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Inorganica Chimica Acta 291 (1999) 39-48

Inorganica Chimica Acta

Syntheses, properties and Mössbauer studies of cyanamide and cyanoguanidine complexes of iron(II). Crystal structures of *trans*-[FeH(NCNH₂)(Ph₂PCH₂CH₂PPh₂)₂][BF₄] and *trans*-[Fe(NCNEt₂)₂(Et₂PCH₂CH₂PEt₂)₂][BF₄]₂

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Received 4 September 1998; accepted 14 December 1998

Abstract

The complexes *trans*-[FeH(NCR)(dppe)_2][BF₄] (1) (R = NH₂, NMe₂, NEt₂ or NC(NH₂)₂; dppe = Ph₂PCH₂CH₂PPh₂) and *trans*-[FeL(NCR)(depe)_2]Y_n (R = NH₂, NMe₂, NEt₂ or NC(NH₂)₂; depe = Et₂PCH₂CH₂PEt₂; Y = BF₄ or BPh₄; (2), L = Br, n = 1; (3), L = NCR, n = 2) have been prepared by treatment of *trans*-[FeHCl(dppe)₂] (in THF and in the presence of Tl[BF₄]) or *trans*-[FeBr₂(depe)₂] (in MeOH and in the presence of [NBu₄][BF₄] or Na[BPh₄]), respectively, with the appropriate cyanamide. NMR and Mössbauer spectral, as well as FAB mass spectrometric data are reported. Mössbauer partial isomer shift (PIS) and partial quadrupole splitting (PQS) parameters have been estimated for the cyanamide and dppe ligands and rationalised, with the overall IS and QS, in terms of π - and σ -electronic effects, the cyanamides behaving as more effective σ -donors and weaker π -acceptors than organonitriles. FAB MS fragmentation patterns are also proposed. The crystal structures of 1 (R = NH₂) and 3 (R = NEt₂, Y = BF₄) are reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Mössbauer study; Crystal structures; Iron complexes; Cyanamide complexes; Cyanoguanidine complexes

1. Introduction

Cyanamide (N=CNH₂) is a recognised substrate of nitrogenase [1] whose coordination chemistry still remains underdeveloped. In pursuit of our interest [2] on the study of its activation, as well as of its derivatives, by a variety of transition metal centres, and in view of the discovery [3] of an alternative nitrogenase containing iron as the only transition metal, we have extended

to dinitrogen-binding iron(II) phosphinic centres the investigation of the reactions of NCNH₂ and its organo-derivatives N=CNMe₂ and N=CNEt₂, as well as its dimeric form, cyanoguanidine, N=CN=NC(NH₂)₂. Therefore, we have prepared three series of cyanamide and cyanoguanidine complexes of the types trans- $[FeH(NCR)(dppe)_2][BF_4]$ (1) $(dppe = Ph_2PCH_2CH_2$ *trans*-[FeBr(NCR)(depe)₂]Y PPh_2), (2) (depe = $Et_2PCH_2CH_2PEt_2$; $Y = BF_4$ or BPh_4) and trans- $[Fe(NCR)_2(depe)_2]Y_2$ (3). Because the bonding properties of such ligands have not yet been fully elucidated, we have applied Mössbauer spectroscopy (which has been successfully used [4] for other low-spin octahedral iron(II) phosphinic complexes) to investigate

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their electron donor/acceptor abilities (in particular partial isomer shifts and quadrupole splittings for these still uncommon ligands were derived), and we have determined the X-ray crystal and molecular structures of two such complexes.

2. Results and discussion

2.1. Syntheses

Treatment of a THF solution of *trans*-[FeHCl-(dppe)₂] with Tl[BF₄] followed by addition of the appropriate cyanamide NCR ($R = NH_2$, NMe₂, NEt₂ or NC(NH₂)₂ (cyanoguanidine)) (in a stoichiometric amount), under an inert atmosphere, for ca. 1 h, leads to the formation of *trans*-[FeH(NCR)(dppe)₂][BF₄] ((1); $R = NH_2$ (1a), NMe₂ (1b), NEt₂ (1c) or NC(NH₂)₂ (1d)) which have been isolated as orange solids (Eq. (1)).

$$trans-[FeHCl(dppe)_2] + NCR + TI[BF_4]$$

$$\stackrel{\text{THF}}{\rightarrow} trans-[FeH(NCR)(dppe)_2][BF_4] + TICl$$
(1)

This preparative method involves replacement of the chloride ligand by the cyanamide (NCR), assisted by the thallium salt, and is analogous to that followed [5] for the synthesis of the related isocyanide complexes trans-[FeH(CNR)(dppe)₂]⁺ (R = alkyl or aryl).

The reaction of *trans*-[FeBr₂(depe)₂] in a methanolic solution with a stoichiometric amount of the appropriate cyanamide (NCR), under an inert atmosphere, for ca. 1 h, leads to the formation of the monocyanamide complexes trans-[FeBr(NCR)(depe)₂]⁺ ((2); $R = NH_2$ (2a), NMe_2 (2b), NEt_2 (2c) or $NC(NH_2)_2$ (2d)) which were isolated as their BF₄⁻ or BPh₄⁻ salts (usually red in colour) upon addition of [NBu₄][BF₄] or Na[BPh₄] (Eq. (i), Scheme 1, $X = NBu_4$ or Na, $Y = BF_4$ or BPh_4 , respectively). However, if a 2-fold molar amount of the cyanamide is used, the dicyanamide species trans- $[Fe(NCR)_2(depe)_2]^{2+}$ ((3); $R = NH_2$ (3a), NMe_2 (3b), NEt_2 (3c) or $NC(NH_2)_2$ (3d)) are obtained (Eq. (ii), Scheme 1), isolated as the BF₄⁻ or BPh₄⁻ salts (red in colour). Complexes 3 can also be obtained by the reaction of the monocyanamide compounds with the corresponding cyanamide (Eq. (iii), Scheme 1).

These reactions are comparable with those reported [6] for *trans*-[FeBr₂(depe)₂] with organonitriles occurring [7] via the stepwise displacement of the bromide ligands.

Complexes 1, 2 and 3 were characterised by IR (Table 1), multinuclear (¹H, ³¹P and ¹³C) NMR (Tables 2 and 3) and Mössbauer (Table 4) spectroscopies, elemental analysis (Table 1), FAB mass spectrometry, as well as, for 1 ($R = NH_2$) or 3 ($R = NEt_2$, $Y = BF_4$), by single-crystal X-ray structural analyses.

