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Iron(II)–nitrile complexes: synthesis, structure and property of *trans*-$[FeH(NCR)(dppe)_2]^+X^-$ (dppe = $Ph_2PCH_2CH_2PPh_2$: R = CH_3, $CH_2CH_2OCH_3$, $CH_2CH_2CH_2Cl$, C_6H_5: X = Cl, BPh_4, BF_4)

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Abstract

Dissolution of *trans*-$FeHCl(dppe)_2$, **1**, in various nitriles under argon led to the formation of complexes of the type *trans*-$[FeH(NCR)(dppe)_2]Cl$ (**2a** (R = CH_3), **3a** (R = CH_2CH_2OMe), **4a** (R = $CH_2CH_2CH_2Cl$), **5a** (R = Ph)) in several hours. Complexes **2a**–**4a** could be further converted to *trans*-$[FeH(NCR)(dppe)_2][BPh_4]$ (**2b**–**4b**) and *trans*-$[FeH(NCR)(dppe)_2][BF_4]$ (**2c**–**4c**) when they were treated with $NaBPh_4$ and $NaBF_4$, respectively. The stability and electrochemical properties of these complexes appeared to depend mainly on their counteranions (Cl^-, BPh_4^-, BF_4^-). Compounds **2b**, **2c**, **3b**, **3c**, **4b** and **4c** reacted with KCN or NaCN to give $[FeH(CN)(dppe)_2]$ (**6**). Compound **6** underwent electrophilic addition at the cyano nitrogen by RSO_3CF_3 (R = Me, H) to give $[FeH(CNR)(dppe)_2][SO_3CF_3]$ (**7a** for R = Me, **7b** for R = H). Crystallographic data for **2b**: monoclinic space group $P2_1/c$, $a = 22.508(1)$ Å, $b = 16.120(1)$ Å, $c = 19.257(1)$ Å, $\beta = 113.86(1)°$, $Z = 4$, $R(wR_2) = 0.0361(0.0882)$. Crystallographic data for **3b**: triclinic space group $P\bar{1}$, $a = 13.240(1)$ Å, $b = 14.732(2)$ Å, $c = 19.807(1)$ Å, $\alpha = 75.276(6)°$, $\beta = 72.466(6)°$, $\gamma = 82.033(6)°$, $Z = 2$, $R(wR_2) = 0.0368(0.0835)$. Crystallographic data for **7a**: monoclinic space group $P2_1/c$, $a = 12.456(1)$ Å, $b = 21.880(3)$ Å, $c = 19.924(3)$ Å, $\beta = 108.08(1)°$, $Z = 4$, $R(wR_2) = 0.0663\ (0.1647)$.

Keywords: Iron nitrile; Crystallographic data; Counteranions; Electrophilic addition

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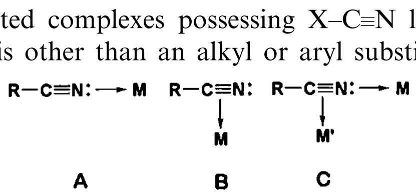
1. Introduction

Nitriles (R–C≡N) are isoelectronic with dinitrogen (N_2) and their transition-metal complexes can serve as convenient precursors for a wide variety of interesting metal complexes. Nitriles have two potential coordination sites, the nitrile nitrogen lone pair (an end-on fashion, **A**) and the carbon–nitrogen triple bond (a side-on fashion, **B**) [1,2]. In addition, a combined mode (**C**) of these two fundamental modes has often been observed in several polynuclear complexes as well as in some related complexes possessing X–C≡N ligands in which X is other than an alkyl or aryl substituent [3].



Nitrile complexes are usually prepared by dissolving a metal halide in the nitrile or replacing CO from carbonyl complexes. They can even be prepared from other nitrile complexes by nitrile exchange reaction [3]. Nitrile complexes provide an example of activation because the electrophilicity of the nitrile α-carbon is enhanced on coordination. For example, coordinated nitriles were reduced to amines in a stepwise manner by

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addition of H^- (a nucleophile) at the α-carbon followed by addition of H^+ (an electrophile) at the nitrile nitrogen [4,5]. In addition, addition of primary amines (RNH_2) to nitrile complexes led to NHR-substituted imine complexes [6].

