Syntheses, properties and Mössbauer studies of mono- and di-nitrile phosphine complexes of iron(II). Crystal structures of *trans*-[Fe(NCR)₂(Et₂PCH₂CH₂PEt₂)₂][BF₄]₂ (R = Me or CH₂C₆H₄OMe-4) †

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Complexes *trans*-[FeL(NCR)(depe)₂]Y$_n$ (R = Me, Et, CH₂C₆H₄OMe-4, C₆H₄OMe-4, C₆H₄Me-4, Ph, C₆H₄F-4 or C₆H₄NO₂-4; depe = Et₂PCH₂CH₂PEt₂; Y = BF₄ or BPh₄; L = Br, *n* = 1 **1**; L = NCR, *n* = 2 **2**) have been prepared by treatment of *trans*-[FeBr₂(depe)₂] (in MeOH and in the presence of [NBu₄][BF₄] or Na[BPh₄]) with a stoichiometric or a twofold molar amount of the appropriate organonitrile. Electronic, NMR and Mössbauer spectral as well as FAB mass spectrometric data are reported. Mössbauer partial isomer shift (p.i.s.) and partial quadrupole splitting (p.q.s.) parameters have been estimated for the nitrile ligands and rationalised, with the overall i.s. and q.s., in terms of π- and σ-electronic effects. The FAB MS fragmentation patterns are also proposed, and the crystal structures of **2** (R = Me or CH₂C₆H₄OMe-4, Y = BF₄) have been determined.

Introduction

The identification of an alternative nitrogenase apparently containing iron as the sole transition metal[1] has triggered a renewed interest in the synthesis and reactivity of iron complexes with substrates of this enzyme, in particular dinitrogen,[2] isocyanides,[3] alkynes,[2a,4] cyclopropene and allenes.[5] Moreover, Mössbauer spectroscopy has been successfully applied to the investigation of a series of iron(II) complexes with ditertiary phosphines,[6–11] namely towards the elucidation of the bonding properties of ligands in terms of their σ and/or π electron donor/acceptor ability. However, nitrile ligands, in spite of their importance in co-ordination chemistry, have only been considered incidentally,[11] and a systematic study of nitrile complexes was not reported.
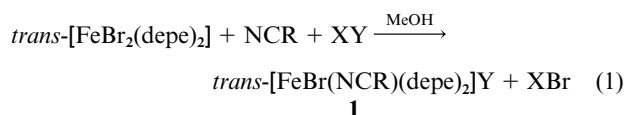
In the present work we have prepared a series of low-spin iron(II) complexes with one or two nitrile ligands, *trans*-[FeBr-(NCR)(depe)₂]Y **1** (R = alkyl or aryl, depe = Et₂PCH₂CH₂-PEt₂; Y = BF₄ or BPh₄) and *trans*-[Fe(NCR)₂(depe)₂]Y₂ **2**, by reaction of *trans*-[FeBr₂(depe)₂] with the appropriate nitrile. Their Mössbauer, electronic, NMR and FAB MS spectra have been investigated, and, for **2** (R = Me or CH₂C₆H₄OMe-4, Y = BF₄), a single-crystal X-ray diffraction analysis has been undertaken. The synthesis of two complexes **1** (R = CH₂C₆-H₄OMe-4) and **2** (R = CH₂C₆H₄OMe-4) had been reported[12] in a preliminary way, together with a kinetic study.
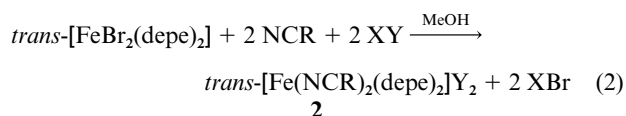
Results and discussion

Syntheses

Reaction of *trans*-[FeBr₂(depe)₂] in a methanolic solution with a stoichiometric amount of the appropriate organonitrile (NCR), under an inert atmosphere, for *ca.* 1 h, leads to the formation of the mononitrile complexes *trans*-[FeBr(NCR)-(depe)₂]⁺ (R = Me **1a**, Et **1b**, CH₂C₆H₄OMe-4 **1c**, C₆H₄OMe-4 **1d**, C₆H₄Me-4 **1e**, Ph **1f**, C₆H₄F-4 **1g** or C₆H₄NO₂-4 **1h**) which were isolated as their BF₄⁻ or BPh₄⁻ salts (usually violet) upon addition of [NBu₄][BF₄] or Na[BPh₄] [eqn. (1), X = NBu₄ or Na, Y = BF₄ or BPh₄, respectively]. However, if a twofold molar amount of the nitrile is used, the dinitrile species *trans*-[Fe(NCR)₂(depe)₂]²⁺ (R = Me **2a**, Et **2b**, CH₂C₆H₄OMe-4 **2c**, C₆H₄OMe-4 **2d**, C₆H₄Me-4 **2e**, Ph **2f**, C₆H₄F-4 **2g** or C₆H₄NO₂-4 **2h**) are obtained [eqn. (2)], isolated as the BF₄⁻ or BPh₄⁻ salts

$$trans\text{-}[FeBr_2(depe)_2] + NCR + XY \xrightarrow{\text{MeOH}}$$

$$trans\text{-}[FeBr(NCR)(depe)_2]Y + XBr \quad (1)$$
$$\mathbf{1}$$

$$trans\text{-}[FeBr_2(depe)_2] + 2\,NCR + 2\,XY \xrightarrow{\text{MeOH}}$$

$$trans\text{-}[Fe(NCR)_2(depe)_2]Y_2 + 2\,XBr \quad (2)$$
$$\mathbf{2}$$

(commonly yellow). Complexes **2** can also be obtained by reaction of the mononitrile compounds with the corresponding organonitrile.

These nitrile reactions are comparable with those reported[11a] for *trans*-[FeCl₂(depe)₂]. They occur *via* the stepwise displacement of the bromide ligands by the nitrile through a mechanism involving rate-limiting dissociation of halide to form [FeBr-(depe)₂]⁺ and [Fe(NCR)(depe)₂]²⁺ which bind NCR to afford **1** or **2**, respectively. This has been demonstrated[12] by stopped-flow mechanistic studies in the case of R = CH₂C₆H₄OMe-4. Complexes **1** and **2** were characterised by IR, UV/VIS (Table 1), multinuclear (¹H, ³¹P, ¹⁹F and ¹³C) NMR (see SUP 57419)

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† *Supplementary data available*: NMR data. Available from BLDSC (No. SUP 57419, 9 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

Table 1 Physical and analytical data for *trans*-[FeBr(NCR)(depe)$_2$]Y^a **1** and *trans*-[Fe(NCR)$_2$(depe)$_2$]Y$_2$^{a} **2**