Table 1

Physical and analytical data for trans-[FeH(NCR)(dppe)₂][BF₄] (1), trans-[FeBr(NCR)(depe)₂]Y^a (2) and trans-[Fe(NCR)₂(depe)₂]Y₂^a (3)

	R	Colour $\nu(N=C)^b$		v(Fe–H) ^b	Analysis (%)°		
					C	Н	Ν
1a	$\mathrm{NH_2}^\mathrm{d}$	orange	2270 m	1850 w,br	64.4(64.8)	4.9(5.2)	2.8(2.8)
1b	NMe ₂	orange	2225 s	1870 w,br	65.4(65.4)	5.5(5.5)	2.4(2.8)
1c	NEt ₂	orange	2215 m	1885 w,br	66.0(65.9)	5.9(5.7)	2.4(2.7)
1d	NC(NH ₂) ₂ ^e	orange	2215 s	1880 w,br	63.4(63.3)	5.6(5.2)	5.3(5.5)
2a	$\mathrm{NH_2}^{\mathrm{d}}$	red	2210 s		37.0(37.2)	6.9(7.4)	3.7(4.1)
2b	NMe ₂	red	2230 s		39.4(39.2)	7.7(7.7)	4.4(4.0)
2c	NEt ₂ ^f	orange	2220 s		60.9(61.0)	8.3(8.1)	2.8(2.9)
2d	NC(NH ₂) ₂ ^e	red	2210 s		36.5(36.7)	7.0(7.3)	7.7(7.8)
3a	NH ₂ ^{d,f}	red	2240 s		69.7(70.6)	7.9(7.8)	4.7(4.7)
3b	NMe ₂	red	2240 s		39.8(39.9)	7.7(7.7)	7.2(7.2)
3c	NEt ₂	red	2225 s		43.3(43.0)	8.2(8.2)	6.6(6.7)
3d	NC(NH ₂) ₂ ^e	red	2220 s		35.8(35.6)	7.0(7.0)	13.6(13.8)

^a $Y = BF_4$ unless stated otherwise.

^b In KBr pellets; values in $\text{cm}^{-1} \pm 2.5$; s, strong; m, medium; w, weak; br, broad.

^c Required values in parentheses.

^d $v(N-H) = 3300-3160 \text{ cm}^{-1}$.

 $v(N-H) = 3460-3280 \text{ cm}^{-1}$.

 $^{f} Y = BPh_{4}.$

Table 2									
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Proton and ${}^{31}P{}^{1}$	H} NMR	data for <i>trans</i> -[F	eH(NCR)(dppe)-	$[BF_{4}]$ (1),	trans-[FeBr(]	NCR)(depe) ₂]Y ^a	(2) and tra	ans-[Fe(NCR),	$(depe)_{2} Y_{2}^{a}$ (3)