Recently, Pombeiro's group prepared a series of iron(II)–isocyanide complexes, *trans*-[FeH(CNR)(dppe)$_2$][A] (R = alkyl or aryl, A = BF_4 or PF_6), by treating *trans*-[FeHCl(dppe)$_2$] (**1**), with appropriate cyanides in the presence of Tl[A] [7]. This group extended this type of chemistry to alkynes and carbon disulfide [8]. In addition, **1** is well known as a precursor for the dinitrogen complex $[FeH(N_2)(dppe)_2]^+$, from which $[FeH(NCCH_3)(dppe)_2][ClO_4]$ and $[FeH(NCPh)(dppe)_2][BPh_4]$ were prepared by replacement of N_2 with the corresponding nitriles [9].When **1** dissolved in nitriles under argon, **1** exhibited an immediate color change from red to orange or yellow. This interesting phenomenon prompted us to investigate as to what the products were and what their structures were. Herein we report the synthesis, structure and properties of iron(II)–nitrile complexes of the type *trans*-$[FeH(NCR)(dppe)_2]^+X^-$ (R = CH_3, $CH_2CH_2OCH_3$, $CH_2CH_2CH_2Cl$, C_6H_5: X = Cl, BPh_4, BF_4).

2. Experimental

Unless otherwise stated, all the reactions were performed with standard Schlenk line and cannula techniques under an argon atmosphere. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for ca. 24 h and washed with distilled water and acetone before use. Glassware was either flame-dried or oven-dried. Hydrocarbon solvents were stirred over concentrated H_2SO_4 for ca. 48 h, neutralized with K_2CO_3, stirred over sodium metal and distilled by vacuum transfer. Benzene, diethyl ether and tetrahydrofuran (THF) were stirred over sodium metal and distilled by vacuum transfer. Dichloromethane and acetonitrile (CH_3CN) were stirred over CaH_2 and distilled by vacuum transfer. NMR solvents (C_6D_6, $CDCl_3$, CD_2Cl_2 and CD_3CN) were degassed by freeze–pump–thaw cycles before use and stored over molecular sieves under argon. $FeCl_2{\cdot}4H_2O$, bis(diphenylphosphino)ethane (dppe = $Ph_2PCH_2CH_2PPh_2$), 4-chlorobutyronitrile ($ClCH_2CH_2CH_2CN$), 3-methoxypropionitrile ($CH_3OCH_2CH_2CN$) and benzonitrile (C_6H_5CN) were purchased from Fluka Chemical. Sodium tetraphenylborate ($NaBPh_4$), sodium tetrafluoroborate ($NaBF_4$), methyl trifluoromethanesulfonate ($MeSO_3CF_3$, MeOTf) and trifluoromethanesulfonic acid (CF_3SO_3H, HOTf) were purchased from Aldrich Chemical. FeHCl(dppe)$_2$, (**1**), was prepared by the literature method [10].

Cyclic voltammetric studies were carried out by using a BAS 100 electrochemical analyzer. Solutions (CH_2Cl_2) were ca. 1 mM in the metal complex and contained 0.1 M tetrabutylammonium tetrafluoroborate ($[^nBu_4N][BF_4]$) supporting electrolyte. For these measurements, a conventional three-electrode cell (Pt-wire working electrode, Pt-plate auxiliary electrode, Ag/AgCl reference electrode) was employed. The $E°$ value for the $[Cp_2Fe]/[Cp_2Fe]^+$ couple was 0.632 V at 300 mV s^{-1} in this cell. All the experiments were carried out under nitrogen.

^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. ^{31}P-NMR spectra were also recorded with a Bruker AMX 500 MHz spectrometer with reference to external 85% H_3PO_4. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Elemental analyses were performed by the Korea Basic Science Center.