Complex	R	Colour	ν(N≡C)^b	λ(log ε)^c	Analysis (%)^d		
					C	H	N
1a	Me^e	Violet	2225w	300(3.53), 400(2.82), 607(2.56)	61.0(60.8)	7.8(7.9)	1.4(1.5)
1b	Et^e	Violet	2220s	308(3.31), 400(2.83), 608(2.51)	60.9(61.2)	8.1(8.0)	1.5(1.5)
1c^f	CH$_2$C$_6$H$_4$OMe-4	Violet	2215w	306(3.95), 400(3.37), 607(3.19)	44.6(44.5)	7.4(7.3)	1.8(1.8)
1d	C$_6$H$_4$OMe-4	Violet	2180m	307(3.32), 409(3.27), 606(2.20)	43.3(43.8)	5.9(5.5)	1.8(1.8)
1e	C$_6$H$_4$Me-4	Violet	2180w	305(3.29), 400(2.98), 605(2.35)	44.6(44.7)	7.2(7.4)	1.8(1.9)
1f	Ph^e	Red	2180s	300(4.90), 413(4.60), 528(3.30), 602(3.12)	62.7(63.1)	7.8(7.6)	0.8(1.4)
1g	C$_6$H$_4$F-4	Red	2190s	305(3.41), 402(3.25), 607(2.72)	42.8(42.9)	6.9(6.9)	1.9(1.9)
1h	C$_6$H$_4$NO$_2$-4	Purple	2175s	305(3.80), 406(3.10), 606(2.85)	41.4(41.4)	6.6(6.7)	3.6(3.6)
2a	Me	Yellow	2250w	335(2.62), 400(2.52)	40.1(39.8)	7.3(7.5)	3.8(3.9)
2b	Et	Yellow	2240m	337(2.83), 401(2.68), 600(2.03)	41.2(41.5)	7.9(7.8)	3.5(3.7)
2c^f	CH$_2$C$_6$H$_4$OMe-4	Yellow	2235w	340(2.71), 400(2.61), 600(2.54)	48.4(48.7)	7.2(7.1)	2.9(3.0)
2d	C$_6$H$_4$OMe-4	Yellow	2200w	340(2.92), 440(2.53), 605(1.70)	47.6(47.6)	6.9(6.9)	3.1(3.1)
2e	C$_6$H$_4$Me-4	Yellow	2200m	357(3.76), 443(2.46), 600(1.85)	49.1(49.4)	7.2(7.1)	3.2(3.2)
2f	Ph	Yellow	2200s	363(4.11), 441(2.83), 610(2.48)	47.9(48.1)	6.9(6.9)	3.3(3.3)
2g	C$_6$H$_4$F-4	Yellow	2205s	366(3.51), 445(2.26), 610(1.64)	46.3(46.2)	6.5(6.4)	3.2(3.2)
2h	C$_6$H$_4$NO$_2$-4	Red	2200s	403(2.93), 445(2.71), 609(1.79)	43.1(43.5)	6.2(6.0)	6.0(6.0)

^{a} Y = BF$_4$ unless stated otherwise. ^{b} In KBr pellets; values in cm^{-1} ± 2.5; s = strong, m = medium, w = weak. ^{c} In CH$_2$Cl$_2$ (240–800 nm); λ ± 4 nm. ^{d} Required values in parentheses. ^{e} Y = BPh$_4$. ^{f} For these compounds the ν(N≡C) and elemental analytical data have been reported.[12]
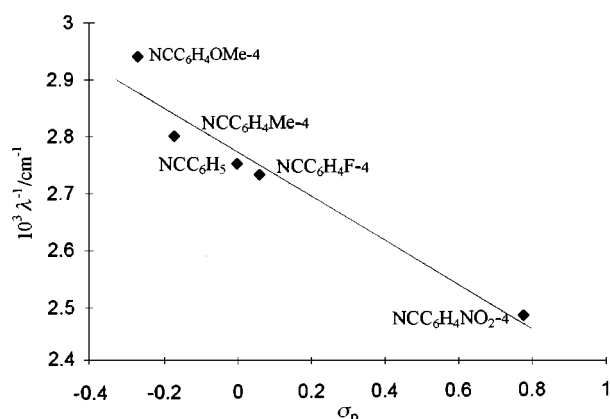
and Mössbauer (Table 2) spectroscopies, elemental analysis (Table 1), FAB mass spectrometry, as well as, for **2** (R = Me or CH$_2$C$_6$H$_4$OMe-4, Y = BF$_4$), by single-crystal X-ray analyses.

Spectroscopic data

The solid-state IR spectra (KBr pellets) of complexes **1** and **2** exhibit ν(NC) values (Table 1) in the range 2250–2180 cm^{-1}. These are considerably lower than those exhibited by the free nitriles ($\Delta\nu = -5$ to -60 cm^{-1}) in agreement with an appreciable π-electron acceptance of the nitrile ligand from the iron(II) metal centre; the $|\Delta\nu|$ shift increases with increasing π-acceptor ability of the nitrile and is more pronounced for complexes **1**, in view of the stronger π-electron release of the {FeBr(depe)$_2$}$^+$ centre in comparison with {Fe(NCR)(depe)$_2$}$^{2+}$. At these metal centres the π-electron effect apparently is more significant than σ-electron release from the ligand to the metal. The σ-electron release from the ligand leads to an increase in ν(NC) upon co-ordination.[13] Other characteristic bands can be identified for the NCC$_6$H$_4$NO$_2$-4 complexes **1h** and **2h** at 1510 and 1340 cm^{-1} due to the aromatic nitro group (asymmetric and symmetric stretching, respectively),[14] and for the methoxyphenyl derivatives **1c**, **1d**, **2c** and **2d** for which the C–O–C asymmetric stretching[14] is found at 1250 cm^{-1}.

In the ^{1}H NMR spectra (in CD$_2$Cl$_2$) (all of the NMR data are available as SUP 57419) the depe resonances occur as sets of complex multiplets which are resolved for some of the complexes. Hence, the resonances of the CH_2CH_2 residue appear as a filled-in doublet centred at δ 2.32–2.00, corresponding to the AA′ part of an A$_2$XX′A′$_2$ (A,A′ = ^{1}H; X,X′ = ^{31}P) spin system. The MeCH_2 protons appear as two doublets ($^2J_{HP} = 15.0$–15.6 Hz) of quartets ($^3J_{HH} = 7.5$–7.8 Hz) at δ 2.38–2.06 and 2.02–1.81, each of them arising from CH_2 coupling to one ^{31}P nucleus (doublet) and to the three protons of the methyl group (quartet). For **2a**, **2c** and **2h** these resonances partially overlap to give a 1:3:4:4:3:1 sextet at δ 2.50–1.65. The resonances of the phenyl protons of the 4-substituted aromatic nitrile complexes occur as two doublets ($^3J_{HH} = 7.5$–9.0 Hz) at δ 8.51–7.02 and 8.27–6.84 for an AB type pattern.