R	Complex	$\delta~(^1\mathrm{H})^\mathrm{b}$	Assignment	J (Hz)	δ (³¹ P) ^c
NH ₂	1a	7.32–7.13 (m, 40H) 6.18 (s, 2H) 2.80–2.60 (m,br, 4H) 2.45 ^g (m,br, 4H) – 22.52 (qt, 1H)	C_6H_5 (dppe) NCN H_2 $1/2Ph_2PCH_2CH_2PPh_2$ $1/2Ph_2PCH_2CH_2PPh_2$ hydride	${}^{2}J_{\rm HP} = 47.8$	- 56.18
NMe ₂	1b	7.72–7.20 (m, 40H) 3.00–2.82 (m,br, 4H) 2.66 (s, 3H) 2.65 (s, 3H) 2.42–2.26 (m,br, 4H) – 22.08 (qt, 1H)	C_6H_5 (dppe) 1/2Ph ₂ PCH ₂ CH ₂ PPh ₂ 1/2NCN(CH ₃) ₂ 1/2NCN(CH ₃) ₂ 1/2Ph ₂ PCH ₂ CH ₂ PPh ₂ hydride	${}^{2}J_{\rm HP} = 47.5$	- 54.60
NEt ₂	1c	7.65–7.10 (m, 40H) 2.94 (q, 4H) 2.80 ^h (m,br, 4H) 2.44–2.30 (m,br, 4H) 0.94 (t, 6H) –22.34 (qt, 1H)	C_6H_5 (dppe) NCN(CH_2CH_3) ₂ 1/2Ph ₂ PC $H_2CH_2PPh_2$ 1/2Ph ₂ PC $H_2CH_2PPh_2$ NCN(CH_2CH_3) ₂ hydride	${}^{3}J_{\rm HH} = 7.1$ ${}^{3}J_{\rm HH} = 7.2$ ${}^{2}J_{\rm HP} = 47.8$	- 55.40°
NC(NH ₂) ₂	1d	7.70–7.02 (m, 40H) 3.00–2.80 (m,br, 4H) 2.50 ^g (m,br, 4H) –22.91 (qt, 1H)	C_6H_5 (dppe) 1/2Ph_2PCH_2CH_2PPh_2 1/2Ph_2PCH_2CH_2PPh_2 hydride	${}^{2}J_{\rm HP} = 47.3$	- 54.28
NH ₂	2a	6.49 (s, 2H) 2.41 (m, 8H) ⁱ 2.26 (dq, 8H) 2.07 (dq, 8H) 1.46 (m, 24H)	NCN H_2 Et ₂ PC H_2 C H_2 PEt ₂ 1/2C H_2 (Et, depe) 1/2C H_2 (Et, depe) C H_3 (depe)	${}^{3}J_{\rm HH} = 7.8, \; {}^{2}J_{\rm HP} = 15.6$ ${}^{3}J_{\rm HH} = 7.8, \; {}^{2}J_{\rm HP} = 15.6$	-70.47
NMe ₂	2b	2.98 (s, 6H) 2.48 (m, 8H) ⁱ 2.33 (dq, 8H) 2.12 (dq, 8H) 1.51 (m, 24H)	NCN $(CH_3)_2$ Et ₂ PCH ₂ CH ₂ PEt ₂ 1/2CH ₂ (Et, depe) 1/2CH ₂ (Et, depe) CH ₃ (depe)	${}^{3}J_{\rm HH} = 7.8, \; {}^{2}J_{\rm HP} = 15.6$ ${}^{3}J_{\rm HH} = 7.6, \; {}^{2}J_{\rm HP} = 15.2$	-74.63
NEt2 ^{d,e}	2c	7.49 (m, 8H) 7.28 (t, 8H) 7.17 (t, 4H) 3.10 (q, 4H) 2.19 (m, 8H) ⁱ 2.03 (dq, 8H) 1.87 (dq, 8H) 1.27 (m, 24H) 0.90 (t, 6H)	$\begin{array}{l} H_o \ (\mathrm{BPh}_4^-) \\ H_m \ (\mathrm{BPh}_4^-) \\ H_p \ (\mathrm{BPh}_4^-) \\ \mathrm{NCN}(\mathrm{C}H_2\mathrm{CH}_3)_2 \\ \mathrm{Et}_2\mathrm{PC}H_2\mathrm{C}H_2\mathrm{PEt}_2 \\ 1/2\mathrm{C}H_2 \ (\mathrm{Et}, \ \mathrm{depe}) \\ 1/2\mathrm{C}H_2 \ (\mathrm{Et}, \ \mathrm{depe}) \\ \mathrm{C}H_3 \ (\mathrm{depe}) \\ \mathrm{NCN}(\mathrm{CH}_2\mathrm{C}H_3)_2 \end{array}$	${}^{3}J_{HH} = 7.0$ ${}^{3}J_{HH} = 7.1$ ${}^{3}J_{HH} = 7.2$ ${}^{3}J_{HH} = 7.8, {}^{2}J_{HP} = 15.6$ ${}^{3}J_{HH} = 7.6, {}^{2}J_{HP} = 15.2$ ${}^{3}J_{HH} = 7.2$	- 74.63
NC(NH ₂) ₂	2d	3.13 (s, 4H) 2.12 (m, 8H) ⁱ 2.07 (dq, 8H) 1.86 (dq, 8H) 1.32 (m, 24H)	NCN $(NH_2)_2$ Et ₂ PCH ₂ CH ₂ PEt ₂ 1/2CH ₂ (Et, depe) 1/2CH ₂ (Et, depe) CH ₃ (depe)	${}^{3}J_{\rm HH} = 7.5, \; {}^{2}J_{\rm HP} = 15.0$ ${}^{3}J_{\rm HH} = 7.6, \; {}^{2}J_{\rm HP} = 15.2$	- 74.06
NH2 ^d	3a	7.48 (m, 16H) 7.08 (t, 16H) 6.93 (t, 8H) 6.78 (s, 2H) ⁱ 2.39 (m, 8H) ⁱ 2.23 (dq, 8H) 2.07 (dq, 8H) 1.44 (m, 24H)	$\begin{array}{l} H_o \ (\mathrm{BPh_4^-}) \\ H_m \ (\mathrm{BPh_4^-}) \\ H_p \ (\mathrm{BPh_4^-}) \\ \mathrm{NCN}H_2 \\ \mathrm{Et_2PC}H_2\mathrm{C}H_2\mathrm{PEt_2} \\ 1/2\mathrm{C}H_2 \ (\mathrm{Et, depe}) \\ 1/2\mathrm{C}H_2 \ (\mathrm{Et, depe}) \\ \mathrm{C}H_3 \ (\mathrm{depe}) \end{array}$	${}^{3}J_{HH} = 7.2$ ${}^{3}J_{HH} = 6.9$ ${}^{3}J_{HH} = 8.1, \; {}^{2}J_{HP} = 16.2$ ${}^{3}J_{HH} = 7.6, \; {}^{2}J_{HP} = 15.2$	-71.31
NMe ₂	3b	2.97 (s, 12H) 2.47 (m, 8H) ⁱ 2.30 (dq, 8H) 2.12 (dq, 8H) 1.51 (m, 24H)	NCN(CH_3) ₂ Et ₂ PC $H_2CH_2PEt_2$ 1/2C H_2 (Et, depe) 1/2C H_2 (Et, depe) C H_3 (depe)	${}^{3}J_{\rm HH} = 7.5, \; {}^{2}J_{\rm HP} = 15.0$ ${}^{3}J_{\rm HH} = 7.7, \; {}^{2}J_{\rm HP} = 15.4$	- 72.77
			2 (1		(continued)

Table 2 (continued)

R	Complex	$\delta \ (^1\mathrm{H})^\mathrm{b}$	Assignment	J (Hz)	$\delta (^{31}\text{P})^{c}$
NEt ₂ ^f	3c	3.06 (q, 8H) 2.24 (m, 8H) ⁱ	NCN $(CH_2CH_3)_2$ Et ₂ PCH ₂ CH ₂ PEt ₂ CH ₂	${}^{3}J_{\rm HH} = 7.1$	-75.28
		1.88 (m, 16H) ^k	CH_2 (Et, depe)	${}^{3}J_{\rm HH} = 8.0, \; {}^{2}J_{\rm HP} = 16.0$	
		1.39 (m, 24H)	CH_3 (depe)		
		1.90 (t, 12H)	$NCN(CH_2CH_3)_2$	${}^{3}J_{\rm HH} = 7.4$	
$NC(NH_2)_2$	3d	3.47 (s, 8H)	$NCN(NH_2)_2$		-71.42
		$2.20 (m, 8H)^{i}$	$Et_2PCH_2CH_2PEt_2$		
		1.97 (dq, 8H)	$1/2CH_2$ (Et, depe)	${}^{3}J_{\rm HH} = 7.4, \ {}^{2}J_{\rm HP} = 14.8$	
		1.82 (dq, 8H)	$1/2CH_2$ (Et, depe)	${}^{3}J_{\rm HH} = 7.2, {}^{2}J_{\rm HP} = 14.4$	
		1.29 (m, 24H)	CH ₃ (depe)		

 a Y = BF₄ unless otherwise stated.

^b In $(CD_3)_2CO$ unless otherwise stated; δ in ppm relative to internal SiMe₄; s, singlet; t, triplet; q, quartet; qt, quintet; dq, doublet of quartets; m, multiplet; br, broad resonance; subscripts *o*, *m*, and *p* denote the *o*-, *m*- and *p*-protons of the phenyl ring, respectively.

^c In (CD₃)₂CO unless otherwise stated; δ (singlet resonance) in ppm relative to external P(OMe)₃.

^d $Y = BPh_4$.

e In CD₂Cl₂.

f In CDCl₃.

^g Partial overlapping with the solvent resonance.

^h Partial overlapping with the NCN(CH_2CH_3)₂ quartet.