2.1. Preparation of [FeH(NCCH$_3$)(dppe)$_2$]Cl (2a)

CH_3CN (15 ml) was added to 0.178 g (0.20 mmol) of **1** at room temperature (r.t.) and the red slurry was stirred for 1 h. The resultant yellow solution was filtered and the solvent was removed under vacuum to give yellow–brown solids. These solids were washed with diethyl ether (2 × 30 ml) and recrystallized from acetonitrile–diethyl ether to give yellow crystals of **2a** (0.132 g, 0.14 mmol, 71%). ^1H-NMR (CD_2Cl_2): δ 7.370–6.710 (40H, m, phenyl, $Ph_2PCH_2CH_2PPh_2$), 2.483 (4H, broad m, $Ph_2PCH_2CH_2PPh_2$), 1.969 (4H, broad m, $Ph_2PCH_2CH_2PPh_2$), 1.340 (3H, s, CH_3CN), -20.762 (1H, quintet, $^2J_{P-H} = 46.5$ Hz, H–Fe). ^{31}P-NMR (CD_2Cl_2): δ 86.555 (d, $^2J_{P-H} = 46.5$ Hz). Anal. Calc. for $C_{54}H_{52}NP_4ClFe$: C, 69.73; H, 5.63; N, 1.51. Found: C, 69.22; H, 5.79; N, 1.78. M.p. (dec.): 118–120°C. IR (KBr): 2250 (CN) cm^{-1}.

2.2. Preparation of [FeH(NCCH$_3$)(dppe)$_2$][BPh$_4$] (2b)

On addition of $NaBPh_4$ (0.411 g, 1.2 mmol) to 30 ml of CH_3CN containing **2a** (0.930 g, 1 mmol), a white powder immediately formed. The resulting slurry was allowed to stir for 1 h and then filtered. The solvent was removed under vacuum to give yellow solids. These solids were extracted with CH_2Cl_2 (2 × 30 ml) and the solvent was removed under vacuum to give yellow solids that were recrystallized from CH_2Cl_2–hexane o give orange crystals of **2b** (1.190 g, 0.98 mmol, 98%). ^1H-NMR ($CDCl_3$): δ 7.438–6.661 (60H, m, phenyl, $Ph_2PCH_2CH_2PPh_2$, BPh_4), 2.407 (4H, broad m, $Ph_2PCH_2CH_2PPh_2$), 1.943 (4H, broad m, $Ph_2PCH_2CH_2$-

PPh$_2$), 0.970 (3H, s, C*H*$_3$CN), −20.793 (1H, quintet, $^2J_{P\text{–}H} = 47$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 138.280–121.804 (Ph), 34.782 (Ph$_2$P*C*H$_2$*C*H$_2$PPh$_2$), 0.735 (*C*H$_3$CN). ^{31}P-NMR (CDCl$_3$): δ 85.468 (d, $^2J_{P\text{–}H} = 47$ Hz). Anal. Calc. for $C_{78}H_{72}BNP_4Fe$: C, 77.17; H, 5.98; N, 1.15. Found: C, 77.51; H, 5.72; N, 1.67. M.p. (dec.): 138–140°C. IR (KBr): 2244 (CN), 1843 (Fe–H) cm^{-1}.

*2.3. Preparation of [FeH(NCCH$_3$)(dppe)$_2$][BF$_4$] (**2c**)*

This compound was prepared in the same method employed to prepare **2b**. NaBF$_4$ (0.165 g, 1.50 mmol) was added to 80 ml of CH$_3$CN containing **2a** (0.931 g, 1.01 mmol) and the resulting solution was allowed to stir for 14 h. Compound **2c** was recrystallized from CH$_2$Cl$_2$–hexane to give orange crystals (0.915 g, 0.93 mmol 92%). ^{1}H-NMR (CDCl$_3$): δ 7.468–6.683 (40H, m, phenyl, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$), 2.674 (4H, broad m, Ph$_2$PC*H*$_2$CH$_2$PPh$_2$), 2.056 (4H, broad m, Ph$_2$PCH$_2$C*H*$_2$PPh$_2$), 1.795 (3H, s, C*H*$_3$CN), −20.974 (1H, quintet, $^2J_{P\text{–}H} = 46.7$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 136.698, 135.139, 133.872, 133.105, 130.489, 130.319, 129.189, 128.335, 33.825 (Ph$_2$P*C*H$_2$*C*H$_2$PPh$_2$), 0.694 (*C*H$_3$CN). ^{31}P-NMR (CDCl$_3$): δ 86.142 (d, $^2J_{P\text{–}H} = 46.7$ Hz). Anal. Calc. for $C_{54}H_{52}BNF_4P_4Fe$: C, 66.08; H, 5.34; N, 1.43. Found: C, 66.43; H, 4.99; N, 1.53. M.p. (dec.): 189–191°C. IR (KBr): 2245 (CN) cm^{-1}.