A *trans* configuration is assigned to the complexes **1** and **2** on the basis of a singlet at δ -74.09 to -79.50 relative to P(OMe)$_3$ in their ^{31}P-{^{1}H} NMR spectra. In the ^{19}F NMR spectra, the [BF$_4$]$^-$ resonance is the expected singlet at δ -151.5 relative to CFCl$_3$, whereas for the NCC$_6$H$_4$F-4 ligand, in **1g** or **2g**, a septet at δ -103.77 or -101.59, respectively, is observed. This multiplet is a consequence of a triplet ($^3J_{FH} = 9.1$–9.3 Hz) (coupling

to the *meta*-protons) of overlapping triplets ($^4J_{FH} = 4.3$–4.6 Hz) (coupling to the *ortho*-protons). In the ^{13}C NMR spectra (both ^{1}H-decoupled and coupled) of complexes **2** the nitrile NCR resonance is usually observed as a singlet in the range δ 138.44–118.71 which corresponds to a downfield shift (by *ca.* 20 ppm) upon co-ordination. The other nitrile carbon resonances were assigned by comparison with those of the free species. However, in the ^{13}C–^{1}H coupled spectrum of **2c** the nitrile *ortho*-carbon resonance is a doublet ($^1J_{CH} = 160.1$ Hz) of distorted quartets ($^2J_{CH} \approx ^3J_{CH} \approx 6.0$ Hz) at δ 130.85. These multiplets result from a doublet (coupling to the *meta*-proton) of triplets (coupling to the methylene protons), partially overlapped. Moreover, in the ^{13}C-{^{1}H} NMR spectra, the resonance of the CH_2CH_2 bridging the phosphorus atoms is a broad quintet (*ca.* 9 Hz) at δ *ca.* 20, arising from coupling to the four ^{31}P nuclei, whereas those of MeCH_2 (at δ *ca.* 18) are broad unresolved signals. These resonances split into 1:3:1 triplets ($^1J_{CH} = 129$ Hz) in the ^{13}C–^{1}H coupled spectra.

The electronic spectra of complexes **1** and **2** have been recorded in dichloromethane (Table 1). For the aromatic dinitrile complexes **2**, the energy of the higher frequency band (in the 340–403 nm wavelength range) decreases linearly with the increase of Hammett's σ_p constant of the substituent in the phenyl ring (Fig. 1) and has been assigned to a metal-to-nitrile charge transfer transition as observed for the related *cis*-[Re(NCR)$_2$(dppe)$_2$][BF$_4$] (R = aryl)[15] or *trans*-[M(CNR)$_2$-

(depe)$_2$][BF$_4$]$_2$ **2** (R = C$_6$H$_4$OMe-4, C$_6$H$_4$Me-4, Ph, C$_6$H$_4$F-4 or C$_6$H$_4$NO$_2$-4) *vs.* Hammett's σ_p constant (for the phenyl substituent of the aromatic nitrile ligands) [$1/\lambda = (-0.39 \pm 0.06)10^{-3}\sigma_p + (2.77 \pm 0.02) \times 10^{-3}$; correlation coefficient $r = 0.94$].

Table 2 Mössbauer isomer shift (i.s.) and quadrupole splitting (q.s.) parameters[a] for *trans*-[FeBr(NCR)(depe)$_2$]Y[b] **1** and *trans*-[Fe(NCR)$_2$(depe)$_2$]Y$_2$[b] **2**, and estimated partial isomer shifts (p.i.s.) and partial quadrupole splittings (p.q.s.) for the nitrile ligands

Experimental					Calculated		p.q.s.[d]	
Complex	R	i.s.	q.s.	$\Gamma_{\frac{1}{2}}$	NCR	p.i.s.[c]	p.q.s.(H) = 0.00 mm s^{-1}	p.q.s.(Cl) = −0.27 mm s^{-1}
1a	Me[e]	0.37	1.16	0.17	NCMe[f]	0.19	0.69	−0.40
1d	C$_6$H$_4$OMe-4	0.36	1.23	0.24	NCC$_6$H$_4$OMe-4[f]	0.18	0.70	−0.39
1g	C$_6$H$_4$F-4	0.31	1.20	0.21	NCC$_6$H$_4$Me-4	0.18	0.69	−0.39
1h	C$_6$H$_4$NO$_2$-4	0.32	1.32	0.22	NCPh	0.17	0.71	−0.37
2a	Me	0.27	1.02	0.26	NCC$_6$H$_4$F-4[f]	0.15	0.70	−0.38
2d	C$_6$H$_4$OMe-4	0.28	0.95	0.18	C$_6$H$_4$NO$_2$-4[f]	0.15	0.74	−0.34
2e	C$_6$H$_4$Me-4	0.27	0.97	0.24				
2f	Ph	0.25	1.05	0.30				
2g	C$_6$H$_4$F-4	0.24	1.09	0.24				
2h	C$_6$H$_4$NO$_2$-4	0.24	1.14	0.17				

[a] Values in mm s^{-1} ± 0.01, recorded at 77 K and referenced against iron foil at 298 K; $\Gamma_{\frac{1}{2}}$ = half width at half height. [b] Y = BF$_4$ unless stated otherwise. [c] Values calculated by using expression p.i.s.(NCR) = i.s. − 0.18 or p.i.s.(NCR) = 0.5 i.s. + 0.04 derived from application of eqn. (3) to the mono- or di-nitrile complexes, respectively (see text). [d] Values calculated, ignoring lattice contributions, by using expression p.q.s.(NCR) = 0.5 q.s. + x [x = 0.08 for p.q.s.(H) = 0.00 mm s^{-1} or −0.99 for p.q.s.(Cl) = −0.27 mm s^{-1}] or p.q.s.(NCR) = 0.25 q.s. + y [y = 0.45 for p.q.s.(H) = 0.00 mm s^{-1} or −0.63 for p.q.s.(Cl) = −0.27 mm s^{-1}] derived from application of eqn. (4) or (5) to the mono- or di-nitrile complexes, respectively. [e] Y = BPh$_4$. [f] Average values for the mono- and di-nitrile complexes.
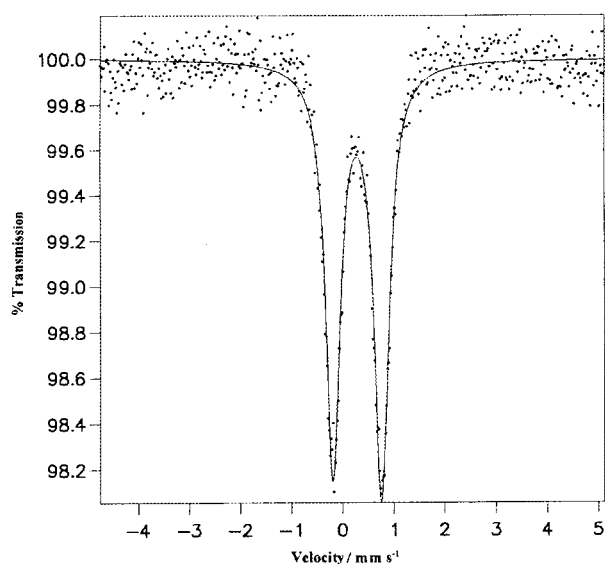

Fig. 2 Mössbauer spectrum of *trans*-[Fe(NCC$_6$H$_4$OMe-4)$_2$(depe)$_2$]-[BF$_4$]$_2$ **2d**, at 77 K and referenced against iron foil at 298 K.