ⁱ Filled-in doublet, not resolved.

^j Lower intensity than expected due to proton exchanging with the solvent water.

^k Multiplet resulting from two doublets of partially overlaped quartets.

2.2. Spectroscopic data

The solid-state IR spectra (KBr pellets) of complexes 1, 2 and 3 exhibit strong v(NC) bands (Table 1) in the range of 2270-2210 cm⁻¹, at slightly higher wavenumbers (by ca. $25-10 \text{ cm}^{-1}$) than those observed for the corresponding free cyanamides, in agreement with the $\eta^1\mbox{-}coordination$ through the cyano group acting mainly as an electron-donor to the metal. The cyanamides appear to behave as weaker π -electron acceptors than organonitriles since v(NC) for the latter species undergoes a shift to lower frequencies upon coordination [6], at the related complexes *trans*-[FeL(NCR)(depe)₂] Y_n $(R = alkyl \text{ or } aryl; Y = BF_4 \text{ or } BPh_4; L = Br, n = 1;$ L = NCR, n = 2). Additional IR broad and strong intensity bands in the range of 3300-3160 cm⁻¹ $(NCNH_2)$ and 3460-3280 cm⁻¹ $[NCNC(NH_2)_2]$ are assigned to v(NH), whereas other strong bands at 1630-1550 cm⁻¹ (NCNH₂) or 1650-1560 cm⁻¹ $[NCNC(NH_2)_2]$ are due to $\delta(NH)$ and/or $\nu(N=C)$. The trans configuration is assigned to all complexes on the basis of a singlet in their ${}^{31}P{}^{1}H$ NMR spectra (Table 2).

Consistent with the *trans* geometry for complexes 1, a quintet resonance is observed in the ¹H NMR spectra (in (CD₃)₂CO) (Table 2) at ca. $\delta - 22$ (²J_{HP} ca. 47 Hz) attributable to Fe–*H*. The resonances of the methylene protons of dppe in 1 occur as two broad multiplets at δ ca. 2–3 thus suggesting two non-equivalent sets of CH₂ groups, whereas the resonances of the $-CH_2CH_2$ –group of depe (complexes 2 or 3) appear as a filled-in

doublet centred at δ 2.48–2.12, corresponding to the AA' part of an A₂XX'A₂' (A,A' = ¹H; X,X' = ³¹P) spin system as found [6] in the ¹H NMR spectra of the analogous organonitrile complexes. For complexes **2** or **3** the MeCH₂– protons appear as two doublets (²J_{HP} = 14.4–16.2 Hz) of quartets (³J_{HH} = 7.2–8.1 Hz) at δ 2.33–1.97 and 2.12–1.39, each of them arising from CH₂ coupling to one ³¹P nucleus (doublet) and to the three protons of the methyl group (quartet). For **3c** these resonances partially overlap to give a 1:3:4:4:3:1 sextet at δ 1.88.

In the ¹³C NMR spectra (both ¹H decoupled and coupled) of complexes **1** (Table 3) the cyano-carbon (N*C*R) resonance is observed as a singlet at δ ca. 125 ppm which corresponds to a slight downfield shift (by ca. 7 ppm) upon coordination. For the cyanoguanidine complex **1d**, the imine carbon NCN*C*(NH₂)₂ resonance occurs at δ 160.38 ppm. The resonances of the different types of carbons at the aromatic rings of the dppe have also been identified (Table 3). Moreover, in the ¹³C{¹H} NMR spectra, the resonance of the $-CH_2CH_2$ - group bridging the phosphorus atoms is a quintet (ca. 12 Hz) at δ ca. 32 ppm, arising from coupling to the four ³¹P nuclei. These resonances split into triplets (¹*J*_{CH} ca. 133 Hz) of those quintets in the ¹³C-¹H coupled spectra.

2.3. Mössbauer data

Mössbauer spectra at 77 K were obtained for complexes 1 ($R = NH_2$ (1a), NMe_2 (1b), NEt_2 (1c) or

Table 3 $^{13}C{^{1}H}$ and ^{13}C NMR data^a for *trans*-[FeH(NCR)(dppe)₂][BF₄] (1)

R	δ	$^{13}C\{^{1}H\}$	$J_{\rm CP}~({\rm Hz})$	¹³ C	${}^{1}J_{\rm CH}$ (Hz)	Assignment
1a NH ₂	133.47	s,br		s,br		C_i (dppe)
-	130.86	d	$17.6 [^{3}J]$	dd	160.6	C_m (dppe)
	128.06	d	$10.1 [^4 J]$	dd	158.4	C_{p} (dppe)
	126.02	d	50.7 $[^2J]$	dd	161.3	C_o (dppe)
	124.61	S		S		NCR
	31.46	qt	12.1	tqt	133.1	$\mathrm{Ph}_{2}\mathrm{P}C\mathrm{H}_{2}C\mathrm{H}_{2}\mathrm{P}\mathrm{Ph}_{2}$
1b NMe ₂	133.80	d	51.5 $[^{1}J]$	d		C_i (dppe)
	131.02	d	25.6 $[^{3}J]$	dd	160.7	C_m (dppe)
	127.98	d	$11.0 [^4J]$	dd	156.7	C_p (dppe)
	126.16	d	41.2 $[^2J]$	dd	160.7	\dot{C}_{a} (dppe)
	125.81	S		с		$NCN(CH_3)_2$
	38.83	S		q	118.1	$NCN(CH_3)_2$
	30.73	qt	12.3 ^b	tqt	133.2	Ph ₂ PCH ₂ CH ₂ PPh ₂
1c NEt ₂	135.87	dm	62.0 $[^{1}J]$	d		C_i (dppe)
	132.99	d	$16.4 [^{3}J]$	dd	161.9	C_m (dppe)
	129.95	d	$10.9 [^4J]$	dd	161.3	C_p (dppe)
	128.21	d	49.5 $[^2J]$	dd	178.0	$\dot{C_o}$ (dppe)
	126.05	S		S		NCN(CH ₂ CH ₃) ₂
	45.25	S		t	139.6	$NCN(CH_2CH_3)_2$
	32.72	qt	12.1 ^b	tqt	133.0	Ph ₂ PCH ₂ CH ₂ PPh ₂
	13.51	S		q	127.6	$NCN(CH_2CH_3)_2$
1d NC(NH ₂) ₂	160.38	S		s		NCNC(NH ₂) ₂
	134.37	s,br		s,br		C_i (dppe)
	131.08	S		d	160.7	C_m (dppe)
	127.80	d	$17.4 [^4J]$	dd	159.4	C_n (dppe)
	126.17	d	$62.2 [^2J]$	dd	161.4	C_{a} (dppe)
	124.33	S		с		NCNC(NH ₂) ₂
	30.83	qt	12.2 ^b	tqt	132.7	$Ph_2PCH_2CH_2PPh_2$

^a In CD₂Cl₂; δ in ppm relative to SiMe₄; s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; br, broad; dm, doublet of multiplets; tqt, triplet of quintets; subscripts *i*, *o*, *m* and *p* denote the *ipso-*, *ortho-*, *meta-* and *para-*carbons, respectively, of the phenyl rings.

