

Synthesis and characterisation of nitrile complexes of iron

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Abstract

The reaction of *cis*-[FeH₂(DMPE)₂] (DMPE = 1,2-bis(dimethylphosphino)ethane) (**1a**) and *trans*-[FeCl₂(DMPE)₂] (**7a**) with acetonitrile, cyanocyclopropane, benzonitrile, *p*-bromobenzonitrile and terephthalonitrile and reaction of *trans*-[FeCl₂(DEPE)₂] (DEPE = 1,2-bis(diethylphosphino)ethane) (**7b**) with acetonitrile, cyanocyclopropane and benzonitrile in methanol solution resulted in a series of nitrile chloride complexes *trans*-[FeCl(N≡C-R)(PP)₂]⁺ and bis-nitrile complexes *trans*-[Fe(N≡C-R)₂(PP)₂]²⁺ of iron. All of the complexes have been characterised spectroscopically and four bis-nitrile complexes have been characterised crystallographically.

Crystals of *trans*-[Fe(N≡CCH₃)₂(DMPE)₂][2PF₆] (**3a**) are monoclinic, space group *P*2₁/*c*, with *a* = 8.697(3), *b* = 9.165(5), *c* = 20.026(5) Å, β = 107.54(3)°, *Z* = 2 and *R* = 0.058 (2300 *F* values). Crystals of *trans*-[Fe(N≡CC₃H₅)₂(DEPE)₂][2BF₄] (**4b**) are monoclinic, space group *P*2₁/*n*, with *a* = 11.146(1), *b* = 15.396(2), *c* = 11.810(2) Å, β = 111.06(1)°, *Z* = 2 and *R* = 0.050 (3011 *F* values). Crystals of *trans*-[Fe(N≡CPh)₂(DMPE)₂][2PF₆] (**5a**) are monoclinic, space group *P*2₁/*n*, with *a* = 11.006(2), *b* = 12.351(3), *c* = 13.650(4) Å, β = 93.60(2)°, *Z* = 2 and *R* = 0.035 (2650 *F* values). Crystals of *trans*-[Fe(*p*-N≡CC₆H₄Br)₂(DMPE)₂][2PF₆][0.5KPF₆] (**6a**) are tetragonal, space group *I*4̄*c*2, with *a* = *b* = 20.015(6), *c* = 21.610(3) Å, β = 90.00°, *Z* = 8 and *R* = 0.049 (2235 *F* values).

1. Introduction

Transition-metal organonitrile complexes have been formed by a variety of different methods including the reaction of metal salts in the presence of suitable nitriles [1] and the replacement of groups such as chloride [2] or molecular nitrogen [3] in metal complexes.

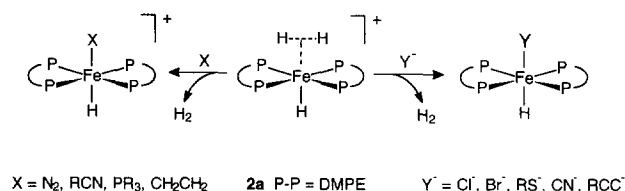
Iron(II) dihydride complexes of the type *cis*-FeH₂(PP)₂ (PP = R₂PCH₂CH₂PR₂; **1a** R = CH₃, DMPE; **1b** R = CH₂CH₃, DEPE) are protonated by weak acids to form a cationic complex containing η²-bound dihydrogen, *trans*-[FeH(H₂)(PP)₂]⁺ (**2**) [4]. In these complexes, molecular hydrogen is only weakly coordinated and may be displaced by a range of neutral ligands (e.g. dinitrogen, nitriles, tertiary phosphines or ethylene) [5] or anions (e.g. halides, thiolates, cyanide or acetylides) [6]. If the conjugate base (B[−]) of the protonating acid (B-H) is itself a good ligand, protonation followed by H₂ displacement results effectively in the substitution of a hydride ligand by B[−] (Scheme 1).

During the course of our continuing study of iron phosphine complexes which possess a rod-like structure [7], we have synthesised a range of nitrile chloride complexes *trans*-[FeCl(N≡C-R)(PP)₂]⁺ and bis-nitrile complexes *trans*-[Fe(N≡C-R)₂(PP)₂]²⁺ of iron incorporating acetonitrile, benzonitrile, *p*-bromobenzonitrile, terephthalonitrile and cyanocyclopropane. In this report, the preparation and spectroscopic characterisation of *trans*-[FeCl(N≡C-R)(PP)₂]⁺ and *trans*-[Fe(N≡C-R)₂(PP)₂]²⁺ complexes is detailed, together with the crystal structures of four representative complexes.

2. Results and discussion

The reaction between *cis*-[FeH₂(DMPE)₂] (**1a**) and excess acetonitrile in methanol cleanly converts the molecular hydrogen complex (**2a**) to the *trans*-bis-acetonitrile complex *trans*-[Fe(N≡CCH₃)₂(DMPE)₂]²⁺ (**3a**). In methanol solvent, the bis-nitrile complex crystallises directly from the reaction mixture over the space of several days, following the addition of a methanol

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Scheme 1.

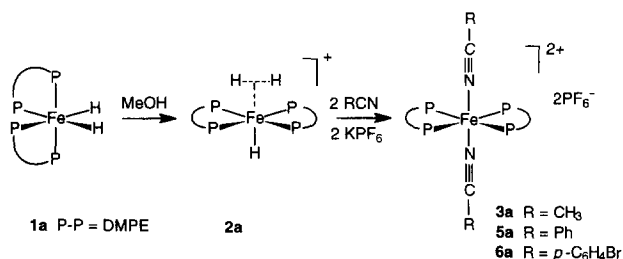
solution of potassium hexafluorophosphate. In an exactly analogous sequence, *cis*-[FeH₂(DMPE)₂] (**1a**) reacts with benzonitrile and *p*-bromobenzonitrile in methanol solution to give the corresponding iron bis-nitrile complexes *trans*-[Fe(N≡CR)₂(DMPE)₂][2PF₆] (R = Ph, **5a**) and (R = *p*-C₆H₄Br, **6a**) (Scheme 2).

In the reactions between (**1a**) and an organic nitrile, a nitrile hydride complex intermediate was detected by ³¹P NMR almost immediately after mixing the two reagents together. The nitrile hydride complexes *trans*-[FeH(N≡CCH₃)(DMPE)₂][PF₆] and *trans*-[FeH(*p*-N≡CC₆H₄Br)(DMPE)₂][PF₆] were isolated by precipitation from the reaction solution, after addition of potassium hexafluorophosphate. Continued stirring of the reaction mixture resulted in formation of the bis-nitrile complexes **3a** and **6a** respectively.

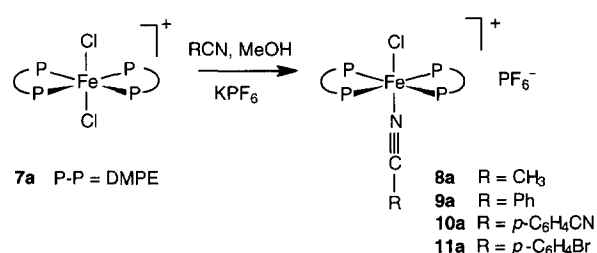
The *trans*-bis-nitrile iron complexes **3–6** were obtained as yellow or orange solids as PF₆[−], BF₄[−] or BPh₄[−] salts which were essentially insoluble in methanol and hexane, slightly soluble in benzene and soluble in THF, acetonitrile, dimethylformamide, chloroform, dichloromethane and acetone. The complexes are moderately air stable and may be kept indefinitely as dry solids under an argon atmosphere.