(dppe)$_2$] (M = Mo or W).[16] In complexes **1** the effect of the R group on the band energy has not been clearly established.

Mössbauer data

Mössbauer spectra at 77 K were obtained for complexes **1** (R = Me **1a**, C$_6$H$_4$OMe-4 **1d**, C$_6$H$_4$F-4 **1g** or C$_6$H$_4$NO$_2$-4 **1h**) and **2** [R = Me **2a**, C$_6$H$_4$OMe-4 **2d** (Fig. 2 as a typical spectrum), C$_6$H$_4$Me-4 **2e**, Ph **2f**, C$_6$H$_4$F-4 **2g** or C$_6$H$_4$NO$_2$-4 **2h**] and the data are presented in Table 2. The dinitrile complexes **2** present lower isomer shift (i.s.) and quadrupole splitting (q.s.) values (in the 0.24–0.28 and 0.95–1.14 mm s^{-1} ranges, respectively) than the mononitrile compounds **1** (0.31–0.37 and 1.16–1.32 mm s^{-1}), both being lower than those quoted[6,17] (0.47 and 1.45 mm s^{-1}) for *trans*-[FeBr$_2$(depe)$_2$]. Since the isomer shift of a complex is known[10] to decrease with an increase of both the σ-electron donor and the π-electron acceptor character of the ligands, i.s. = −constant · (σ + π), and the quadrupole splitting decreases with a decrease of the π-electron acceptance and with an increase of the σ-donor ability of the ligands, q.s. = constant · (π − σ), the above ordering can be rationalised by considering that the nitrile ligands act not only as stronger π-electron acceptors (as expected, since Br$^-$ is not a π acceptor)
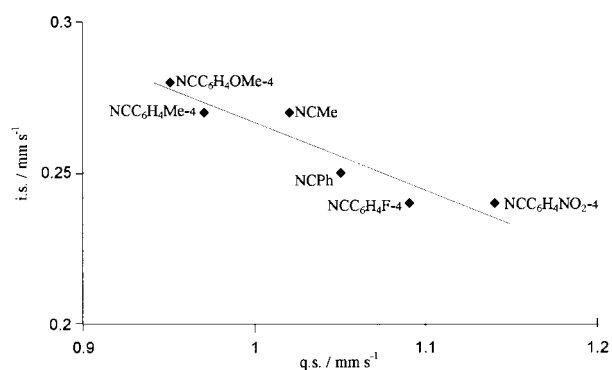
Fig. 3 Plot of i.s. *vs.* q.s. values for *trans*-[Fe(NCR)$_2$(depe)$_2$][BF$_4$]$_2$ **2** (R = Me, C$_6$H$_4$OMe-4, C$_6$H$_4$Me-4, Ph, C$_6$H$_4$F-4 or C$_6$H$_4$NO$_2$-4) [i.s. = (−0.22 ± 0.04) q.s. + (0.49 ± 0.04); correlation coefficient r = 0.88].
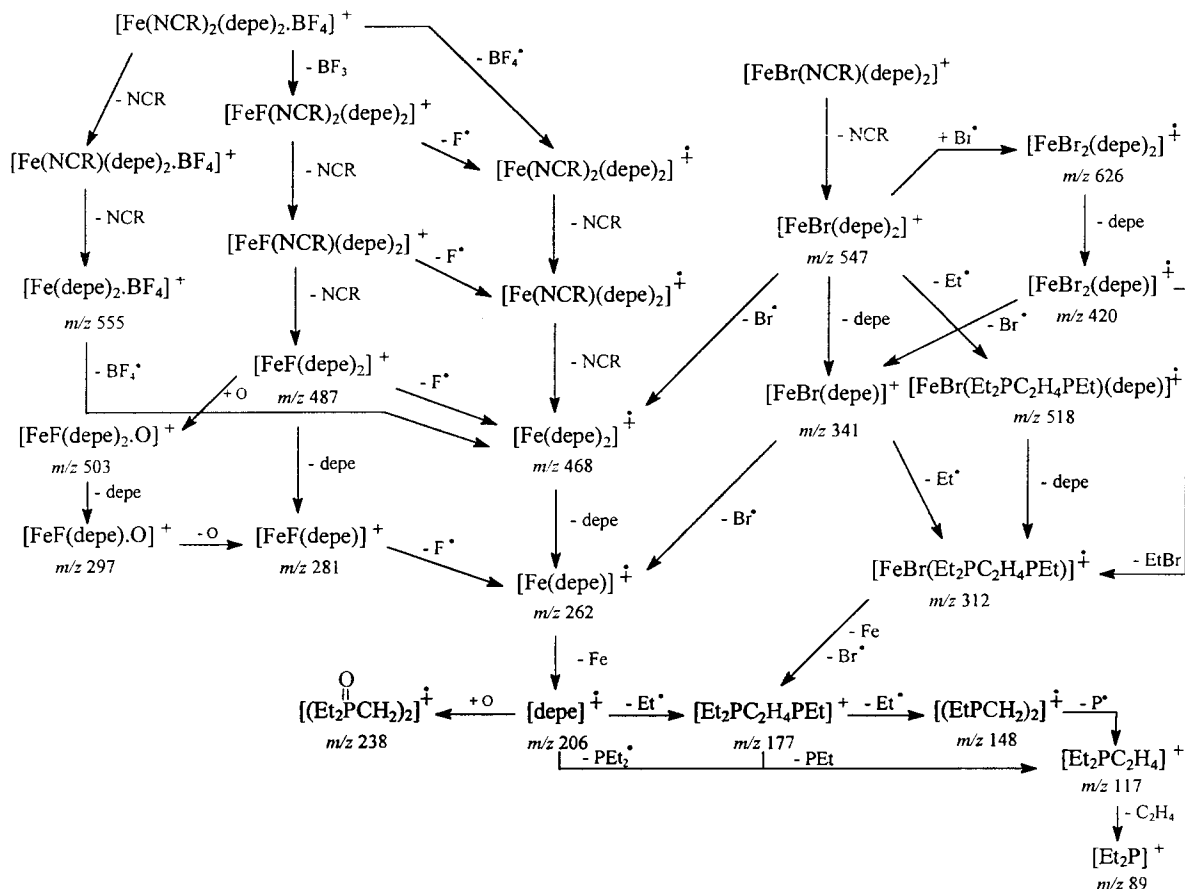
but also as more effective σ-electron donors than bromide. This is in accord with the observed lability of the bromide ligand at the iron(II) centre, which can be replaced easily by a nitrile (see the preparation of complexes **1** and **2**), and also with known[6] lower values of the partial i.s. and partial q.s. (see below) associated with the nitrile ligands in comparison with bromide.