^b Owing to virtual coupling to the four equivalent phosphorus nuclei.

^c Partial overlapping with the phenyl ring resonance.

NC(NH₂)₂ (1d)), 2 (R = NH₂ (2a) or NEt₂ (2c)) and 3 (R = NH₂ (3a), NMe₂ (3b), NEt₂ (3c) or NC(NH₂)₂ (3d)) and the data are presented in Table 4. A typical spectrum is shown in Fig. 1 (for 1d).

Complexes 2 and 3 present IS (e.g. IS = 0.24 - 0.28mm s⁻¹ for *trans*-[Fe(NCR)₂(depe)₂]²⁺ (R = alkyl or aryl)) and QS values (QS = 1.16 - 1.23 mm s⁻¹ for trans-[FeBr(NCR)(depe)₂]⁺) [6] higher and lower, respectively, than those of the analogous mono- and di-organonitrile complexes. Since the isomer shift of a complex decreases [4e] with an increase of both the σ -electron donor and the π -electron acceptor character of the ligands, $IS = -constant \times (\sigma + \pi)$, and the QS decreases with a decrease of the π -electron acceptance and with an increase of the σ -donor ability of the ligands, $QS = constant \times (\pi - \sigma)$, these results indicate a weaker π -electron acceptor ability of the cyanamide ligands compared with the organonitriles, consistent with the IR results discussed above. Moreover, all our cyanamide complexes present lower IS and QS values than those quoted (0.47 and 1.45 mm s⁻¹ [4a,8] and 0.47 and 1.51 mm s⁻¹ [9]) for *trans*-[FeBr₂(depe)₂], indicating that the cyanamide ligands act as more effective σ -electron donors than bromide, in agreement with the observed lability, towards displacement reactions, of the latter ligand at the {Fe^{II}(depe)₂} centre.

The Mössbauer spectral data were also analysed in terms of the point-charge model [4e], and partial isomer shifts (PIS) and partial quadrupole splittings (PQS) were derived (Table 4). In this model the observed IS is the sum of the PIS of the individual ligands (Eq. (2)), whereas the QS is given by a difference of partial values for the ligands, according to expressions dependent upon the composition and structure, i.e. Eqs. (3) and (4) for the general types *trans*-[FeACB₄] and *trans*-[FeA₂B₄], which include our complexes 1, 2 and 3 (A = NCR, B = dppe/2 (1) or depe/2 (2 or 3), C = H (1) or Br (2)), respectively.

$$=\Sigma$$
 PIS

IS

QS = 2PQS(A) + 2PQS(C) - 4PQS(B)(3)

$$QS = 4PQS(A) - 4PQS(B)$$
(4)

By application of these equations to our data for complexes 2 and 3 (and considering that PIS = -0.02(B) and 0.26 (C) mm s⁻¹, PQS(B) = 0.45 or -0.63 mm s⁻¹ (with reference to PQS(H) = 0.00 or to PQS(Cl) = -0.27 mm s⁻¹, respectively), and PQS(C) = 0.82 or -0.27 mm s⁻¹ (with reference to PQS(H) = 0.00 or to PQS(Cl) = -0.27 mm s⁻¹, respectively) [4a], we have estimated the PIS and PQS values for the cyanamide

Table 4

Mössbauer isomer shift (IS) and quadrupole splitting (QS) parameters^a for *trans*-[FeH(NCR)(dppe)_2][BF₄] (1), *trans*-[FeBr(NCR)(depe)_2][BF₄] (2) and *trans*-[Fe(NCR)_2(depe)_2]Y₂^b (3), and estimated partial isomer shifts (PIS) and partial quadrupole splittings (PQS) for the cyanamide ligands

R	IS	5	QS	$\Gamma_{1/2}$	
Experimental					
1a NH ₂	0.	29	0.80	0.21	
1b NMe ₂	0.	28	0.90	0.16	
1c NEt ₂	0.	27	0.94	0.15	
$1d NC(NH_2)_2$	0.	26	1.02	0.14	
2a NH ₂	0.	33	1.03	0.34	
$2c \text{ NEt}_2^e$	0.	35	0.99	0.21	
3a NH ₂ ^e	0.	33	1.13	0.21	
3b NMe ₂	0.	31	1.08	0.12	
3c NEt ₂	0.	32	1.05	0.18	
3d NC(NH ₂) ₂	0.	34	1.01	0.16	
Calculated					
NCR	PIS ^c	PQS	d		
		PQS 0.	$d(H) = 00 \text{ mm s}^{-1}$	$PQS(Cl) = -0.27 \text{ mm s}^{-1}$	_
NH ₂ ^f	0.18	0.67		-0.41	
NMe ₂	0.20	0.72		-0.36	
NEt ₂ ^f	0.19	0.65		-0.43	
NC(NH ₂) ₂	0.21	0.70		-0.38	
dppe/2	0.00	0.11		-0.98	

^a Values in mm s⁻¹ \pm 0.01, recorded at 77 K and referenced against iron foil at 298 K; $\Gamma_{1/2}$ = half width at half height.

^b $Y = BF_4$ unless stated otherwise.

^c Values calculated by using the expression PIS(NCR) = IS -0.18 or PIS(NCR) = 0.5 IS +0.04 derived from application of Eq. (2) to complexes **2** or **3**, respectively, or the expression PIS(dppe/2) = 0.25 IS -0.25 PIS(NCR) -0.018 derived from application of Eq. (2) to complexes **1**.

