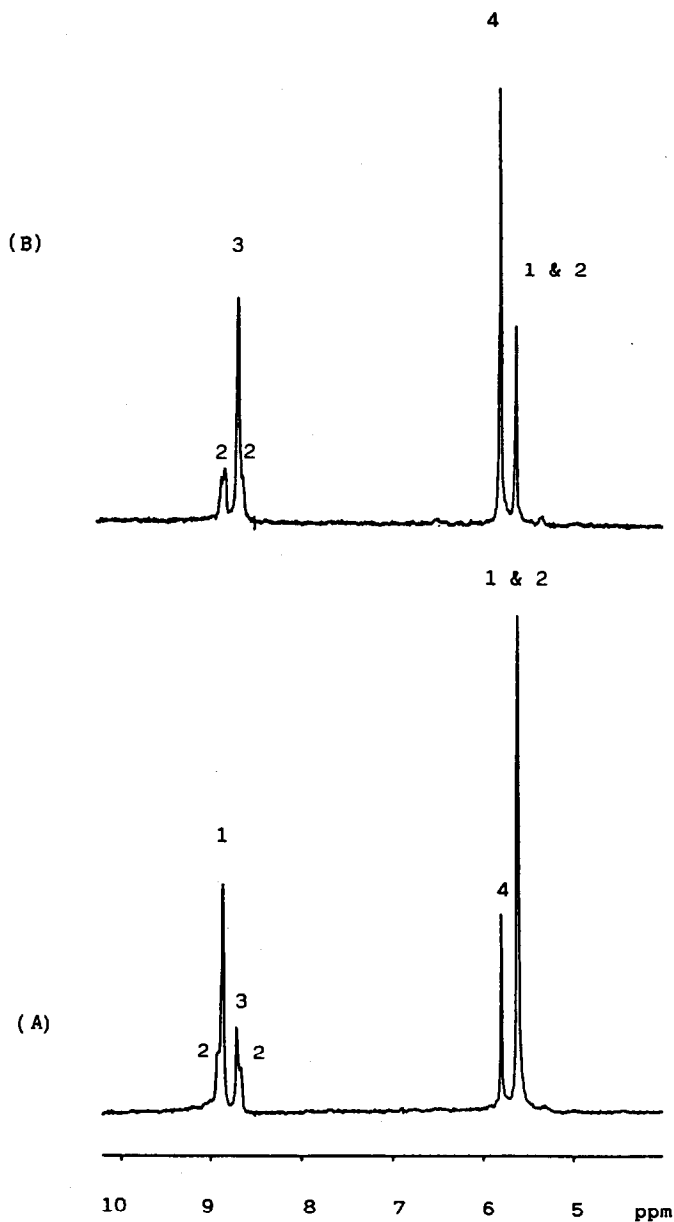

(III)

Fig. 3. 80 MHz ^{1}H NMR spectra of [Cp(CO)$_2$Fe-pyrazine-Fe(CO)$_2$Cp](ClO$_4$)$_2$ (**d**) in DMSO-d_6. (A): spectrum of a freshly prepared solution. (B): spectrum of the same solution after 1 h at room temperature. 1: [Cp(CO)$_2$Fe-pz-Fe(CO)$_2$Cp]$^{2+}$ (**d**); 2: [CpFe(CO)$_2$pz]$^+$ (**e**); 3: free pyrazine; and 4: [CpFe(CO)$_2$(DMSO)]$^+$. See equations 1 and 2 in the text.

The two singlets at 5.60 and 5.78 ppm are indicative of the presence of at least two cyclopentadienyl-containing complexes. Eventually, only one complex is present (5.78 ppm) and we assume this to be [CpFe(CO)$_2$(DMSO)]$^+$ since all the pyrazine ligand has become free.

TABLE 3

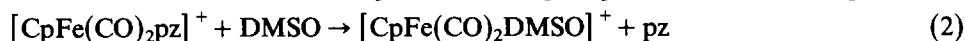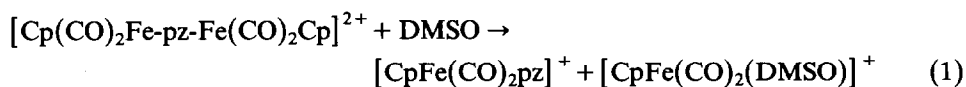ROOM TEMPERATURE ^{57}Fe MÖSSBAUER PARAMETERS ^{a}

Compound	δ ^{b}(mms^{-1})	Δ(mms^{-1})	Γ_{exp}(mms^{-1})
(a)	0.102(6)	1.88(2)	0.28(1)
(b)	0.103(7)	1.83(2)	0.28(1)
(c)	0.099(5)	1.86(1)	0.28(1)
(d)	0.091(7)	1.92(2)	0.36(2)

^{a} Number in parentheses represents the standard deviation of the final digit indicated. ^{b} Relative to natural α-iron foil.

The other singlet (5.60 ppm) falls in the same region as for other complexes containing aromatic amines ([CpFe(CO)$_2$pyr]$^+$ in DMSO-d_6, δ(C$_5$H$_5$) 5.66 ppm) and is assigned to both of the complexes (d) and (e).