For complexes **2** a reasonable linear correlation appears to be observed between i.s. and q.s. values [i.s. = (−0.22 ± 0.04) q.s. + (0.49 ± 0.04); correlation coefficient r = 0.88] with a *negative* slope (Fig. 3) suggesting that π effects are dominant for these ligands and this is consistent with the IR results discussed above. A linear correlation with a *positive* slope has been reported[10] for *trans*-[FeH(L)(depe)$_2$][BPh$_4$] with L ligands (NCMe, NCPh, isocyanides or phosphites) presenting dominant σ effects in their co-ordination (however, CO and N$_2$ do not follow such a correlation due to the significance of their π acceptance). For complexes **1** no relationship is apparent, and therefore neither σ nor π contributions appear to predominate in the co-ordination of the nitriles.

The Mössbauer spectral data were also analysed in terms of the point-charge model[10] and partial isomer shifts (p.i.s.) and partial quadrupole splittings (p.q.s.) were derived (Table 2). In this model the observed isomer shift is the sum of the partial isomer shifts of the individual ligands [eqn. (3)], whereas the

$$\text{i.s.} = \Sigma \text{ p.i.s.} \tag{3}$$

quadrupole splitting is given by a difference of partial values for the ligands, according to expressions dependent upon the com-

Scheme 1 (fragmentation diagram)

$[Fe(NCR)_2(depe)_2.BF_4]^+$

$-NCR$ → $[Fe(NCR)(depe)_2.BF_4]^+$

$-BF_3$ → $[FeF(NCR)_2(depe)_2]^+$

$-BF_4^\bullet$ → $[Fe(NCR)_2(depe)_2]^{\ddagger}$

$-F^\bullet$

$[FeF(NCR)_2(depe)_2]^+$ → $-NCR$ → $[FeF(NCR)(depe)_2]^+$ → $-F^\bullet$

$[Fe(NCR)(depe)_2.BF_4]^+$ → $-NCR$ → $[Fe(depe)_2.BF_4]^+$ m/z 555

$[Fe(NCR)_2(depe)_2]^{\ddagger}$ → $-NCR$ → $[Fe(NCR)(depe)_2]^{\ddagger}$ → $-NCR$

$[FeF(NCR)(depe)_2]^+$ → $-NCR$ → $[FeF(depe)_2]^+$ m/z 487 → $-F^\bullet$

$[Fe(depe)_2.BF_4]^+$ → $-BF_4^\bullet$ → $+O$ → $[FeF(depe)_2.O]^+$ m/z 503

$[FeF(depe)_2]^+$ → $-F^\bullet$ → $[Fe(depe)_2]^{\ddagger}$ m/z 468

$[FeF(depe)_2.O]^+$ → $-depe$ → $[FeF(depe).O]^+$ m/z 297 → $-O$ → $[FeF(depe)]^+$ m/z 281 → $-F^\bullet$

$[FeF(depe)_2]^+$ → $-depe$ → $[FeF(depe)]^+$ m/z 281

$[Fe(depe)_2]^{\ddagger}$ → $-depe$ → $[Fe(depe)]^{\ddagger}$ m/z 262

$[Fe(depe)]^{\ddagger}$ → $-Fe$ → $[depe]^{\ddagger}$ m/z 206

$[(Et_2PCH_2)_2]^{\ddagger}$ m/z 238 ← $+O$ — $[depe]^{\ddagger}$ m/z 206 → $-Et^\bullet$ → $[Et_2PC_2H_4PEt]^+$ m/z 177 → $-Et^\bullet$ → $[(EtPCH_2)_2]^{\ddagger}$ m/z 148 → $-P^\bullet$ → $[Et_2PC_2H_4]^+$ m/z 117 → $-C_2H_4$ → $[Et_2P]^+$ m/z 89

$-PEt_2^\bullet$ … $-PEt$ → $[Et_2PC_2H_4]^+$

Right side:

$[FeBr(NCR)(depe)_2]^+$ → $-NCR$ → $[FeBr(depe)_2]^+$ m/z 547

$+Br^\bullet$ → $[FeBr_2(depe)_2]^{\ddagger}$ m/z 626 → $-depe$ → $[FeBr_2(depe)]^{\ddagger}$ m/z 420

$[FeBr(depe)_2]^+$ → $-Br^\bullet$ → $[Fe(depe)_2]^{\ddagger}$; → $-depe$ → $[FeBr(depe)]^+$ m/z 341 ; $-Et^\bullet$ → $[FeBr(Et_2PC_2H_4PEt)(depe)]^{\ddagger}$ m/z 518

$[FeBr_2(depe)]^{\ddagger}$ → $-Br^\bullet$ → $[FeBr(Et_2PC_2H_4PEt)(depe)]^{\ddagger}$

$[FeBr(depe)]^+$ → $-Et^\bullet$ → $[FeBr(Et_2PC_2H_4PEt)]^{\ddagger}$ m/z 312 ; → $-Br^\bullet$ → $[Fe(depe)]^{\ddagger}$

$[FeBr(Et_2PC_2H_4PEt)(depe)]^{\ddagger}$ → $-depe$ → $[FeBr(Et_2PC_2H_4PEt)]^{\ddagger}$; ← $-EtBr$

$[FeBr(Et_2PC_2H_4PEt)]^{\ddagger}$ m/z 312 → $-Fe$, $-Br^\bullet$ → $[Et_2PC_2H_4PEt]^+$

Scheme 1 Proposed general fragmentation pattern for complexes *trans*-[FeBr(NCR)(depe)₂][BF₄] **1** and *trans*-[Fe(NCR)₂(depe)₂][BF₄]₂ **2** under FAB conditions.

position and structure, *i.e.* eqns. (4) and (5) for the general types

$$q.s. = 2\,p.q.s.(A) + 2\,p.q.s.(C) - 4\,p.q.s.(B) \qquad (4)$$

$$q.s. = 4\,p.q.s.(A) - 4\,p.q.s.(B) \qquad (5)$$

trans-[FeACB₄] and *trans*-[FeA₂B₄], which include our complexes **1** and **2** (A = NCR, B = depe/2, C = Br), respectively. By application of these equations to our data {and considering that p.i.s. = −0.02 (B) and 0.26 (C) mm s⁻¹, p.q.s.(B) = 0.45 or −0.63 mm s⁻¹ [with reference to p.q.s.(H) = 0.00 or to p.q.s.(Cl) = −0.27 mm s⁻¹, respectively], and p.q.s.(C) = 0.82 or −0.27 mm s⁻¹ [with reference to p.q.s.(H) = 0.00 or to p.q.s.(Cl) = −0.27 mm s⁻¹, respectively]},[6] we have estimated the p.i.s. and p.q.s. values for the nitrile ligands (Table 2).