^d Values calculated, ignoring lattice contributions, by using the expression PQS(NCR) = $0.5 \text{ QS} + x (x = 0.08 \text{ for PQS}(H) = 0.00 \text{ mm s}^{-1} \text{ or } x = -0.99 \text{ for PQS}(Cl) = -0.27 \text{ mm s}^{-1}) \text{ or PQS}(NCR) = 0.25 \text{ QS} + y (y = 0.45 \text{ for PQS}(H) = 0.00 \text{ mm s}^{-1} \text{ or } y = -0.63 \text{ for PQS}(Cl) = -0.27 \text{ mm s}^{-1}) \text{ derived from application of Eqs. (3) or (4) to complexes$ **2**or**3** $, respectively, or the expression PQS(dppe/2) = 0.5 PQS(NCR) - 0.25 QS - z (z = 0.00 \text{ for PQS}(H) = 0.00 \text{ mm s}^{-1} \text{ or } z = 0.55 \text{ for PQS}(Cl) = -0.27 \text{ mm s}^{-1}) \text{ derived from application of Eq. (3) to complexes$ **1**.

^e $Y = BPh_4$.

^f Average values for the mono- and di-cyanamide complexes.



Fig. 1. Mössbauer spectrum of trans-[FeH(NCNC(NH₂)₂)(dppe)₂]-[BF₄] (1d) at 77 K and referenced against iron foil at 298 K.

ligands (Table 4). The application of Eqs. (2) and (3) to complexes 1, leads us to estimate the PIS and PQS values for the dppe ligand.

In comparison with the related organonitriles or N₂ ligands, the cyanamides present slightly higher PIS values (0.18–0.21 versus 0.15–0.19 [6] or 0.09 [4a] mm s⁻¹) but PQS values (0.65–0.72 mm s⁻¹) are in the lower limit of the range for those exhibited by the other ligands (0.69–0.74 [6] or 0.78 [4a] mm s⁻¹, respectively). Hence, the cyanamide ligands present weaker summed σ -donor and π -acceptor contributions (higher PIS), in particular behaving as more effective σ -donors but weaker π -acceptors (lower PQS) than organonitriles or dinitrogen.

2.4. FAB MS

The FAB mass spectra of the complexes *trans*-[FeL-(NCR)(depe)₂] Y_n (R = NH₂, NMe₂, NEt₂ or NC(NH₂)₂; Y = BF₄ or BPh₄; (2), L = Br, n = 1; (3), L = NCR, n = 2) were run in 3-nitrobenzyl alcohol (NBA) matrices and the corresponding molecular ions were clearly detected (with the expected bromine isotopic pattern for complexes 2).

For the dicyanamide complexes **3b**, **3c** or **3d** the peak detected at the highest m/z is due to the monocationic aggregate [Fe(NCR)₂(depe)₂ · BF₄]⁺ in accord with the behaviour observed [6,10] for some $[ML_n^{2+}][Y^-]_2$ type salts, but such a species is not detected for the [BPh₄]⁻ salt **3a**. The fluoro-ions [FeF(depe)₂]⁺ (m/z 847) and [FeF(NCR)(depe)]⁺ are also detected for the [BF₄]⁻ salts and can be considered to be formed by fluorination of [Fe(depe)₂]^{•+} (m/z 468) or [Fe(NCR)(depe)]^{•+} under FAB MS conditions.



Scheme 2. Proposed general fragmentation pattern for complexes *trans*-[FeBr(NCR)(dppe₂)][BF₄] (2) and *trans*-[Fe(NCR)₂(dppe₂)]Y₂ (3) under FAB conditions.

The fragmentation pathways can be initiated by the elimination of the monodentate ligands from the molecular ion—see the general proposed fragmentation pattern depicted in Scheme 2—to give $[Fe(depe)_2]^{\bullet+}$ (m/z 468) which undergoes similar fragmentation patterns for all the mono- and di-cyanamide complexes, as observed for the related organonitrile complexes [6]. This indicates the possible generation of a low oxidation state iron–diphosphine centre by reduction of a parent complex.

For complexes 2, elimination of a diphosphine ligand occurs only after the loss of the cyanamide ligand, as observed in complexes 1 [11], in accord with the stronger coordination of the chelating diphosphine. The molecular ion of the liberated diphosphine, depe^{•+}, follows a fragmentation pathway analogous to that exhibited by a genuine sample of depe. In contrast to the behaviour observed [6] for the organonitrile complexes, in the cyanamide complexes the diphosphine ligand itself cannot undergo partial fragmentation.

In addition, the dibromide ion $[\text{FeBr}_2(\text{depe})_2]^{\bullet+}$ was detected at m/z 626 with the expected bromine isotopic pattern. It conceivably results from the reaction of $[\text{FeBr}(\text{depe})_2]^+$ with Br[•] under FAB MS conditions, and not from contamination with *trans*-[FeBr₂(depe)₂] since the presence of this complex was not detected (e.g. by NMR or elemental analysis) in any of the cyanamide complexes. Loss of depe generates a fragment ion at m/z 420 with the same bromine isotopic pattern, assigned to $[\text{FeBr}_2(\text{depe})]^{\bullet+}$.

2.4.1. Crystal structures of trans-[FeH(NCNH₂)(dppe)₂]-[BF₄] and trans-[Fe(NCNEt₂)₂(depe)₂][BF₄]₂

The molecular structures of trans-[FeH(NCNH₂)- $(dppe)_2$ [BF₄] (1a) and trans-[Fe(NCEt₂)₂(depe)₂][BF₄]₂ (3c) have been determined by X-ray diffraction studies. They are shown in Fig. 2 and selected bond lengths and angles are listed in Table 5. For 1a, the iron atom is octahedrally coordinated and displaced out of the equatorial plane (-0.103(2) Å) of the four P atoms towards the coordinated nitrogen atom of the cyanamide. The Fe–H separation, 1.59(9) Å, is comparable to the value of 1.53(9) Å [12] found in [FeH(N₂)(Ph₂PC₂H₄PPhC₂- $H_4PPhC_2H_4PPh_2$]Br · EtOH and agrees with the value of 1.53 Å estimated [13] as the sum of the iron and hydrogen covalent radii. The Fe-P bond distances (2.244(4) Å, averaged value) are shorter than in trans- $[Fe(NCMe)_2(dppe)_2][BF_4]_2 \cdot CH_2Cl_2$ (2.331(3) Å, averaged value) [14] in agreement with the greater electron donor character of the hydride and cyanamide ligands than that of acetonitrile, and are comparable to those of $[FeH(N_2)(depe)_2]^+$ (2.240(2) Å) [15]. The Fe-N bond distance of **1a** has a value, 1.95(1) Å, comparable to that of *trans*-[Fe(NCMe)₂(dppe)₂][BF₄]₂ \cdot CH₂Cl₂ (1.913(6) Å) [14] and $[FeH(N_2)(depe)_2]^+$ (1.825(7) Å) [15]. While the $[Fe(NCMe)_2(dppe)_2]^{2+}$ complex cation is centrosymmetric and as a consequence the P atoms of each dppe ligand are perfectly trans to each other, in our complex 1a the trans angles for P(1)-Fe-P(2) and P(3)-Fe-P(4) are 176.2(2) and 173.3(2)°, respectively. The dppe ligands have an about gauche conformation

of the ethylenic chain with P(1)-C(14)-C(15)-P(3) and P(2)-C(40)-C(41)-P(4) torsion angles of -44(1) and $34(1)^{\circ}$, respectively, consistent with the NMR results discussed above.