*2.4. Preparation of [FeH(NCCH$_2$CH$_2$OMe)(dppe)$_2$]Cl (**3a**)*

MeOCH$_2$CH$_2$CN (20 ml) was added to 0.267 g (0.3 mmol) of **1** at r.t. and the resulting solution was stirred for 2 h. The solvent was removed under vacuum and washed with diethyl ether (2 × 30 ml) to give yellow solids of **3a** (0.252 g, 0.26 mmol, 86.2%). ^{1}H-NMR (CDCl$_3$): δ 7.436–6.702 (40H, m, phenyl, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$), 3.341 (3H, s, *Me*OCH$_2$CH$_2$CN), 2.613 (4H, broad m, Ph$_2$PC*H*$_2$CH$_2$PPh$_2$), 2.373 (2H, broad m, MeOC*H*$_2$CH$_2$CN), 2.042 (4H, broad m, Ph$_2$PCH$_2$C*H*$_2$PPh$_2$), 1.876 (2H, broad m, MeOCH$_2$C*H*$_2$CN), −20.762 (1H, quintet, $^2J_{P\text{–}H} = 46.8$ Hz, *H*–Fe). ^{31}P-NMR (CDCl$_3$): δ 85.347 (d, $^2J_{P\text{–}H} = 46.8$ Hz). Anal. Calc. for $C_{56}H_{56}NOP_4ClFe$: C, 69.04; H, 5.79; N, 1.44. Found: C, 69.24; H, 5.26; N, 1.11. M.p. (dec.): 139–141°C. IR (KBr): 2236 (CN), 1886 (Fe–H) cm^{-1}.

*2.5. Preparation of [FeH(NCCH$_2$CH$_2$OMe)(dppe)$_2$][BPh$_4$] (**3b**)*

MeOCH$_2$CH$_2$CN (10 ml) containing **1** (0.178 g, 0.20 mmol) was stirred for 4 h and then NaBPh$_4$ (0.075 g, 0.22 mmol) was added. The resulting solution was allowed to stir for an additional 1 h and filtered and the solvent was removed under vacuum to give yellow solids. These solids were extracted with 20 ml of CH$_2$Cl$_2$ and the solvent was removed. The resulting bright yellow solids were washed with THF (2 × 20 ml) and recrystallized from CH$_2$Cl$_2$–hexane to give orange crystals of **3b** (0.21 g, 0.17 mmol, 85%). ^{1}H-NMR (CD$_2$Cl$_2$): δ 7.392–6.698 (40H, m, phenyl), 3.314 (3H, s, *Me*OCH$_2$CH$_2$CN), 3.203 (2H, t, $J = 5.6$ Hz, MeOC*H*$_2$CH$_2$CN), 2.601 (4H, broad m, Ph$_2$PC*H*$_2$CH$_2$PPh$_2$), 2.087 (4H, broad m, Ph$_2$PCH$_2$C*H*$_2$PPh$_2$), 2.052 (2H, t, $J = 5.6$ Hz, MeOCH$_2$C*H*$_2$CN), −20.355 (1H, quintet, $^2J_{P\text{–}H} = 47.0$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$): δ 136.610, 135.872, 135.174, 133.842, 133.021, 130.685, 130.351, 128.691, 128.449, 126.254, 122.366 (Ph), 67.070 (*Me*OCH$_2$CH$_2$CN), 59.511 (MeO*CH*$_2$CH$_2$CN), 33.133 (Ph$_2$P*C*H$_2$*C*H$_2$PPh$_2$), 22.488 (MeOCH$_2$*C*H$_2$CN). ^{31}P-NMR (CD$_2$Cl$_2$): δ 84.985 (d, $^2J_{P\text{–}H} = 47.0$ Hz). Anal. Calc. for $C_{80}H_{76}BNOP_4Fe$: C, 76.38; H, 6.09; N, 1.11. Found: C, 76.54; H, 6.43; N, 1.25. M.p. (dec.): 150–152°C. IR (KBr): 2236 (CN), 1842 (Fe–H) cm^{-1}.