In comparison with the aromatic nitriles, acetonitrile appears to exhibit a slightly higher p.i.s. (0.19 *vs.* 0.15–0.18 mm s⁻¹) and its p.q.s. (0.69 mm s⁻¹) is in the lower limit of the observed range (0.69–0.74 mm s⁻¹). This is in accord with the expected weaker π-electron acceptance of the alkyl cyanide (with an increasing effect on p.i.s. and a decreasing effect on p.q.s.) in comparison with the aromatic ones. The p.q.s. value we have obtained for NCMe is comparable with that (0.64)[6] previously reported, but our study gives a p.i.s. value which is significantly higher than that previously proposed[6] (0.11 mm s⁻¹) on the basis of the Mössbauer data for the hydride complexes [FeH(NCMe)(depe)₂][BPh₄] and [FeH(NCMe)(dmpe)₂][BF₄] (dmpe = Me₂PCH₂CH₂PMe₂). The previous p.i.s. value disagrees with the higher values obtained in the present study for the aromatic nitriles, but if the new p.i.s. value (0.19 mm s⁻¹) is used to calculate the i.s. for these hydride–acetonitrile complexes (a calculated value of 0.18 mm s⁻¹ is obtained for both compounds) then there is no satisfactory agreement with the measured values (0.11 or 0.10 mm s⁻¹).[6] These observations

suggest that the p.i.s. of the hydride and/or of the acetonitrile ligand can depend on the binding properties of the ligand in *trans* position, thus corroborating a suggestion presented by others[17] for the possibility of such type of behaviour for good π acceptors (*e.g.* isocyanides or carbonyl) and good σ donors (such as hydride).

An alternative explanation, involving the re-estimate of the p.i.s. of NCMe, could also be put forward. In fact if we consider the p.i.s. of this ligand as the average of the above values (0.19 and 0.11 mm s⁻¹, the new and the old one, respectively), *i.e.* 0.15 mm s⁻¹ and use this value to calculate the i.s. of those hydride complexes and of our nitrile compounds **1a** and **2a**, a satisfactory agreement (within 0.07 mm s⁻¹)[18] with the measured values is achieved. However, this approach would imply that the p.i.s. would be insufficiently sensitive to the difference in π-electron acceptance between alkyl and aryl cyanides, since the average p.i.s. value for NCMe would lie in the range observed for the latter nitriles.

In comparison with related unsaturated molecules, such as N₂, C₂H₄, CNMe or CO, the nitrile ligands present higher p.i.s. values (0.15–0.19 *vs.* 0.09,[6] 0.12,[6] −0.02[6] or −0.13[6] mm s⁻¹) and p.q.s. values (0.69–0.74 mm s⁻¹) which are in the upper limit of the range for those exhibited by the other ligands (0.78,[6] 0.42,[6] 0.33[6] or 0.43[6] mm s⁻¹, respectively). Hence, the nitrile ligands present weaker summed π-acceptance and σ-donor contributions (high p.i.s.), in particular behaving as weak σ donors but appreciable π acceptors (high p.q.s.) approaching N₂ in this respect (the others being stronger σ donors).

FAB mass spectra

In the FAB mass spectra of the complexes *trans*-[FeBr(NCR)(depe)₂][BF₄] (R = Me **1a**, Et **1b** or C₆H₄NO₂-4 **1h**) run in 3-nitrobenzyl alcohol matrices the corresponding molecular ions are clearly detected with the expected bromine isotopic

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for *trans*-[Fe(NCR)$_2$(depe)$_2$][BF$_4$]$_2$ (R = Me **2a** or CH$_2$C$_6$H$_4$OMe-4 **2c**)

		2c	
	2a	1	2
About the Fe atom			
Fe–P(1)	2.2736(11)	2.293(4)	2.281(5)
Fe–P(2)	2.2832(8)	2.308(4)	2.292(4)
Fe–N(1)	1.896(2)	1.898(11)	1.901(13)
P(1)–Fe–N(1)	88.71(8)	88.5(4)	89.5(4)
P(2)–Fe–N(1)	89.34(8)	89.5(4)	92.0(3)
P(1)–Fe–P(2)	84.88(3)	83.8(2)	84.8(2)
In the nitrile ligands			
N(1)–C(1)	1.131(4)	1.14(2)	1.15(2)
C(1)–C(2)	1.454(4)	1.48(2)	1.42(2)
Fe–N(1)–C(1)	178.2(3)	177.7(12)	176.0(13)
N(1)–C(1)–C(2)	179.4(4)	176(2)	178(2)

pattern. The fragmentation pathways (see the proposed general pattern depicted in Scheme 1) can be initiated by loss of the nitrile ligand to form [FeBr(depe)$_2$]$^+$ (*m/z* 547 for ^{79}Br or 549 for ^{81}Br), followed by Fe–Br bond homolysis to give the iron(I) ion [Fe(depe)$_2$]$^{·+}$ (*m/z* 468) which undergoes similar fragmentation patterns for all the mono- and di-nitrile complexes. Elimination of a diphosphine ligand occurs only after the loss of the nitrile ligand, as is known in other cases [19] in accord with the stronger co-ordination of the chelating diphosphine relative to the nitrile ligand. In this way [FeBr(depe)$_2$]$^+$ gives [FeBr(depe)]$^+$ [*m/z* 341 (^{79}Br) or 343 (^{81}Br)] which, upon Fe–Br bond homolysis, forms [Fe(depe)]$^{·+}$ (*m/z* 262). The molecular ion of the liberated diphosphine, depe$^{·+}$, follows a fragmentation pathway analogous to that exhibited by a genuine sample of depe. The diphosphine ligand itself can undergo partial fragmentation still in the presence of one of the monodentate coligands and of the other diphosphine and its fragmentation processes are analogous for all the complexes **1**, generally being initiated by ethyl (Et$^·$) elimination.