For *trans*-[Fe(NCNEt₂)₂(depe)₂][BF₄]₂ (**3c**), the iron atom lies on a crystallographic inversion center with the two depe ligands in the equatorial plane and the two cyanamide ligands mutually *trans* in an octahedral coordination geometry. The depe ligands have a *cis* conformation of the ethylenic chain with a P-C-C-P torsional angle of 0°, in agreement with the NMR results. The same conformation of the bridging ethylene has been found in *trans*-[FeCl₂(dmpe)₂] [16], but not in



Fig. 2. Molecular structures of (a) *trans*-[FeH(NCNH₂)(dppe)₂][BF₄] (1a) and (b) *trans*-[Fe(NCNEt₂)₂(depe)₂][BF₄]₂ (3c).

Table 5

Selected bond distances (Å) and angles (°) for *trans*-[FeH(NCNH₂)-(dppe)₂][BF₄] (**1a**) or *trans*-[Fe(NCNEt₂)₂(depe)₂][BF₄]₂ (**3c**)

	1a	3c
About the Fe atom		
Fe-P(1)	2.261(4)	2.282(2)
Fe–P(2)	2.249(4)	2.276(3)
Fe-P(3)	2.229(4)	_
Fe–P(4)	2.238(4)	_
Fe-N(1)	1.95(1)	1.908(8)
Fe–H	1.59(9)	_
P-Caliph. av.	1.85(1)	1.84(2)
P-Cphen. av.	1.84(1)	_
P-Cethylen. av.	1.50(2)	-
P(1)–Fe–N(1)	86.9(3)	89.6(2)
P(2)-Fe-N(1)	93.8(3)	88.7(2)
P(3)-Fe-N(1)	96.9(3)	-
P(4)-Fe-N(1)	92.9(3)	_
P(1)-Fe-P(2)	83.6(1)	85.5(1)
P(1)-Fe-P(3)	176.2(2)	-
P(2)-Fe-P(4)	173.3(2)	_
H(1)–Fe–N(1)	171(5)	_
In the cyanamide ligan	ds	
N(1)-C	1.15(2) C(1)	1.14(1) C(11)
N(2)–C	1.34(2) C(1)	1.36(1) C(11)
N(2)–C(12)	-	1.58(3)
N(2)–C(14)	_	1.50(2)
Fe-N(1)-C	174(1) C(1)	176(1) C(11)
C(11)-N(2)-C(12)	_	113(1)
C(11)-N(2)-C(14)	_	119(1)
N(1)-C-N(2)	177(2) C(1)	178(1) C(11)

trans-[FeI₂(depe)₂] which was *gauche* with a P-C-C-P torsional angle of 50.0(2)° [17].

The Fe–P bond distances of 2.277(3) Å (Fe–P(1)) and 2.285(2) Å (Fe–P(2)) (Table 5) are slightly shorter than those in [FeI₂(depe)₂] (2.295(1) and 2.323(1) Å) [17], but comparable to the values of 2.260(2) and 2.268(3) Å found in [FeCl₂(depe)₂] [18]. These complexes exhibit different conformations of the bridging ethylene in the diphosphine ligands, and the isomerization process due to the conformational changes which could be related either to the hindrance of the substituent at the phosphorus atoms, or to that of the ligands in the axial positions.

The Fe–N bond distance of 1.919(7) Å (Table 5) is comparable to the value of 1.913(6) Å [14] reported for *trans*-[Fe(NCMe)₂(dppe)₂][BF₄]₂ · CH₂Cl₂ and to that of 1.894(4) Å [17] in [Fe(NCMe)₂(opdp)₂]I₂. The *N*-amine atom of the diethylcyanamide ligand has a planar geometry (the sum of the angles around N(2) is 359(1)°) rather than pyramidal as observed in *mer*-[ReCl₂(NCNEt₂)(PMePh₂)₃] [2f] and in the free ligands dimethylcyanamide (NCNMe₂) [19] and cyanamide (NCNH₂) [20,21].

The linear NC-NEt₂ ligand (the N-C-N angle is $178(1)^{\circ}$) has a C(11)-N(2) bond distance of 1.32(1) Å

which is shorter than the analogous distance in *mer*-[ReCl₂(NCNEt₂)(PMePh₂)₃] (1.34(1) Å) [2f] and in free NCNMe₂ and NCNH₂ (1.351 [19] and 1.346 Å [20], microwave results). Therefore, the lone pair of the amine N atom is delocalized into the π -bonding of the cyano group, with resulting shortening of the Et₂N– CN bond and enhancement of the electron donor ability of the diethylcyanamide ligand towards the cationic Fe(II) metal centre, in agreement with the IR and Mössbauer results discussed above. Similar behaviour is found in *trans*-[Pt(CF₃)(NCNEt₂)(PPh₃)₂][BF₄] [2d], and in *trans*-[Cr(NCNEt₂)(CO)₅] [22]. Hence, the canonical form (**a**) presents a significant contribution in the VB representation of the cyanamide ligand.

$$\dot{M} = N = C = \dot{N}Et_2$$

3. Experimental

3.1. Syntheses

All manipulations were routinely performed under an atmosphere of dinitrogen using standard vacuum and inert-gas flow techniques. Solvents were purified by standard procedures and freshly distilled immediately prior to use. The complexes *trans*-[FeHCl(dppe)₂] and *trans*-[FeBr₂(depe)₂] were prepared by literature methods [9,23]. The cyanamides were used as purchased from Aldrich.