Reaction of *trans*-[FeCl₂(DMPE)₂] (**7a**) with excess acetonitrile in methanol solvent resulted in the almost quantitative precipitation of *trans*-[FeCl(N≡CCH₃)(DMPE)₂][PF₆] (**8a**) after addition of potassium hexafluorophosphate. A similar procedure was used to synthesise iron nitrile chloride complexes **9a**, **10a** and **11a** from benzonitrile, terephthalonitrile and *p*-bromobenzonitrile respectively (Scheme 3).

Cyanocyclopropane, however, reacts with **7a** to directly form the bis-nitrile complex **4a**. This could result from the greater solubility of *trans*-[FeCl(N≡CC₃H₅)(DMPE)₂]⁺ compared with **8a–11a**



Scheme 2.



Scheme 3.

under the reaction conditions, allowing further reaction to form the bis-nitrile complex **4a**. It has been reported that **7a** reacts with excess acetonitrile and sodium tetraphenylborate to form the bis-nitrile complex *trans*-[Fe(N≡CCH₃)₂(DMPE)₂][2BPh₄] after 18 h under refluxing conditions [8]. In the case of *trans*-[FeCl₂(DEPE)₂] (**7b**), both the acetonitrile chloride and the bis-acetonitrile salts may be isolated at room temperature [9]. Under the reaction conditions employed, only the bis-nitrile complexes were isolated when **7b** reacted with acetonitrile, cyanocyclopropane or benzonitrile.

The nitrile groups of the bis-nitrile complexes can be exchanged in the presence of terminal acetylenes. *Trans*-[Fe(N≡CPh)₂(DMPE)₂]²⁺ (**5a**) affords the bis-acetylide *trans*-Fe(C≡CPh)₂(DMPE)₂ when added to a solution of phenylacetylene in methanol solution in the presence of sodium methoxide.

2.1. Spectroscopic characterisation of *trans*-[FeCl(N≡C-R)(PP)₂]⁺ and *trans*-[Fe(N≡C-R)₂(PP)₂]²⁺ complexes

All of the bis-nitrile and nitrile chloride complexes synthesised are diamagnetic and all show one singlet resonance in the ³¹P NMR spectrum, indicative of a *trans* geometry in which the four phosphorus atoms of the chelating ligands are equivalent. The ³¹P chemical shifts typically occur in the range 58–66 ppm and are very similar for both nitrile chloride and bis-nitrile complexes generated from the same nitrile.

The ³¹P NMR spectra of the nitrile hydride complexes (acquired without proton decoupling) appear as doublets, with coupling to the iron-bound hydride (²J_{PH} ≈ 50 Hz). The ³¹P chemical shifts of the nitrile hydride complexes occur at approximately 69 ppm, i.e. approximately 10 ppm downfield of the corresponding bis-nitrile and nitrile chloride complexes.

The ¹³C NMR spectra of both the bis-nitrile and nitrile chloride complexes indicate a small upfield shift of the resonances associated with the cyano carbon atom of the nitrile ligand on complexation (Table 1). It was not possible to unequivocally assign the resonances for all the quaternary carbon atoms in compounds **4b** and **10a**.

Table 1
 ^{13}C chemical shifts of the nitrile carbon in complexed and non-complexed nitriles

Complex	δ (ppm)	RC $\equiv$ N	δ (ppm)
<i>trans</i> -[FeCl(N $\equiv$ CCH ₃)(DMPE) ₂][PF ₆] (8a)	98.1 ^a	CH ₃ C $\equiv$ N	117.7 ^b
<i>trans</i> -[FeH(N $\equiv$ CCH ₃)(DMPE) ₂][PF ₆]	124.1 ^a		
<i>trans</i> -[Fe(N $\equiv$ CCH ₃) ₂ (DMPE) ₂][2PF ₆] (3a)	112.1 ^c		
<i>trans</i> -[Fe(N $\equiv$ CCH ₃) ₂ (DEPE) ₂][2BPh ₄] (3b)	105.2 ^a		
<i>trans</i> -[FeCl(N $\equiv$ CPh)(DMPE) ₂][PF ₆] (9a)	110.4 ^a	PhC $\equiv$ N	118.7 ^b
<i>trans</i> -[Fe(N $\equiv$ CPh) ₂ (DMPE) ₂][2PF ₆] (5a)	110.8 ^c		
<i>trans</i> -[Fe(N $\equiv$ CPh) ₂ (DEPE) ₂][2BPh ₄] (5b)	112.0 ^d		
<i>trans</i> -[FeCl(<i>p</i> -N $\equiv$ CC ₆ H ₄ Br)(DMPE) ₂][BPh ₄] (11a)	109.4 ^a	<i>p</i> -BrC ₆ H ₄ C $\equiv$ N	117.7 ^b
<i>trans</i> -[FeH(<i>p</i> -N $\equiv$ CC ₆ H ₄ Br)(DMPE) ₂][PF ₆]	112.1 ^d		
<i>trans</i> -[Fe(<i>p</i> -N $\equiv$ CC ₆ H ₄ Br) ₂ (DMPE) ₂][2PF ₆] (6a)	109.8 ^d		

^a Solvent acetonitrile-*d*₃; ^b solvent chloroform-*d*₁; ^c solvent DMF-*d*₇; ^d solvent acetone-*d*₆.

The ^1H NMR spectra (^{31}P decoupled) of the complexes reflect the symmetry of the ligand environment. In the bis-nitrile complexes, two singlet resonances associated with the methyl and methylene protons of the

DMPE ligand were observed. In the case of the nitrile chloride and nitrile hydride compounds, which no longer possess a plane of symmetry containing all four phosphorus atoms, more complex spectra were observed.

Table 2
 Crystal data for the complexes **3a**, **4b**, **5a** and **6a**

Complex	3a	4b	5a	6a
Chemical formula	C ₁₆ H ₃₈ F ₁₂ FeN ₂ P ₆	C ₂₈ H ₅₈ B ₂ F ₈ FeN ₂ P ₄	C ₂₆ H ₄₂ F ₁₂ FeN ₂ P ₆	C ₂₆ H ₄₂ Br ₂ F ₁₅ FeN ₂ P _{6.5} K _{0.5}
<i>M</i> _r	728.23	776.13	852.3	1104.12
Crystal system	monoclinic	monoclinic	monoclinic	tetragonal
Crystal colour	yellow	orange	yellow	yellow
Crystal habit	plate	plate	prism	columnar
Crystal dimensions (mm ³)	0.30 × 0.65 × 0.10	0.14 × 0.28 × 0.25	0.28 × 0.28 × 0.13	0.39 × 0.18 × 0.16
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	$\bar{I}4c2$
<i>Z</i>	2	2	2	8
<i>a</i> (Å)	8.697(3)	11.146(1)	11.006(2)	20.015(6)
<i>b</i> (Å)	9.165(5)	15.396(2)	12.351(3)	20.015(6)
<i>c</i> (Å)	20.026(5)	11.810(2)	13.650(4)	21.610(3)
β (°)	107.54(3)	111.06(1)	93.60 (2)	90.00
<i>V</i> (Å ³)	1522(1)	1891.0(5)	1852(1)	8657(3)
<i>D</i> _x (Mg m ⁻³)	1.589	1.362	1.528	1.52
Radiation source	Mo K α	Mo K α	Mo K α	Mo K α
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Diffractionmeter	Enraf–Nonius	Enraf–Nonius	Enraf–Nonius	Enraf–Nonius
Monochromator	Graphite	Graphite	Graphite	Graphite
θ range (°)	1 < θ < 30	1 < θ < 25	1 < θ < 25	1 < θ < 25
Scan type	$\omega/2\theta$	$\omega-4/3\theta$	$\omega-2\theta$	$\omega-\theta$
No. of reflections measured	4430	3633	3487	4139
No. of observed reflections	2300	3011	2650	2235
Criterion of observed	$I > 3\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
Range of <i>h</i>	0 to 12	–13 to 13	–13 to 13	0 to 23
Range of <i>k</i>	0 to 12	0 to 18	0 to 14	0 to 23
Range of <i>l</i>	–27 to 26	0 to 14	0 to 16	0 to 25
Number of variables	299	263	226	278
<i>R</i>	0.058	0.050	0.035	0.049
<i>R</i> _w	0.056	0.0508	0.041	0.050
Shift/e.s.d.	0.06	< 0.259	< 0.005	< 0.05
Refinement	XTAL 3.2	SHELX-76	SHELX-76	SHELX-76
Data reduction	XTAL 3.2	Enraf–Nonius SDP [24]	Enraf–Nonius SDP	Enraf–Nonius SDP
Solution	XTAL 3.2	SHELXS-86 [25]	SHELXS-86	SHELXS-86
H atoms	Refined	Calc.	Calc.	Calc.
Weighting scheme	Statistical	Statistical	Statistical	Statistical