*2.6. Preparation of [FeH(NCCH$_2$CH$_2$OMe)(dppe)$_2$][BF$_4$] (**3c**)*

This compound was prepared by the same method employed to prepare **3b**. NaBF$_4$ (0.22 g, 0.2 mmol) was added to 15 ml of MeOCH$_2$CH$_2$CN containing **3a** (0.097 g, 0.1 mmol) and the resulting solution was stirred for 2 h. **3c** was recrystallized from CH$_2$Cl$_2$–hexane to give orange crystals (0.065 g, 0.063 mmol, 63.4%). ^{1}H-NMR (CDCl$_3$): δ 7.460–6.719 (40H, m, phenyl), 3.339 (3H, s, *Me*OCH$_2$CH$_2$CN), 2.616 (4H, broad m, Ph$_2$PC*H*$_2$CH$_2$PPh$_2$), 2.423 (2H, broad m, MeOC*H*$_2$CH$_2$CN), 2.051 (4H, broad m, Ph$_2$PCH$_2$C*H*$_2$PPh$_2$), 1.759 (2H, broad m, MeOCH$_2$C*H*$_2$CN), −20.774 (1H, quintet, $^2J_{P\text{–}H} = 36.6$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 136.517, 136.447, 135.196, 135.139, 133.913, 133.133, 130.571, 129.309, 128.409 (Ph), 67.786 (*Me*OCH$_2$CH$_2$CN), 59.588 (MeO*C*H$_2$CH$_2$CN), 33.487 (Ph$_2$P*C*H$_2$*C*H$_2$PPh$_2$), 23.209 (MeOCH$_2$*C*H$_2$CN). ^{31}P-{^{1}H}-NMR (CDCl$_3$): δ 85.558 (d, $^2J_{P\text{–}H} = 36.6$ Hz). Anal. Calc. for $C_{56}H_{56}BNOF_4P_4Fe$: C, 65.58; H, 5.50; N, 1.37. Found: C, 65.53; H, 4.91; N, 1.15. M.p. (dec.): 165–167°C. IR (KBr): 2239 (CN), 1875 (Fe–H) cm^{-1}.

*2.7. Preparation of [FeH(NCCH$_2$CH$_2$CH$_2$Cl)(dppe)$_2$]Cl (**4a**)*

ClCH$_2$CH$_2$CH$_2$CN (10 ml) was added to 0.178 g (0.20 mmol) of **1** at r.t. and the solution was stirred for 1 h. The resultant solution was filtered and the solvent was removed under vacuum and washed with diethyl ether (2 × 30 ml) to give yellow solids of **4a** (0.191 g, 0.19.mmol, 95%). ^{1}H-NMR (CDCl$_3$): δ 7.421–6.789 (40H, m, phenyl), 3.212 (2H, broad m,

$\mathrm{ClC}H_2\mathrm{CH_2CH_2CN}$), 2.734 (4H, broad m, $\mathrm{Ph_2PC}H_2\mathrm{CH_2Ph_2}$), 2.081 (4H, broad m, $\mathrm{Ph_2PCH_2C}H_2\mathrm{PPh_2}$), 1.667 (2H, broad m, $\mathrm{ClCH_2C}H_2\mathrm{CH_2CN}$), 1.602 (2H, t, $J = 7$ Hz, $\mathrm{ClCH_2CH_2C}H_2\mathrm{CN}$), -21.022 (1H, quintet, $^2J_{\mathrm{P-H}} = 36.6$ Hz, *H*–Fe). ^{31}P-NMR ($\mathrm{CD_2Cl_2}$): δ 85.317 (d, $^2J_{\mathrm{P-H}} = 36.6$ Hz). Anal. Calc. for $\mathrm{C_{56}H_{55}NP_4Cl_2Fe}$: C, 67.76; H, 5.58; N, 1.41. Found: C, 67.39; H, 4.77; N, 1.47. M.p. (dec.): 130–132°C. IR (KBr): 2232 (CN), 1860 (Fe–H) cm^{-1}.