These results and the conductivity measurements obtained for this complex in DMSO, indicated that complex (d) reacts with the solvent as shown in eq. 1 and 2.

$$[Cp(CO)_2Fe\text{-}pz\text{-}Fe(CO)_2Cp]^{2+} + DMSO \rightarrow$$

$$[CpFe(CO)_2pz]^+ + [CpFe(CO)_2(DMSO)]^+ \quad (1)$$

$$[CpFe(CO)_2pz]^+ + DMSO \rightarrow [CpFe(CO)_2DMSO]^+ + pz \quad (2)$$

Mössbauer spectra

Each of the compounds studied in this work gives a clear well-resolved quadrupole doublet spectrum. The Mössbauer effect parameters (room temperature) listed in Table 3 are in good agreement with those for other low spin cyclopentadienyliron(II) compounds [21,22]. All are characterized by small positive isomer shifts and quadrupole splitting of ca. 2 mm s^{-1}. Complexes (a), (b), and (c) show almost identical isomer shifts and this can be attributed to the similar basicity of the three amines (see Table 4). Surprisingly, compound (d), which contains the less basic amine, shows the lowest isomer shift. This must be attributed to the π-acceptor ability of pyrazine, which leads to an increase in the electron density at iron by removing d electron density, and the associated synergistic effect which increases the basicity of the ligand [26].

The quadrupole splitting E_Q, observed for the compounds studied here are fairly constant and fall in the same range as observed for similar compounds. Bancroft et al. [27] have attributed this invariance to the ability of the cyclopentadienyl and carbonyl ligands to change their bonding properties substantially in order to neutralize the changes in electron asymmetry.

TABLE 4

BASICITY OF THE AMINE LIGANDS

Amine	pK_a	Reference
1,8-naphthyridine	3.39	23
3,5-dimethylpyrazole	3.12	24
pyridazine	2.33	25
pyrazine	0.65	25

Conclusions

The relative orientation of the nitrogen lone pair determines the coordination mode of the ligands studied. When the angle between the lone pairs is $< 180°$, coordination through one nitrogen atom sterically hinders the other, making it unavailable for coordination to another metal center. On the other hand, the unfavorable orientation of the nitrogen lone pairs on the naph and pyr ligands does not lead to chelation either. For L = pz, the *trans* arrangement of the nitrogen atoms, and the basicity increase of one nitrogen of pyrazine on coordination of the other nitrogen to an electron rich central atom [26] result in formation of the dinuclear complex (**d**). The insolubility of this species precludes the preparation and isolation of the mononuclear complex.

Unlike other six-coordinated complexes of a d^6 central atom, the compounds studied here do not, in the range of temperatures studied, show any dynamic process rendering the two nitrogen atoms of the ligand equivalent. A dissociative path is probably precluded by a strong nitrogen–iron bond. An intramolecular path, which could be reasonably assumed for complex (**a**), and is less likely but still possible for complex (**c**), does not take place, for either steric or electronic reasons; our data do not allow us to decide which of these two effects is the more important. Nevertheless, EH-MO calculations on model systems indicate the existence of a high energy barrier owing to electronic effects for the exchange of a six coordinated iron atom between the two nitrogen atoms of naphthyridine or pyridazine by an intramolecular route [28].

Experimental

Chemical analyses were carried out at the "Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.)". NMR spectra were recorded with a Bruker WP 80 SYFT or a Varian XL-200 spectrometer. IR spectra were recorded with a Perkin–Elmer 681 spectrophotometer. Mössbauer spectra were obtained with a constant acceleration spectrometer coupled to a conventional multichannel analyzer working in the multiscale mode and with ^{57}Co/Rh as a single-line source. The Mössbauer spectra were obtained with unground polycrystalline samples, and were calibrated against $Na_2[Fe(CN)_5NO] \cdot 2H_2O$; they were fitted to Lorentzian curves by the least squares method.

Preparative methods

Reactions were performed in Schlenk-type flasks under dry deoxygenated argon. All the solvents were distilled and degassed before use. Pyrazine and pyridazine were purchased, and used without further purification. The amines 1,8-naphthyridine [14] and 3,5-dimethylpyrazole [15] and the starting compounds $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ [16] and $\eta^5\text{-}C_5H_5Fe(CO)_2I$ [17] were prepared by published methods. [CpFe(CO)$_2$THF]ClO$_4$ was prepared by a slight modification of the method reported in the literature [18], and its CH_2Cl_2 solution was used directly.

Preparation of [CpFe(CO)$_2$L]ClO$_4$ (L = naphthyridine (a), 3,5-dimethylpyrazole (b)) and [Cp(CO)$_2$Fe-pz-Fe(CO)$_2$Cp](ClO$_4$)$_2$ (d)

A mixture of CpFe(CO)$_2$I (0.30 g, 1 mmol) and AgClO$_4$ (0.20 g, 1 mmol) in THF

(10 ml) was stirred at room temperature for 3 h. The solvent was evaporated, the residue extracted with CH_2Cl_2, and the resulting solution filtered through Celite. The appropriate amine (2 mmol) was added to the solution, and after stirring at room temperature for 10 h (naphthyridine) or 5 h (pyrazine), or at the reflux temperature for 1 h (3,5-DMP), the solution was filtered and concentrated to half its volume then ether (10 ml) was added. The yellow powder which separated was filtered off, washed with ether, and dried. Yields were about 60% (**a**), 40% (**b**), 80% (**d**). Compounds (**a**) and (**b**) can be recrystallized from acetone/ether.

Preparation of [CpFe(CO)₂(pyr)]ClO₄

A solution of $[CpFe(CO)_2]_2$ (0.30 g, 1 mmol) and pyridazine (0.16 g, 2 mmol) in acetone (15 ml) was stirred at room temperature for 15 min then $AgClO_4$ (0.40 g, 2 mmol) was added. After 4 h stirring, the solution was filtered through Celite, and concentrated to half its original volume then ether (15 ml) was added. The yellow powder was filtered off, washed with ether, and dried. Yield about 85%. The product can be recrystallized from acetone/ether.

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