3a = *trans*-[Fe(N $\equiv$ CCH₃)₂(DMPE)₂][2PF₆], **4b** = *trans*-[Fe(N $\equiv$ CC₃H₅)₂(DEPE)₂][2BF₄], **5a** = *trans*-[Fe(N $\equiv$ CC₆H₅)₂(DMPE)₂][2PF₆], **6a** = *trans*-[Fe(*p*-N $\equiv$ CC₆H₄Br)₂(DMPE)₂][2PF₆].

The α methylene hydrogens of the ethyl groups of the DEPE complexes are diastereotopic and show a multiplet pattern in the ^1H NMR spectrum. In addition, the ^1H NMR spectra of the nitrile hydride complexes show a high field quintet at approximately -22 ppm, indicating coupling to four equivalent phosphorus atoms ($^2J_{\text{PH}} \approx 50$ Hz).

The stretching frequency of the $\text{N}\equiv\text{C}$ bond changed little in the case of the bis-acetonitrile (**3a**) and acetonitrile chloride (**8a**) complexes ($\pm 5\text{ cm}^{-1}$) compared to that of the free ligand. Benzonitrile, however, showed a shift in frequency, to lower energy, on complexation (13 and 32 cm^{-1} for **5a** and **9a** respectively) and this suggests an increased degree of metal to ligand ($d_{\pi} \rightarrow \pi^*$) backbonding in the aryl nitrile ligands compared to the alkylnitrile ligands.

2.2. X-ray crystallography

The solid state structures of four bis-nitrile complexes (**3a**, **4b**, **5a** and **6a**) have been determined by single crystal X-ray diffraction techniques (Table 2, Figs. 1–4). All of the complexes are octahedral with the phosphorus atoms of the chelating ligands in the complexes forming an equatorial plane with the nitrile ligands adopting axial positions *trans* to one another. The crystal structure of *trans*- $[\text{Fe}(\text{N}\equiv\text{CCH}_3)_2(\text{DMPE})_2][2\text{BPh}_4]$ has been determined by other workers [8], and the bond lengths and angles of the cation correspond to those determined for **3a** (Table 3).

The complexes of alkyl nitriles **3a** and **4b** possess a

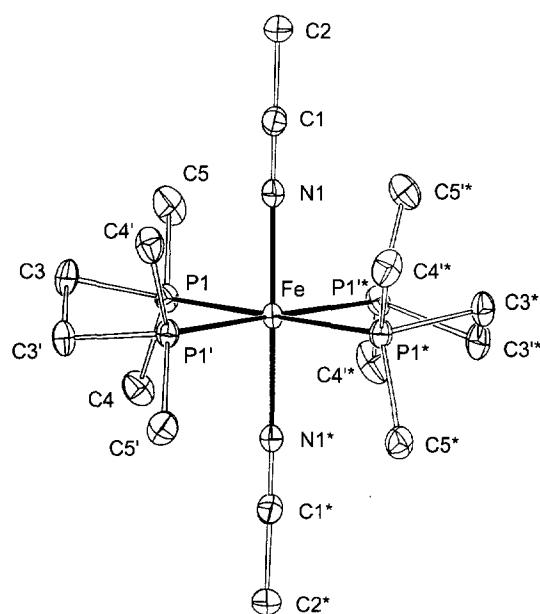


Fig. 1. View of the complex *trans*- $[\text{Fe}(\text{N}\equiv\text{CCH}_3)_2(\text{DMPE})_2][2\text{PF}_6]$ (**3a**) showing atom labelling. Atoms labelled * are related by inversion to the asymmetric unit.

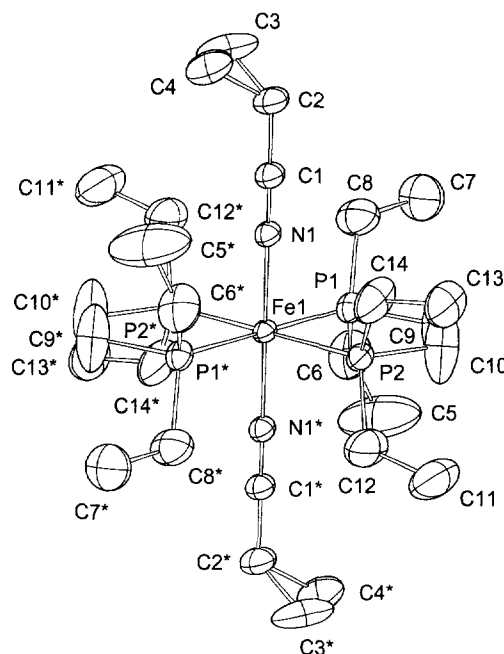


Fig. 2. View of the complex *trans*- $[\text{Fe}(\text{N}\equiv\text{CC}_3\text{H}_5)_2(\text{DEPE})_2][2\text{BF}_4]$ (**4b**) showing atom labelling. Atoms labelled * are related by inversion to the asymmetric unit.

similar Fe–N bond length to that of the benzonitrile complex **5a**, though a longer Fe–N bond length than that of the *p*-bromobenzonitrile complex **6a**. The $\text{C}\equiv\text{N}$ distance in complexes **3a**, **4b** and **6a** was within the

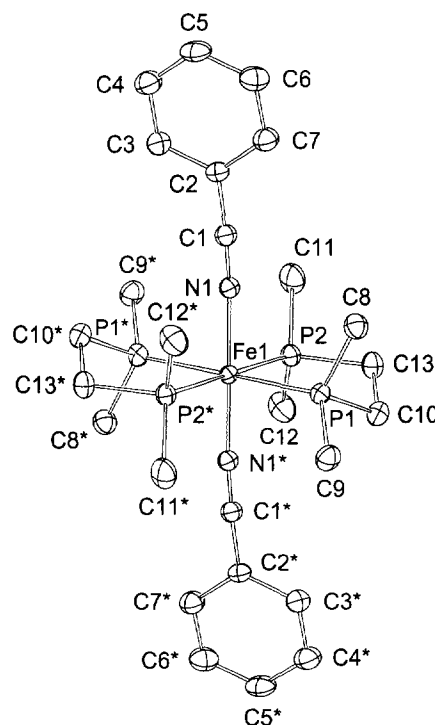


Fig. 3. View of the complex *trans*- $[\text{Fe}(\text{N}\equiv\text{CPh})_2(\text{DMPE})_2][2\text{PF}_6]$ (**5a**) showing atom labelling. Atoms labelled * are related by inversion to the asymmetric unit.