For complexes *trans*-[Fe(NCR)$_2$(depe)$_2$][BF$_4$]$_2$ (R = Me **2a**, Et **2b** or C$_6$H$_4$NO$_2$-4 **2h**) the peak detected at the highest *m/z* is due to the monocationic aggregate [Fe(NCR)$_2$(depe)$_2$·BF$_4$]$^+$ as expected on the basis of the known behaviour observed [20] for [ML$_n^{2+}$][Y$^-$]$_2$ type salts. The ions [Fe(NCR)(depe)$_2$·BF$_4$]$^+$, [Fe(NCR)$_2$(depe)$_2$]$^{·+}$ and [FeF(NCR)$_2$(depe)$_2$]$^+$ are also detected in all the cases and can be considered to be formed by elimination of a nitrile ligand, of BF$_4^·$ or of BF$_3$, respectively, from the above aggregate (Scheme 1). Loss of the nitrile ligands from the fluoro-complex leads to the fragment ion [FeF-(depe)$_2$]$^+$ (*m/z* 487) from which the oxoiron ions [FeF-(depe)$_2$·O]$^+$ (*m/z* 503) and [FeF(depe)·O]$^+$ (*m/z* 297) are conceivably derived, the matrix being the source of the oxygen atom. Similarly to the behaviour of the mononitrile compounds, at complexes **2** elimination of the chelating diphosphine ligand occurs only after the loss of the NCR ligands.

Crystal structures of *trans*-[Fe(NCR)$_2$(depe)$_2$][BF$_4$]$_2$ (R = Me or CH$_2$C$_6$H$_4$OMe-4)

The molecular structures of *trans*-[Fe(NCR)$_2$(depe)$_2$][BF$_4$]$_2$ (R = Me **2a** or CH$_2$C$_6$H$_4$OMe-4 **2c**) have been obtained by X-ray diffraction studies. They are depicted in Fig. 4 and selected bond lengths and angles are listed in Table 3. For both complexes the iron atom lies on a centre of symmetry and exhibits an approximately octahedral co-ordination with the four P atoms in the equatorial positions, whereas the nitrile ligands occupy the apical positions. These ligands are practically normal to the equatorial plane, with P–Fe–N angles,

(a)

(b)
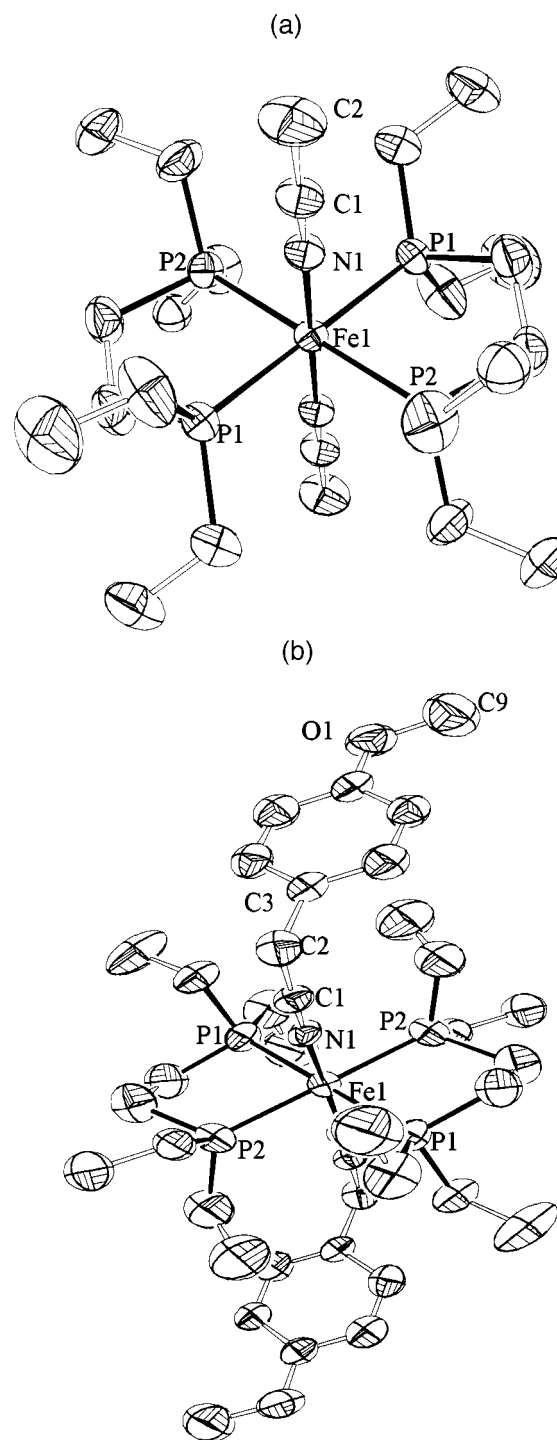
Fig. 4 Molecular structures of *trans*-[Fe(NCMe)$_2$(depe)$_2$][BF$_4$]$_2$ **2a** (a) and *trans*-[Fe(NCCH$_2$C$_6$H$_4$OMe-4)$_2$(depe)$_2$][BF$_4$]$_2$ **2c** (b).

ranging from 88.5(4) to 92.0(3)°, comparable to the ones found in the literature (88.2–91.8°).[21–23] In both complexes the nitrile ligands have an essential linear co-ordination [Fe–N–C 178.2(3)° for **2a** and 177.7(12)/176.0(13)° for **2c**, and N–C–C 179.4(4)° for **2a** and 176(2)/178(2)° for **2c**]. The Fe–N distances 1.896(2) and 1.898(11)/1.901(13) Å are in the lower range of the values normally reported (1.903 [24]–1.916 Å [25]), even though slightly longer than the extremely short distance found [1.867(12) Å] [23] in the complex *trans*-[Fe(NCMe)$_2$(Ph$_2$PCH$_2$-PPh$_2$)$_2$]$^{2+}$. The average metal–phosphorus bond length is similar to that observed [2.290(1) Å] [26] for *trans*-[FeBr$_2$(depe)$_2$].