*2.8. Preparation of [FeH($\mathrm{NCCH_2CH_2CH_2Cl}$)(dppe)$_2$][$\mathrm{BPh_4}$] (**4b**)*

$\mathrm{NaBPh_4}$ (0.034 g, 0.1 mmol) was added to 10 ml of THF containing **4a** (0.05 g, 0.05 mmol) and then the resulting solution was stirred for 2 h. The solvent was removed under vacuum to give yellow solids, which were extracted with 20 ml of $\mathrm{CH_2Cl_2}$. The solvent was again removed and the resulting yellow solids were washed with diethyl ether (2 × 10 ml) and recrystallized from $\mathrm{CH_2Cl_2}$–hexane to give orange crystals of **4b** (0.043 g, 0.034 mmol, 67.4%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.465–6.651 (60H, m, phenyl), 2.830 (2H, broad t, $J = 5.5$ Hz, $\mathrm{ClC}H_2\mathrm{CH_2CH_2CN}$), 2.470 (4H, broad m, $\mathrm{Ph_2PC}H_2\mathrm{CH_2PPh_2}$), 2.024 (4H, broad m, $\mathrm{Ph_2PCH_2C}H_2\mathrm{PPh_2}$), 1.739 (2H, broad m, $\mathrm{ClCH_2C}H_2\mathrm{CH_2CN}$), 1.177(2H, m, $\mathrm{ClCH_2CH_2C}H_2\mathrm{CN}$), -20.701 (1H, quintet, $^2J_{\mathrm{P-H}} = 47$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR ($\mathrm{CD_2Cl_2}$): δ 136.614, 135.628, 134.781, 133.660, 130.706, 129.129, 128.544, 126.312, 122.404 (Ph), 43.498 ($\mathrm{Cl}C\mathrm{H_2CH_2CH_2CN}$), 32.910 ($\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$), 28.322 ($\mathrm{ClCH_2CH_2}C\mathrm{H_2CN}$), 18.303 ($\mathrm{ClCH_2}C\mathrm{H_2CH_2CN}$). ^{31}P-NMR ($\mathrm{CD_2Cl_2}$): δ 84.080 (d, $^2J_{\mathrm{P-H}} = 47$ Hz). Anal. Calc. for $\mathrm{C_{80}H_{75}BNP_4ClFe}$: C, 75.28; H, 5.92; N, 1.10. Found: C, 75.08; H, 5.43; N, 1.13. M.p. (dec.): 151–153°C. IR (KBr): 2248 (CN), 1841.2 (Fe–H) cm^{-1}.

*2.9. Preparation of [FeH($\mathrm{NCCH_2CH_2CH_2Cl}$)(dppe)$_2$][$\mathrm{BF_4}$] (**4c**)*