Table 3
Selected bond lengths (Å) and angles (°) for complexes **3a**, **4b**, **5a** and **6a**

Complex	$r(\text{Fe}-\text{N})$	$r(\text{Fe}-\text{P})$	$r(\text{C}\equiv\text{N})$	$r(\text{NC}-\text{C})$	$\angle\text{P}-\text{Fe}-\text{P}$	$\angle\text{P}-\text{Fe}-\text{N}$	$\angle\text{Fe}-\text{N}-\text{C}$	Reference
<i>trans</i> -[Fe(N≡CCH ₃) ₂ (DMPE) ₂][2PF ₆] (3a)	1.917(5)	2.255(2)	1.127(8)	1.45(1)	85.17(6)	89.8(1)	178.6(4)	This work
		2.263(2)				90.3(1)		
<i>trans</i> -[Fe(N≡CCH ₃) ₂ (DMPE) ₂] ²⁺	1.905(7)	2.264(4)	1.129(7)	1.463(10)	84.8(2)	89.0(2)	178.1(5)	[8]
		2.270(4)				90.1(2)		
<i>trans</i> -[Fe(N≡CCH ₃) ₂ (DPPM) ₂] ²⁺	1.867(12)	2.281(4)	1.125(15)	1.525(22)	73.0(1)	87.3(3)	172.3(11)	[10]
		2.285(4)						
<i>trans</i> -[Fe(N≡CCH ₃) ₂ (OPDP) ₂] ²⁺	1.894(4)	2.337(1)			81.1(1)	90.4(1)		[11]
		2.343(1)				91.8(1)		
<i>trans</i> -[Fe(N≡CCH ₃) ₂ (DPPE) ₂] ²⁺	1.916(10)	2.321(3)	1.13(2)	1.45(2)	82.57(9)	89.4(2)	170.6(11)	[12]
<i>trans</i> -[Fe(N≡CC ₃ H ₅) ₂ (DEPE) ₂][2BF ₄] (4b)	1.913(3)	2.284(2)	1.130(5)	1.443(6)	85.1(0)	89.9(1)	179.0(4)	This work
		2.295(1)				90.5(1)		
<i>trans</i> -[Fe(N≡CPh) ₂ (DMPE) ₂][2PF ₆] (5a)	1.917(5)	2.255(2)	1.150(4)	1.433(4)	84.9(0)	87.8(1)	174.6(2)	This work
		2.263(2)				88.8(1)		
<i>trans</i> -[Fe(<i>p</i> -N≡CC ₆ H ₄ Br) ₂ (DMPE) ₂][2PF ₆] (6a)	1.893(7)	2.259(3)	1.129(10)	1.444(13)	85.4(1)	89.9(2)	178.1(8)	This work
		2.265(3)				90.2(2)		

DPPM = Ph₂PCH₂PPh₂; OPDP = *o*-phenylene-bis(diphenylphosphine); DPPE = Ph₂PCH₂CH₂PPh₂.

range 1.127–1.130 Å, which is significantly shorter than the corresponding distance in **5a** (1.150 Å). In contrast, the NC–C bond length was significantly longer in **3a**, **4b** and **6a** than in **5a**. The Fe–P distances of the three DMPE complexes **3a**, **5a** and **6a** are similar and significantly shorter than the Fe–P distances measured in the DEPE complex **4b**. The increased Fe–P distances in the complex with DEPE ligands reflects the differing steric requirement of the phosphine ligands. The ‘bite’ angle (P–Fe–P angle within the chelating phosphine ligand) in all four of the DMPE and DEPE complexes **3a**, **4b**, **5a** and **6a** was approximately 85°.

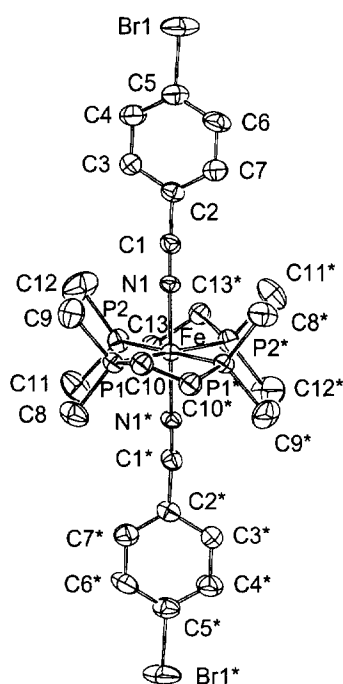


Fig. 4. View of the complex *trans*-[Fe(*p*-N≡CC₆H₄Br)₂(DMPE)₂][2PF₆] (**6a**) showing atom labelling. Atoms labelled * are related by inversion to the asymmetric unit.

The structures of related bis-nitrile iron complexes containing bidentate phosphines have been reported previously [8,10–12]. The Fe–P distances in the DMPE and DEPE complexes **3a**, **4b**, **5a** and **6a** were shorter than in the cations [Fe(N≡CCH₃)₂(DPPM)₂]²⁺ [10], [Fe(N≡CCH₃)₂(OPDP)₂]²⁺ [11], and [Fe(N≡CCH₃)₂(DPPE)₂]²⁺ [12], and this correlates with the larger P–Fe–P ‘bite’ angle of the DMPE and DEPE chelating ligands. While the length of the C≡N bond does not vary significantly in the four acetonitrile complexes studied, the length of the Fe–N bond was longer in **3a** and [Fe(N≡CCH₃)₂(DPPE)₂]²⁺ than [Fe(N≡CCH₃)₂(DPPM)₂]²⁺ or [Fe(N≡CCH₃)₂(OPDP)₂]²⁺. The M–N bond is shorter in the iron nitrile complexes than in [Mo₂(μ-F)(N≡CCH₃)₈O₂][3BF₄] [13], [(η⁶-C₆H₆)Ru(N≡CCH₃)₂Cl][BF₄] [14], [Ru(S-2,3,5,6-(CH₃)₄C₆H₃)(N≡CCH₃)₂][PF₆] [15], *mer*-[RuH(NC-CHCOOCH₃)(NCCH₂COOCH₃)(PPh₃)₃] [16], [Re(*p*-NCC₆H₄CH₃)₂(Ph₂PCH₂CH₂PPh₂)₂][ReF₂(Ph₂-PCH₂CH₂PPh₂)₂][2BF₄] [17] or [Re(*p*-NCC₆H₄-CH₃)₂(Ph₂PCH₂CH₂PPh₂)₂][BF₄] [18].

3. Experimental section

All reactions and manipulations were performed under an inert atmosphere of nitrogen or argon, in a dry box or using Schlenk apparatus. Tetrahydrofuran (THF), benzene and light petroleum (b.p. 60–70 °C) were distilled from sodium benzophenone ketyl under nitrogen prior to use. Methanol (500 ml) was dried by distillation from magnesium. Deuterated solvents were obtained from Merck and Aldrich and used as received. Nitriles were obtained from Aldrich and purified by distillation or recrystallisation before use. *Cis*-[FeH₂(DMPE)₂] (**1a**), *trans*-[FeCl₂(DMPE)₂] (**7a**) and *trans*-[FeCl₂(DEPE)₂] (**7b**) were prepared according to literature procedures

[19]. ^1H (400.1 MHz), ^{31}P (162.0 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer at 300 K, in the solvents indicated. ^1H and ^{13}C NMR spectra were referenced to residual solvent resonances and ^{31}P NMR spectra were referenced to external, neat trimethyl phosphite, taken to be 140.85 ppm at 300 K. UV–visible spectra were recorded as THF solutions on a Hitachi 150-20 spectrometer. Infrared spectra were recorded on a Perkin Elmer FTIR 1600 spectrometer with the sample in a Nujol mull. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were performed by National Analytical Laboratories (N.A.L.) or the University of New South Wales Analytical Service. All solvents and liquid reagents were degassed by three to five freeze–pump–thaw cycles prior to use. Nitrogen (> 99.5%) and argon were obtained from Commonwealth Industrial Gases (C.I.G.) and used as received.