IR measurements were carried out on a Perkin-Elmer 683 spectrophotometer and ¹H, ³¹P and ¹³C NMR spectra were recorded on a Varian Unity 300 spectrometer, at the Centro de Química Estrutural. Mössbauer spectra were determined at the Nitrogen Fixation Laboratory on an E.S. Technology MS-105 Mössbauer spectrometer with a 25 mCi ⁵⁷Co source in a rhodium matrix, recorded at 77 K and referenced against iron foil at 298 K. The FAB mass spectrometric measurements were performed on a Trio 2000 spectrometer at the Centro de Química Estrutural. Positive-ion FAB mass spectra were obtained by bombarding NBA matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Nominal molecular masses were calculated using the most abundant isotopes, i.e. ⁵⁶Fe (92%), ⁷⁹Br (50.7%) and the expected natural abundance isotope cluster patterns were observed for the various ion clusters. However, further complexity due to addition (from the matrix) or loss of hydrogen was usually not taken into account. Mass calibration for data system acquisition was achieved using CsI.

3.1.1. trans-[FeH(NCR)(dppe)_2][BF₄] (1; $R = NH_2$ (1a), NMe₂ (1b), NEt₂ (1c) or NC(NH₂)₂ (1d))

Complexes 1 were prepared by a common method, and a typical procedure is given below for the com-

pound (1a, $R = NH_2$). Tl[BF₄] (72.8 mg, 0.25 mmol) was added to a solution of *trans*-[FeHCl(dppe)₂] (0.20 g, 0.22 mmol) in THF (60 cm³) and the suspension was stirred for ca. 10 min at room temperature (r.t.). The colour changed to pale pink and powdered cyanamide (9.4 mg, 0.22 mmol) was then added slowly immediately giving an orange suspension. The precipitate of TlCl was filtered off and the filtrate concentrated in vacuo. Cooling to ca. -18° C led to the precipitation of 1a as an orange solid which was filtered off, washed with a THF/Et₂O (1:5) mixture and recrystallized from CH₂Cl₂/Et₂O and dried in vacuo (ca. 80% yield).

3.1.2. trans-[FeBr(NCR)(depe)_2]Y (2; $R = NH_2$ (2a), NMe_2 (2b), NEt_2 (2c) or $NC(NH_2)_2$ (2d); $Y = BF_4$ or BPh_4) and trans-[Fe(NCR)_2(depe)_2]Y_2 (3; $R = NH_2$ (3a), NMe_2 (3b), NEt_2 (3c) or $NC(NH_2)_2$ (3d); $Y = BF_4$ or BPh_4)

The general procedure followed in the syntheses of complexes 2 and 3 involved the addition of the appropriate cyanamide in a stoichiometric (2) or 2-fold (3) molar ratio to a solution of *trans*-[FeBr₂(depe)₂] in MeOH (50 cm³). The solution was left to stir overnight at r.t. and [NBu₄][BF₄] or Na[BPh₄] in methanol was then added (in a 1:1 (2) or 2:1 (3) molar ratio, relative to the starting complex). Cooling to ca. -18° C led to the precipitation of the mono- or di-cyanamide complex usually as a red solid which was filtered-off, washed with MeOH/Et₂O (1:4) and dried in vacuo (ca. 70% average yield).

3.2. Crystallography

X-ray data were collected on a Philips PW1100 (Febo system) diffractometer, using graphite-monochromated radiation, λ (Mo K α) = 0.71069 Å, at r.t. Data collection parameters are summarized in Table 6. The orientation matrix and cell dimensions were determined by least-squares refinement of the angular positions of 30 reflections. Three standard reflections were monitored every 180 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for LP and for absorption as described by North et al. [24]. No correction was made for extinction.

The positions of the heavy atoms were found from Patterson syntheses [25]. All non-H atoms were located in the subsequent Fourier maps. The structures were refined by full-matrix least-squares. Anisotropic temperature factors for the non-hydrogen atoms, except those of the phenyls, refined isotropically, were applied in **1a**. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 U_{eq} of the parent carbon atom). The hydride atom was found in a final difference Fourier and refined isotropically. The non-hydrogen atoms in **3c** were refined anisotropically.

Table 6

Crystal data and details of refinement for *trans*-[FeH(NCNH₂)-(dppe)₂][BF₄] (**1a**) and *trans*-[Fe(NCNEt₂)₂(depe)₂][BF₄]₂ (**3c**)

Compound	1a	3c
Empirical formula	C ₅₃ H ₅₁ BF ₄ FeN ₂ P ₄	$C_{30}H_{68}B_2F_8FeN_4P_4$
Formula weight	982.6	838.3
Temperature (°C)	23	23
Crystal size (mm)	0.28 imes 0.21 imes 0.30	$0.36 \times 0.32 \times 0.40$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	Pbca
Ζ	4	4
a (Å)	21.573(4)	16.446(3)
b (Å)	16.556(3)	18.203(3)
c (Å)	13.471(3)	14.617(3)
β (°)	90.04(3)	_
V (Å ³)	4811(2)	4376(1)
$D_{\text{calc}} \text{ (g cm}^{-3})$	1.35	1.27
θ Range (°)	3–26	3–26
F(000)	2040	1766
μ (Mo K α) (mm ⁻¹)	5.01	5.31
Reflections collected	3125	4289
Observed reflections $[I \ge 3\sigma(I)]$	2964	1805
GOF	1.09	1.16
$R = \Sigma[F_{\rm o} - F_{\rm c}] / \Sigma F_{\rm o} $	0.062	0.073

Only the hydrogen atoms of the ethylene chain were introduced in calculated positions as in **1a**, while the hydrogens of the ethyl groups were omitted due to some disordering in the ethyl moieties. It was not possible to refine rational disordered models for these carbon atoms and they were thus refined at full occupancy even though high thermal parameters were present. Structure refinement and final geometrical calculations were carried out with SHELXL-93 [26] and PARST [27] programs, and the drawings with ORTEP II [28]. Final atomic coordinates, thermal parameters and structure factors are available from the authors.

Acknowledgements

This work has been partially supported by the JNICT and the Institute for the International Scientific and Technological Co-operation (ICCTI) (Portugal)/ The British Council (UK) and the JNICT or ICCTI/ CNR (Italy) protocols of collaboration, the PRAXIS XXI Programme and the Foundation for Science and Technology (FCT) (Portugal), and the BBSRC (UK). We also thank Mr Indalécio Marques (Centro de Química Estrutural) for running the FAB mass spectra.

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