$\mathrm{NaBF_4}$ (0.022 g, 0.2 mmol) was added to 10 ml of $\mathrm{ClCH_2CH_2CH_2CN}$ containing **4a** (0.095 g, 0.1 mmol) and then the resulting solution was stirred for 2 h. The solvent was removed under vacuum to give yellow solids, which were extracted with 15 ml of $\mathrm{CH_2Cl_2}$. The solvent was removed again and the resulting yellow solids were recrystallized from $\mathrm{CH_2Cl_2}$–hexane to give yellow crystals of **4c** (0.037 g, 0.034 mmol, 67.4%). ^{1}H-NMR ($\mathrm{CD_2Cl_2}$): δ 7.458–7.140 (40H, m, phenyl, $Ph_2\mathrm{PCH_2CH_2P}Ph_2$), 3.272 (2H, t, $J = 6$ Hz, $\mathrm{ClC}H_2\mathrm{CH_2CH_2CN}$), 2.599 (4H, broad m, $\mathrm{Ph_2PC}H_2\mathrm{CH_2PPh_2}$), 2.258 (2H, *t*, $J = 7$ Hz, $\mathrm{ClCH_2CH_2C}H_2\mathrm{CN}$), 2.059 (4H, broad m, $\mathrm{Ph_2PCH_2C}H_2\mathrm{PPh_2}$), 1.526 (2H, broad m, $\mathrm{ClCH_2C}H_2\mathrm{CH_2CN}$), -20.599 (1H, quintet, $^2J_{\mathrm{P-H}} = 36.6$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR ($\mathrm{CD_2Cl_2}$): δ 136.062, 135.005, 133.714, 133.066, 130.586, 129.208, 128.445 (phenyl), 43.824 ($\mathrm{Cl}C\mathrm{H_2CH_2CH_2CN}$), 33.269 ($\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$), 28.508 ($\mathrm{ClCH_2CH_2}C\mathrm{H_2CN}$), 18.432 ($\mathrm{ClCH_2}C\mathrm{H_2CH_2CN}$). ^{31}P-NMR ($\mathrm{CD_2Cl_2}$): δ 84.654 (d, $^2J_{\mathrm{P-H}} = 36.6$ Hz). Anal. Calc. for $\mathrm{C_{56}H_{55}BNF_4P_4ClFe}$: C, 64.42; H, 5.31; N, 1.34. Found: C, 64.77; H, 5.12; N, 1.54. M.p. (dec.): 172–174°C. IR (KBr): 2232 (CN).

*2.10. Preparation of [FeH(NCPh)(dppe)$_2$]Cl (**5a**)*

PhCN (10 ml) was added to 0.178 g (0.20 mmol) of **1** at r.t. and the solution was stirred for 1 h. The color of the solution changed from red–violet to yellow. The resultant solution was filtered and the solvent was removed under vacuum and washed with benzene (2 × 30 ml) to give yellow solids of **5a** (0.181 g, 0.18 mmol, 91%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.805–6.769 (45H, m, phenyl), 2.550 (4H, broad m, $\mathrm{Ph_2PC}H_2\mathrm{CH_2PPh_2}$), 2.095 (4H, broad m, $\mathrm{Ph_2PCH_2C}H_2\mathrm{PPh_2}$), -19.224 (1H, quintet, $^2J_{\mathrm{P-H}} = 49.8$ Hz, *H*–Fe). ^{31}P-NMR ($\mathrm{CDCl_3}$): δ 83.779 (d, $^2J_{\mathrm{P-H}} = 49.8$ Hz). Anal. Calc. for $\mathrm{C_{59}H_{54}NP_4ClFe}$: C, 71.42; H, 5.49; N, 1.41. Found: C, 71.28; H, 5.12; N, 1.43. M.p. (dec.): 118–120°C. IR (KBr): 2050 (CN) cm^{-1}.

*2.11. Preparation of [FeH(CN)(dppe)$_2$] (**6**)*

*2.11.1. Reaction of **2b** with NaCN*

To a mixed solvent (20 ml) THF–MeOH (1:1) were added **2b** (0.121 g, 0.1 mmol) and NaCN (0.007 g, 0.15 mmol) and the resulting solution was stirred for 8 h. The solvent was removed under vacuum and the remaining solids were extracted with 20 ml of dichloromethane and washed with hexane (2 × 20 ml) to give a yellow powder of **6** (0.081 g, 0.09 mmol, 88%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.516–6.990 (40H, m, phenyl, $Ph_2\mathrm{PCH_2CH_2P}Ph_2$), 2.467 (4H, broad m, $\mathrm{Ph_2PC}H_2\mathrm{CH_2PPh_2}$), 1.983 (4H, broad m, $\mathrm{Ph_2PCH_2C}H_2\mathrm{PPh_2}$), -14.748 (1H, quintet, $^2J_{\mathrm{P-H}} = 46$ Hz, *H*–Fe). ^{13}C{^{1}H}-NMR ($\mathrm{CDCl_3}$): δ 164.421 (*C*N), 139.591, 138.536, 134.685, 134.206, 129.259, 129.098, 127.671 (phenyl), 34.143 (t, $J_{\mathrm{P-C}} = 13.1$ Hz, $\mathrm{Ph_2P}C\mathrm{H_2CH_2PPh_2}$). ^{31}P-NMR ($\mathrm{CDCl_3}$): δ 90.175 (d, $^2J_{\mathrm{P-H}} = 46$ Hz). Anal. Calc. for $\mathrm{C_{53}H_{49}NP_4Fe}$: C, 72.36; H, 5.61; N, 1.59. Found: C, 72.54; H, 5.25; N, 1.72. M.p. (dec.): 188–190°C. IR (KBr): 2050 (CN) cm^{-1}.