3.1. *Trans*-[Fe(N≡CCH₃)₂(DMPE)₂][2PF₆] (3a)

Cis-[FeH₂(DMPE)₂] (1a, 40 mg, 112 μmol) in methanol (1 ml) was added to acetonitrile (46 mg, 1.12 mmol) in methanol (1 ml) and the solution was stirred for 30 min. Potassium hexafluorophosphate (50 mg, 272 μmol) in methanol (1 ml) was added and the solution was stirred for a further 2 h at ambient temperature. The resultant precipitate was collected by filtration and washed with methanol (1 ml) to yield *trans*-[FeH(N≡CCH₃)(DMPE)₂][PF₆] as a yellow powder (28 mg, 46%); m.p. > 300 °C (decomposed without melting). ^{31}P NMR (acetone-*d*₆): δ 69.8 (d, $^2J_{\text{PH}}$ = 49 Hz). ^1H NMR (acetone-*d*₆): δ -22.44 (1H, quintet, $^2J_{\text{PH}}$ = 49 Hz, FeH), 1.95 (12H, s, PCH₃), 1.98 (12H, s, PCH₃), 2.23–2.51 (8H, m, CH₂), 2.76 (3H, s, CCH₃). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (acetone-*d*₆): δ 2.7 (CCH₃), 13.7 (CH₃), 20.9 (CH₃), 30.7 (CH₂), 124.1 (N≡C). ν_{max} (Nujol): 2232 (N≡C) cm⁻¹.

A solution of *cis*-[FeH₂(DMPE)₂] (1a, 40 mg, 111 μmol), acetonitrile (30 mg, 1.03 mmol) and potassium hexafluorophosphate (93 mg, 500 μmol) in methanol (2 ml) was stirred for 2 days. The resultant precipitate was collected by filtration and recrystallised from ethanol to yield *trans*-[Fe(N≡CCH₃)₂(DMPE)₂][2PF₆] (3a) as a yellow powder (33 mg, 41%). $^{31}\text{P}\{^1\text{H}\}$ NMR (DMF-*d*₇): δ 60.6. $^1\text{H}\{^{31}\text{P}\}$ NMR (DMF-*d*₇): δ 1.62 (24H, s, PCH₃), 2.27 (8H, s, CH₂), 2.40 (6H, s, CH₃). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (DMF-*d*₇): δ 3.74 (CCH₃), 11.1 (CH₃), 27.8 (CH₂), 112.1 (N≡C). λ_{max} (THF, log ε): 213 (2.11), 256 (2.73). ν_{max} (Nujol): 2257 (N≡C) cm⁻¹.

3.2. *Trans*-[Fe(N≡CCH₃)₂(DEPE)₂][2BPh₄] (3b)

Acetonitrile (10 mg, 0.34 mmol) was added to *trans*-[FeCl₂(DEPE)₂] (7b, 30 mg, 83 μmol) dissolved in dry

methanol (3 ml) and the solution was stirred for 10 min. A saturated solution of sodium tetraphenylborate (1 ml) was added and the resultant precipitate was collected by filtration to yield *trans*-[Fe(N≡CCH₃)₂(DEPE)₂][2BPh₄] (3b) as a cream coloured powder (45 mg, 68%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone-*d*₆): δ 65.9. $^1\text{H}\{^{31}\text{P}\}$ NMR (acetone-*d*₆): δ 1.50 (24H, s, CH₃CH₂), 2.23 (8H, m, CH₃CH₂), 2.33 (8H, m, CH₃CH₂), 2.49 (6H, s, NCCCH₃), 2.50 (8H, s, CH₂), 6.92 (8H, m, ArCH), 7.06 (16H, m, ArCH), 7.49 (16H, m, ArCH). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (acetone-*d*₆): δ 5.6 (NCCCH₃), 9.7 (CH₂CH₃), 18.4 (CH₂CH₃), 20.7 (CH₂), 105.2 (N≡C), 122.6 (ArCH), 126.3 (ArCH), 137.4 (ArCH), 164.25 (J_{BH} = 50 Hz, 4 lines, BC). ν_{max} (Nujol): 2255 (N≡C) cm⁻¹. Anal. Found: C, 72.7; H, 8.2; N, 2.4. FeC₇₂H₉₄P₄N₂B₂ Calc.: C, 72.74; H, 7.97; N, 2.36%.

3.3. *Trans*-[Fe(N≡CC₃H₅)₂(DMPE)₂][2BF₄] (4a)

Trans-[FeCl₂(DMPE)₂] (7a, 45 mg, 105 μmol) was dissolved in methanol (5 ml) to give a red solution. Addition of cyanocyclopropane (0.25 ml, 4.1 mmol) gave a purple coloured solution which turned orange after stirring at ambient temperature overnight. Sodium tetrafluoroborate (23 mg, 210 μmol) was added and the solution was stirred for a further hour. Concentration of the solution gave a yellow precipitate which was removed by filtration. The solid was washed with cold methanol and *n*-hexane and then dried in vacuo to give *trans*-[Fe(N≡CC₃H₅)₂(DMPE)₂][2BF₄] (4a) as a yellow solid (37 mg, 72%). $^{31}\text{P}\{^1\text{H}\}$ NMR (methanol-*d*₄): δ 59.1. ^1H NMR (methanol-*d*₄): δ 0.99 (4H, m, CHCHH), 1.05 (4H, m, CHCHH), 1.56 (24H, br s, CH₃), 1.74 (2H, m, CH), 2.28 (8H, br m, PCH₂). $^{13}\text{C}\{^{31}\text{P}, ^1\text{H}\}$ (methanol-*d*₄): δ -0.8 (CH), 8.7 (CCH₂), 12.3 (PCH₃), 29.7 (PCH₂), 141.2 (N≡C). ν_{max} (Nujol): 2054 (N≡C) cm⁻¹. Anal. Found: C, 36.4; H, 6.6; N, 4.1. FeC₂₀H₄₂P₄N₂B₂F₈ Calc.: C, 36.18; H, 6.38; N, 4.22%.

3.4. *Trans*-[Fe(N≡CC₃H₅)₂(DEPE)₂][2BF₄] (4b)

Trans-[FeCl₂(DEPE)₂] (7b, 50 mg, 93 μmol) was dissolved in methanol (5 ml) and cyanocyclopropane (0.25 ml, 4.1 mmol) was added. After stirring at ambient temperature overnight, sodium tetrafluoroborate (22 mg, 200 μmol) was added and the solution was stirred for 1 h. Concentration of the solution gave a yellow precipitate which was removed by filtration. The solid was washed with cold methanol and *n*-hexane and then dried in vacuo to give *trans*-[Fe(N≡CC₃H₅)₂(DEPE)₂][2BF₄] (4b) as a yellow solid (47 mg, 78%). $^{31}\text{P}\{^1\text{H}\}$ NMR (methanol-*d*₄): δ 64.9. ^1H NMR (methanol-*d*₄): δ 1.03 (4H, m, CHCHH), 1.07 (4H, m, CHCHH), 1.37 (24H, dd, J_{HH} = 7.5, 7.5 Hz,

CH_2CH_3), 1.94 (8H, dq, $J_{\text{HH}} = 7.5$, 15.0 Hz, $\text{CH}-\text{HCH}_3$), 2.03 (2H, m, CH), 2.18 (8H, dq, $J_{\text{HH}} = 7.5$, 15.0 Hz, CHHCH_3), 2.34 (8H, m, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (methanol- d_4): δ -0.4 (CH), 8.8 (CCH_2), 9.5 (CCH_3), 18.7 (PCH_2CH_3), 21.1 (PCH_2). ν_{max} (Nujol): 2066 ($\text{N}\equiv\text{C}$) cm^{-1} .