In the NCCH$_2$C$_6$H$_4$OMe-4 ligand the angle C(1)–C(2)–C(3) is 110.5(13)/113.4(13)°, showing an almost perfect sp^3 hybridisation on the C(2) atom. The methoxy group is coplanar with the phenyl ring and they are nearly parallel to the equatorial

Table 4 Room-temperature crystal data and details of refinement for *trans*-[Fe(NCMe)$_2$(depe)$_2$][BF$_4$]$_2$ **2a** and *trans*-[Fe(NCCH$_2$C$_6$H$_4$OMe-4)$_2$-(depe)$_2$][BF$_4$]$_2$ **2c**

	2a	2c
Empirical formula	C$_{24}$H$_{54}$B$_2$F$_8$FeN$_2$P$_4$	C$_{38}$H$_{66}$B$_2$F$_8$FeN$_2$O$_2$P$_4$
M	724.04	936.28
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
Z	4	4
$a/Å$	17.265(4)	15.732(2)
$b/Å$	14.8580(5)	17.723(2)
$c/Å$	13.528(5)	16.723(3)
$\beta/°$	93.414(10)	96.330(10)
$U/Å^3$	3464(2)	4634.3(11)
$D_c/g\ cm^{-3}$	1.388	1.342
θ Range/°	1.8 to 30	1.7 to 25
$F(000)$	1520	1968
μ(Mo-Kα)/mm^{-1}	0.682	0.530
Index ranges h,k,l	0, −19 to 24, 20–18	−18 to −21, −19 to 0, 0–19
Reflections collected	5175	8421
Independent reflections (R_{int})	5024 (0.0443)	8107 (0.0894)
Data/restraints/parameters	4050/0/190	6010/260/517
Goodness of fit on F^2	0.991	1.068
R	0.0833 (5024)	0.31
R [$F_o > 4\sigma(F_o)$]	0.0569 (3593)	0.1361 (2800)
Largest difference peak and hole/e Å^{-3}	0.831, −0.352	0.946, −0.428

plane defined by the metal and the four phosphorus atoms. The P–C–C–P linkages have a *gauche* conformation,[27] with each carbon below and above the co-ordination plane.

Experimental

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 dibromide complex *trans*-[FeBr$_2$(depe)$_2$] was prepared by literature methods[26] and the syntheses of **1c** and **2c** have been reported.[12] The nitriles were used as purchased from Aldrich and Kodak & Lancaster Synthesis. The IR measurements were carried out on a Perkin-Elmer 683 spectrophotometer, ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer and electronic spectra on a JASCO 7800 UV/VIS 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 ^{57}Co 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 3-nitrobenzyl alcohol 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.* ^{56}Fe (92%), ^{79}Br (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.

Syntheses

***trans*-[FeBr(NCR)(depe)$_2$]Y (R = Me 1a, Et 1b, CH$_2$C$_6$H$_4$-OMe-4 1c, C$_6$H$_4$OMe-4 1d, C$_6$H$_4$Me-4 1e, Ph 1f, C$_6$H$_4$F-4 1g or C$_6$H$_4$NO$_2$-4 1h; Y = BF$_4$ or BPh$_4$).** Complexes **1** were prepared by adding the appropriate nitrile in the stoichiometric molar ratio to a methanolic solution of *trans*-[FeBr$_2$(depe)$_2$]. The solution was stirred for *ca.* 1 h at room temperature and [NBu$_4$][BF$_4$] or Na[BPh$_4$] in methanol was then added (in a 1:1 molar ratio relative to the starting complex). Cooling to *ca.* −18 °C led to the precipitation of the corresponding mono-

nitrile complex (*ca.* 65% average yield). As a typical example, *trans*-[FeBr(NCC$_6$H$_4$NO$_2$-4)(depe)$_2$][BF$_4$] **1h** was prepared as follows: *trans*-[FeBr$_2$(depe)$_2$] (0.240 g, 0.382 mmol) was dissolved in MeOH (50 cm^3) and NCC$_6$H$_4$NO$_2$-4 (51.7 mg, 0.349 mmol) in MeOH (2 cm^3) was added dropwise. The solution was stirred for 1 h at room temperature followed by addition of [NBu$_4$][BF$_4$] (126.4 mg, 0.384 mmol) in methanol (2 cm^3). Cooling to *ca.* −18 °C led to the precipitation of **1h** as a purple solid which was filtered off, washed with MeOH–Et$_2$O (1:4) and dried *in vacuo* (*ca.* 70% yield).

***trans*-[Fe(NCR)$_2$(depe)$_2$]Y$_2$ (R = Me 2a, Et 2b, CH$_2$C$_6$H$_4$-OMe-4 2c, C$_6$H$_4$OMe-4 2d, C$_6$H$_4$Me-4 2e, Ph 2f, C$_6$H$_4$F-4 2g or C$_6$H$_4$NO$_2$-4 2h; Y = BF$_4$ or BPh$_4$).** Complexes **2** were prepared by adding the appropriate nitrile in a twofold molar ratio to a methanolic solution of *trans*-[FeBr$_2$(depe)$_2$]. The solution was left to stir overnight at room temperature and [NBu$_4$][BF$_4$] or Na[BPh$_4$] in methanol was then added (in a 2:1 molar ratio, relative to the starting complex). Cooling to *ca.* −18 °C led to the precipitation of the dinitrile complex as a yellow solid (*ca.* 55% average yield). As a typical example, *trans*-[Fe(NCC$_6$H$_4$-OMe-4)$_2$(depe)$_2$][BF$_4$]$_2$ **2d** was prepared as follows: *trans*-[FeBr$_2$(depe)$_2$] (0.230 g, 0.366 mmol) was dissolved in MeOH (50 cm^3) and a solution of NCC$_6$H$_4$OMe-4 (100.9 mg, 0.758 mmol) in MeOH (3 cm^3) then added dropwise. The solution was left to stir overnight at room temperature and [NBu$_4$][BF$_4$] (254.4 mg, 0.772 mmol) in methanol (5 cm^3) then added dropwise. Cooling to *ca.* −18 °C led to the precipitation of **2d** as a yellow solid which was filtered off and recrystallised from CH$_2$Cl$_2$–Et$_2$O (*ca.* 65% yield).

Crystallography

X-Ray data were collected by the ω–2θ scan mode, on an Enraf-Nonius TURBO CAD4 diffractometer equipped with a rotating anode using graphite monochromated radiation, λ(Mo-Kα) = 0.71069 Å. Data collection parameters are summarised in Table 4. Three standard reflections were monitored during data collection to test the crystal stability. Using the CAD4 software, data were corrected for Lorentz-polarisation effects and empirically for absorption. In both structures the positions of the Fe atoms were obtained by a three-dimensional Patterson synthesis and located at special positions $\bar{1}$. Two different molecules were found in the asymmetric unit of complex **2c**. In **2a** the boron atoms lie on a twofold axis, on (0, *y*, 0.25)

and $(0.5, y, 0.75)$, respectively. All the non-hydrogen atoms were located in subsequent Fourier-difference maps and refined with anisotropic thermal motion parameters. The hydrogen atoms were inserted in calculated positions and refined isotropically with fixed distances to the parent carbon atom. The structure solution and refinement were done with SHELXS 86[28] and SHELXL 93,[29] respectively, and illustrations were drawn with ORTEP II.[30] The atomic scattering factors and anomalous scattering terms were taken from ref. 31 All calculations were carried out at the Centro de Química Estrutural.

CCDC reference number 186/1109.

See http://www.rsc.org/suppdata/dt/1998/3311/ for crystallographic files in .cif format.

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