3.5. *Trans*-[Fe($\text{N}\equiv\text{CPh}$)₂(DMPE)₂][2PF₆] (5a)

Benzonitrile (100 mg, 970 μmol) was added to *cis*-[FeH₂(DMPE)₂] (1a, 40 mg, 111 μmol) dissolved in dry methanol (3 ml) and the solution was stirred for 10 min. Potassium hexafluorophosphate (93 mg, 500 μmol) was added and the resultant precipitate was collected by filtration after 4 days. The residue was recrystallised from ethanol to yield *trans*-[Fe($\text{N}\equiv\text{CPh}$)₂(DMPE)₂][2PF₆] (5a) as a yellow powder (31 mg, 33%); m.p. > 250 °C (decomposed without melting). $^{31}\text{P}\{^1\text{H}\}$ NMR (DMF- d_7): δ 59.6. $^1\text{H}\{^{31}\text{P}\}$ NMR (DMF- d_7): δ 1.82 (24H, s, CH_3), 2.47 (8H, s, CH_2), 7.58–7.82 (10H, m, CH). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (DMF- d_7): δ 11.3 (CH_3), 28.1 (CH_2), 110.8 ($\text{N}\equiv\text{C}$), 129.5 (CH), 132.8 (CH), 134.0 (CH), 134.2 (C). λ_{max} (THF, log ϵ): 213 (3.01), 262 (4.08), 357 nm (3.22). ν_{max} (Nujol): 2215 ($\text{N}\equiv\text{C}$) cm^{-1} . Anal. Found: C, 36.5; H, 5.3. $\text{FeC}_{26}\text{H}_{42}\text{P}_6\text{N}_2\text{F}_{12}$ Calc.: C, 36.64; H, 4.97%.

3.6. *Trans*-[Fe($\text{N}\equiv\text{CPh}$)₂(DEPE)₂][2BPh₄] (5b)

Benzonitrile (50 mg, 0.49 mmol) was added to *trans*-[FeCl₂(DEPE)₂] (7b, 30 mg, 83 μmol) dissolved in dry methanol (3 ml) and the solution was stirred for 10 min. A saturated methanol solution of sodium tetraphenylborate was added and the resultant precipitate was collected by filtration to yield *trans*-[Fe($\text{N}\equiv\text{CPh}$)₂(DEPE)₂][2BPh₄] (5b) as a yellow powder (58 mg, 78%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δ 65.3. $^1\text{H}\{^{31}\text{P}\}$ NMR (acetone- d_6): δ 1.57 (24H, s, CH_2CH_3), 2.42 (8H, m, CHHCH_3), 2.54 (8H, m, CHHCH_3), 2.65 (8H, s, CH_2), 6.92 (8H, m, ArCH), 7.07 (16H, m, ArCH), 7.48 (16H, m, ArCH), 7.75–7.87 (10H, m, ArCH). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (acetone- d_6): δ 9.8 (CH_2CH_3), 18.5 (CH_2CH_3), 20.8 (CH_2), 112.0 ($\text{N}\equiv\text{C}$), 122.6 ($\text{ArCH}-\text{BPh}_4$), 126.4 ($\text{ArCH}-\text{BPh}_4$), 130.7 (ArCH), 131.2 (ArCH), 133.9 (ArCH), 137.5 ($\text{ArCH}-\text{BPh}_4$), 164.8 ($J_{\text{BH}} = 50$ Hz, 4 lines, BC). ν_{max} (Nujol): 2212 ($\text{N}\equiv\text{C}$) cm^{-1} . Anal. Found: C, 74.9; H, 7.7; N, 2.1. $\text{FeC}_{82}\text{H}_{98}\text{P}_4\text{N}_2\text{B}_2$ Calc.: C, 75.01; H, 7.52; N, 2.13%.

3.7. *Trans*-[Fe(*p*-N $\equiv\text{CC}_6\text{H}_4\text{Br}$)₂(DMPE)₂][2PF₆] (6a)

A solution of *cis*-[FeH₂(DMPE)₂] (1a, 40 mg, 112 μmol) in methanol (1 ml) was added to *p*-bromobenzonitrile (203 mg, 1.12 mmol) in methanol (1 ml) and the solution was stirred for 30 min. Potassium hex-

afluorophosphate (93 mg, 500 μmol) in methanol (1 ml) was added and the solution was stirred for a further 2 h at ambient temperature. The resultant precipitate was collected by filtration and washed with methanol (1 ml) and benzene (4 ml) to yield *trans*-[FeH(*p*-N $\equiv\text{CC}_6\text{H}_4\text{Br}$)(DMPE)₂][PF₆] (6a) as an orange powder (29 mg, 38%); m.p. 231–236 °C (dec.). ^{31}P NMR (acetone- d_6): δ 68.8 (d, $^2J_{\text{PH}} = 51$ Hz). ^1H NMR (acetone- d_6): δ -22.12 (1H, quintet, $^2J_{\text{PH}} = 50$ Hz, FeH), 1.68 (12H, s, CH_3), 1.74 (12H, s, CH_3), 2.05–2.23 (8H, m, CH_2), 7.74 (2H, m, CH), 7.86 (2H, m, CH). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (acetone- d_6): δ 13.4 (CH_3), 20.6 (CH_3), 30.6 (CH_2), 112.1 ($\text{N}\equiv\text{C}$), 127.2 (C), 132.2 (CH), 132.8 (C), 133.4 (CH). ν_{max} (Nujol): 2174 ($\text{N}\equiv\text{C}$) cm^{-1} .

A solution of *cis*-[FeH₂(DMPE)₂] (1a, 40 mg, 112 μmol) in methanol (1 ml) was added to a solution of *p*-bromobenzonitrile (203 mg, 1.12 mmol) in methanol (1 ml) and the mixture was stirred for 3 days at room temperature. The resultant precipitate was collected by filtration and washed with methanol (1 ml) and benzene (4 ml) to yield *trans*-[Fe(*p*-N $\equiv\text{CC}_6\text{H}_4\text{Br}$)₂(DMPE)₂][2PF₆] (6a) as a yellow coloured powder (52 mg, 65%); m.p. > 300 °C (decomposed without melting). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δ 59.8. $^1\text{H}\{^{31}\text{P}\}$ NMR (acetone- d_6): δ 2.04 (24H, s, CH_3), 2.65 (8H, s, CH_2), 7.87 (4H, m, CH), 7.93 (4H, m, CH). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (acetone- d_6): δ 11.1 (CH_3), 28.1 (CH_2), 109.8 ($\text{N}\equiv\text{C}$), 128.9 (C), 132.8 (CH), 133.9 (C), 134.3 (CH). ν_{max} (Nujol): 2217 ($\text{N}\equiv\text{C}$) cm^{-1} .

3.8. *Trans*-[FeCl($\text{N}\equiv\text{CCH}_3$)(DMPE)₂][PF₆] (8a)

Trans-[FeCl₂(DMPE)₂] (7a, 100 mg, 235 μmol) was dissolved in methanol (3 ml) and acetonitrile (50 mg, 1.22 mmol) added. The solution was stirred for 30 min. Potassium hexafluorophosphate (50 mg, 272 μmol) was added to the solution and the resultant precipitate collected by filtration and recrystallised from ethanol to give *trans*-[FeCl($\text{N}\equiv\text{CCH}_3$)(DMPE)₂][PF₆] (8a) as a yellow crystalline solid (101 mg, 74%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetonitrile- d_3): δ 59.5. $^1\text{H}\{^{31}\text{P}\}$ NMR (acetonitrile- d_3): δ 1.54 (12H, s, PCCH_3), 1.55 (12H, s, PCCH_3), 1.67 (3H, s, CH_3), 1.69 (8H, m, CH_2). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (acetonitrile- d_3): δ 4.4 (CCH_3), 11.1 (PCH_3), 11.2 (PCH_3), 28.1 (CH_2), 98.1 ($\text{N}\equiv\text{C}$). λ_{max} (THF, log ϵ): 212 (2.25), 252 nm (2.71). ν_{max} (Nujol): 2247 ($\text{N}\equiv\text{C}$) cm^{-1} .

3.9. *Trans*-[FeCl($\text{N}\equiv\text{CPh}$)(DMPE)₂][PF₆] (9a)

Benzonitrile (80 mg, 780 μmol) was added to *trans*-[FeCl₂(DMPE)₂] (7a, 80 mg, 187 μmol) dissolved in dry methanol (3 ml) and the solution was stirred for 30 min. Potassium hexafluorophosphate (40 mg, 220 μmol) was added and the resultant precipitate was

collected by filtration to yield *trans*-[FeCl(N≡CPh)(DMPE)₂][PF₆] (**9a**) as an orange/red powder (74 mg, 62%); m.p. 281–284 °C (dec.). ³¹P{¹H} NMR (dichloromethane-*d*₂): δ 59.3. ¹H{³¹P} NMR (dichloromethane-*d*₂): δ 1.50 (12H, s, CH₃), 1.56 (12H, s, CH₃), 2.23 (8H, m, CH₂), 7.29 (2H, m, Ar-*H*), 7.43 (2H, m, Ar-*H*), 7.49 (1H, m, Ar-*H*). ¹³C{¹H, ³¹P} NMR (acetonitrile-*d*₃): δ 11.1 (CH₃), 11.2 (CH₃), 28.2 (CH₂), 110.4 (N≡C), 129.7 (CH), 132.7 (CH), 134.6 (CH), 134.7 (C). λ_{max} (THF, log ε): 212 (2.03), 271 (3.44), 350 nm (3.49). ν_{max} (CHCl₃): 2196 (N≡C) cm⁻¹. An analogous procedure was adopted to form *trans*-[FeCl(N≡CPh)(DMPE)₂][BPh₄]. Anal. Found: C, 63.1; H, 6.8. FeC₄₃H₅₇P₄NCIB Calc.: C, 63.45; H, 7.06%.

3.10. *Trans*-[FeCl(*p*-N≡CC₆H₄C≡N)(DMPE)₂][PF₆] (**10a**)

Terephthalonitrile (120 mg, 0.94 mmol) in dry methanol (6 ml) was added to *trans*-[FeCl₂(DMPE)₂] (**7a**, 20 mg, 47 μmol) dissolved in dry methanol (2 ml) and the solution was stirred for 30 min. Potassium hexafluorophosphate (40 mg, 220 μmol) was added and the volume of the solution was reduced to 4 ml. The resultant precipitate was collected by filtration. The solid was washed with methanol (1 ml) and pentane (4 ml) to yield *trans*-[FeCl(*p*-N≡CC₆H₄C≡N)(DMPE)₂][PF₆]

Table 4

Final atomic coordinates for *trans*-[Fe(N≡CCH₃)₂(DMPE)₂][2PF₆] (**3a**) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	1	0.7756(1)	0.75
N(1)	0.9247(5)	0.7755(5)	0.8307(2)
C(1)	0.8831(6)	0.7738(6)	0.8788(3)
C(2)	0.8317(8)	0.7693(9)	0.9413(3)
P(1)	0.8100(2)	0.6090(1)	0.69736(8)
C(3)	0.6381(7)	0.7043(7)	0.6371(3)
C(4)	0.7158(9)	0.5113(8)	0.7533(4)
C(5)	0.850(1)	0.4677(8)	0.6421(5)
P(1')	0.8109(2)	0.9426(2)	0.69867(8)
C(3')	0.6160(8)	0.8480(8)	0.6696(4)
C(4')	0.824(1)	1.0304(8)	0.6196(4)
C(5')	0.770(1)	1.0927(9)	0.7510(5)
P(3)	0.6867(2)	0.7299(2)	0.42741(8)
F(1)	0.7957(5)	0.7182(9)	0.5044(2)
F(2)	0.648(2)	0.567(1)	0.414(1)
F(3)	0.5788(6)	0.7452(8)	0.3511(2)
F(4)	0.728(3)	0.887(2)	0.429(1)
F(5)	0.539(2)	0.759(3)	0.4544(8)
F(6)	0.833(2)	0.700(2)	0.3995(7)
F(2')	0.756(7)	0.586(3)	0.437(2)
F(4')	0.636(6)	0.885(4)	0.444(2)
F(5')	0.554(5)	0.656(6)	0.448(1)
F(6')	0.830(3)	0.789(7)	0.409(1)

Occupancy factor 0.66(3) for F(2), F(4), F(5), F(6).

Occupancy factor 0.34(3) for F(2'), F(4'), F(5'), F(6').

Table 5

Final atomic coordinates for *trans*-[Fe(N≡CC₃H₅)₂(DEPE)₂][2BF₄] (**4b**) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	0	0	0
P(1)	0.0045(1)	0.0358(1)	0.1901(1)
P(2)	0.0708(1)	0.1386(1)	-0.0052(1)
N(1)	0.1742(3)	-0.0393(2)	0.0672(3)
C(1)	0.2773(4)	-0.0624(3)	0.1052(4)
C(2)	0.4089(4)	-0.0914(4)	0.1573(5)
C(3)	0.5140(6)	-0.0290(7)	0.1644(10)
C(4)	0.4971(7)	-0.0544(6)	0.2714(9)
C(5)	0.2255(10)	-0.0160(10)	0.3843(11)
C(6)	0.0992(9)	-0.0290(6)	0.3238(6)
C(7)	-0.1492(8)	0.0766(5)	0.3306(7)
C(8)	-0.1461(7)	0.0386(6)	0.2127(6)
C(9)	0.0627(10)	0.1466(5)	0.2230(7)
C(10)	0.0900(12)	0.1893(5)	0.1376(8)
C(11)	0.3058(7)	0.2293(6)	0.0194(9)
C(12)	0.2251(7)	0.1524(4)	-0.0236(10)
C(13)	-0.0045(7)	0.3081(4)	-0.1051(8)
C(14)	-0.0353(7)	0.2131(4)	-0.1137(9)
B(1)	0.1902(8)	0.2133(6)	0.6078(9)
F(1)	0.2952(6)	0.2053(5)	0.7071(5)
F(2)	0.2184(9)	0.2411(7)	0.5185(7)
F(3)	0.1319(7)	0.2864(6)	0.6319(9)
F(4)	0.1165(14)	0.1535(10)	0.6027(15)
F(5)	0.2475(45)	0.1563(40)	0.5543(28)
F(6)	0.0828(20)	0.1750(20)	0.5363(26)

(**10a**) as a magenta coloured powder (28 mg, 90%); m.p. > 280 °C (decomposed without melting). ³¹P{¹H} NMR (dichloromethane-*d*₂): δ 58.6. ¹H{³¹P} NMR (dichloromethane-*d*₂): δ 1.51 (12H, s, CH₃), 1.56 (12H, s, CH₃), 2.00–2.14 (4H, m, CH₂), 2.14–2.28 (4H, m, CH₂), 7.38 (2H, m, Ar-*H*), 7.70 (2H, m, Ar-*H*). ¹³C{¹H, ³¹P} NMR (acetone-*d*₆): δ 12.9 (CH₃), 13.0 (CH₃), 30.0 (CH₂), 133.1 (ArCH), 134.2 (ArCH). ν_{max} (Nujol): 2191 (N≡C) cm⁻¹.

3.11. *Trans*-[FeCl(*p*-N≡CC₆H₄Br)(DMPE)₂][BPh₄] (**11a**)

p-Bromobenzonitrile (32 mg, 176 μmol) was added to *trans*-[FeCl₂(DMPE)₂] (**7a**, 48 mg, 112 μmol) dissolved in dry methanol (5 ml) and the solution was stirred for 30 min. Sodium tetraphenylborate (40 mg, 67 μmol) in methanol (3 ml) was added and the resultant precipitate was collected by filtration to yield *trans*-[FeCl(*p*-N≡CC₆H₄Br)(DMPE)₂][BPh₄] (**11a**) as a red powder (85 mg, 84%). ³¹P{¹H} NMR (acetone-*d*₆): δ 60.1. ¹H{³¹P} NMR (acetone-*d*₆): δ 1.77 (12H, s, CH₃), 1.81 (12H, s, CH₃), 2.41 (8H, m, CH₂), 7.62, 7.83 (2H, m, Ar-*H*), 6.63, 7.08, 7.49 (20H, m, Ar-*H*). ¹³C{¹H, ³¹P} NMR (acetone-*d*₆): δ 12.7 (CH₃), 12.9 (CH₃), 30.2 (CH₂), 112.4 (N≡C), 122.6 (ArCH-BPh₄), 126.4 (ArCH-BPh₄), 128.5 (N≡CC), 134.1

(CH), 134.4 (CBr), 134.9 (CH), 137.5 (ArCH–BPh₄), 165.5 ($J_{\text{BH}} = 50 \text{ Hz}$, 4 lines, BC). λ_{max} (THF, log ϵ): 211 (3.64), 255 (4.02), 364 nm (2.09). ν_{max} (CHCl₃): 2226 (N≡C) cm⁻¹.

3.12. X-ray crystallography

The crystallographic data for complexes **3a**, **4b**, **5a** and **6a** are summarised in Table 2. Cell constants were determined by a least-squares fit to the setting values of 25 independent reflections. For complex **3a**, the PF₆⁻ groups were disordered, the disorder being essentially modelled as a two site rotational displacement about the central phosphorus site. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 computer program implemented by Hall [20] or SHELX-76 [21].

In complex **6a**, both PF₆⁻ counterions were rotationally disordered and the P–C–C–P chelate rings are conformationally disordered. The complex co-crystallised with 0.5KPF₆ per molecule of **6a**.

Scattering factors and anomalous dispersion corrections used for Fe were taken from the *International Tables* [22], and all others were those supplied in SHELX-76 [21]. Non-hydrogen atom coordinates are listed in Tables 4–7. The atomic nomenclature is defined in Figs. 1–4 [23]. Listings of H atom coordinates, anisotropic thermal parameters, close intermolecular contacts and observed and calculated structure factor

Table 6
Final atomic coordinates ($\times 10^4$) for *trans*-[Fe(N≡CPh)₂(DMPE)₂][2PF₆] (**5a**) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	0	5000	5000
P(1)	1943(1)	5601(1)	5079(1)
P(2)	–441(1)	6658(1)	5615(1)
N(1)	289(2)	4495(2)	6299(2)
C(1)	470(3)	4271(2)	7112(2)
C(2)	689(3)	4096(2)	8146(2)
C(3)	1707(3)	4572(3)	8626(2)
C(4)	1896(3)	4454(3)	9631(3)
C(5)	1097(3)	3869(3)	10143(2)
C(6)	112(3)	3384(3)	9667(3)
C(7)	–114(3)	3492(3)	8668(2)
C(8)	2459(3)	6233(3)	3986(2)
C(9)	3206(3)	4720(3)	5457(3)
C(10)	2038(3)	6681(3)	5998(2)
C(11)	–1419(3)	7597(3)	4914(3)
C(12)	–1049(4)	6686(3)	6822(3)
C(13)	962(3)	7443(3)	5789(3)
P(3)	5458(1)	5486(1)	7891(1)
F(1)	5782(2)	5808(2)	6814(1)
F(2)	5129(3)	5169(2)	8964(2)
F(3)	5019(3)	4352(2)	7476(2)
F(4)	5928(3)	6602(2)	8287(2)
F(5)	4153(2)	5957(3)	7667(2)
F(6)	6780(3)	4981(3)	8095(2)

Table 7

Final atomic coordinates for *trans*-[Fe(*p*-N≡CC₆H₄Br)₂(DMPE)₂][2PF₆][0.5KPF₆] (**6a**) with estimated standard deviations in parentheses

Atom	x	y	z	Occupation
Fe	0.8202(1)	0.8202(1)	0.7500	
P(1)	0.8365(1)	0.9218(1)	0.7939(1)	
P(2)	0.7192(1)	0.8041(1)	0.7940(1)	
Br(1)	0.6236(1)	1.0015(1)	0.4121(1)	
K	1.0000	1.0000	1.0000	
P(3)	0.5000	1.0000	0.2500(1)	
F(1)	0.4251(5)	1.0043(6)	0.2641(8)	0.75
F(2)	0.4971(12)	0.9548(9)	0.3051(6)	0.75
N(1)	0.7787(3)	0.8618(4)	0.6813(3)	
C(1)	0.7532(5)	0.8848(5)	0.6399(4)	
C(2)	0.7239(4)	0.9133(5)	0.5849(4)	
C(3)	0.6690(6)	0.9563(6)	0.5917(5)	
C(4)	0.6398(6)	0.9827(6)	0.5402(5)	
C(5)	0.6651(5)	0.9684(6)	0.4845(5)	
C(6)	0.7186(5)	0.9266(7)	0.4774(5)	
C(7)	0.7480(6)	0.8998(6)	0.5279(5)	
C(8)	0.8447(7)	0.9286(6)	0.8763(5)	
C(9)	0.7781(7)	0.9882(5)	0.7763(6)	
C(10)	0.9104(11)	0.9600(11)	0.7592(11)	0.65
C(10')	0.9294(17)	0.9400(17)	0.7847(19)	0.35
C(11)	0.7116(6)	0.8058(7)	0.8757(5)	
C(12)	0.6500(6)	0.8577(8)	0.7714(8)	
C(13)	0.6959(11)	0.7132(12)	0.7859(15)	0.55
C(13')	0.7307(15)	0.6800(14)	0.7409(18)	0.45
P(4)	1.0789(1)	0.8646(1)	0.9153(1)	
F(3)	1.0029(6)	0.8722(7)	0.9268(8)	0.75
F(4)	0.0936(13)	0.8920(10)	0.8497(9)	0.75
F(5)	0.1157(21)	0.8093(11)	0.9427(17)	0.75
F(6)	1.1034(4)	0.9211(5)	0.9610(6)	0.75
F(3')	1.1529(5)	0.8615(14)	0.9003(11)	0.75
F(4')	1.0586(4)	0.8067(5)	0.8737(4)	0.75
F(5')	1.0503(11)	0.9314(8)	0.8897(9)	0.75
F(6')	1.0644(15)	0.8397(20)	0.9761(6)	0.75

amplitudes for complexes **3a**, **4b**, **5a** and **6a** have been deposited as supplementary material.

4. Conclusion

Bis-nitrile complexes were synthesised from the iron dihydride complex *cis*-[FeH₂(DMPE)₂] and nitrile chloride or bis-nitrile complexes were synthesised from *trans*-[FeCl₂(DMPE)₂] or *trans*-[FeCl₂(DEPE)₂]. All of the complexes are stable as dry powders under an argon atmosphere. All the bis-nitrile complexes have structures with the nitrile ligands mutually *trans* as determined by NMR spectroscopy and by X-ray diffraction on four examples.

5. Supplementary material available

Tables of full crystallographic details including thermal parameters, hydrogen and non-hydrogen atom posi-

tional and thermal parameters, least-squares planes calculations, bond lengths and bond angles for **3a**, **4b**, **5a** and **6a** (23 pages); tables of calculated and observed structure factors for **3a**, **4b**, **5a** and **6a** (50 pages).

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