*2.11.2. Reaction of **2b**, **2c**, **3b**, **3c**, **4b** or **4c** with KCN*

To a mixed solvent (20 ml) THF–MeOH (1:1) were added **2b** (0.150 g, 0.12 mmol) and KCN (0.012 g, 0.18 mmol) and the solution was stirred for 6 h. The color of the solution changed from orange to yellow–green. The solvent was removed under vacuum and the remaining solids were extracted with 30 ml of dichloromethane and washed with hexane (2 × 20 ml) to give yellow powder of **6** (0.085 g, 0.09 mmol, 77%).

To a mixed solvent (20 ml) CH_2Cl_2–MeOH (1:1) were added **2c** (0.098 g, 0.1 mmol) and KCN (0.10 g, 0.15 mmol) and the solution was stirred for 7 h. The solvent was removed under vacuum and the remaining solids were extracted with 20 ml of dichloromethane and washed with hexane (2 × 20 ml) to give yellow powder of **6** (0.066 g, 0.08 mmol, 75%).

To a mixed solvent (20 ml) THF–MeOH (1:1) were added **3b** (0.126 g, 0.1 mmol) and KCN (0.010 g, 0.15 mmol) and the solution was stirred for 8 h. The solvent was removed under vacuum and the remaining solids were extracted with 30 ml of dichloromethane and washed with hexane (2 × 20 ml) to give yellow powder of **6** (0.076 g, 0.086 mmol, 86%).

To a mixed solvent (20 ml) THF–MeOH (1:1) were added **3c** (0.103 g, 0.1 mmol) and KCN (0.010 g, 0.15 mmol) and the solution was stirred for 12 h. The solvent was removed under vacuum and the remaining solids were extracted with 30 ml of dichloromethane and washed with hexane (2 × 20 ml) to give yellow powder of **6** (0.080 g, 0.09 mmol, 90%).

To a mixed solvent (20 ml) THF–MeOH (1:1) were added **4b** (0.128 g, 0.1 mmol) and KCN (0.010 g, 0.15 mmol) and the solution was stirred for 12 h. The solvent was removed under vacuum and the remaining solids were extracted with 30 ml of dichloromethane and washed with hexane (2 × 20 ml) to give yellow powder of **6** (0.066 g, 0.075 mmol, 75%).

To a mixed solvent (10 ml) CH_2Cl_2–MeOH (1:1) were added **4c** (0.052 g, 0.05 mmol) and KCN (0.005 g, 0.08 mmol) and the solution was stirred for 12 h. The solvent was removed under vacuum and the remaining solids were extracted with 30 ml of dichloromethane and washed with hexane (2 × 20 ml) to give **6** as a yellow powder (0.020 g, 0.023 mmol, 46%).

2.12. Preparation of $[FeH(CNR)(dppe)_2][SO_3CF_3]$

2.12.1. $[FeH(CNMe)(dppe)_2][SO_3CF_3]$ (**7a**)

Methyl trifluoromethanesulfonate ($MeSO_3CF_3$, 10 μl, 0.088 mmol) was added to 30 ml of CH_2Cl_2 containing **6** (0.072 g, 0.082 mmol) and then the resulting solution was allowed to stir for 14 h. The color of the solution turned from yellow to yellow–green. The solvent was removed under vacuum to give yellow–green solids, which were recrystallized from CH_2Cl_2–hexane to give **7a** (0.05 g, 0.048 mmol, 61%). ^{1}H-NMR ($CDCl_3$): δ 7.446–6.836 (40H, m, phenyl, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 3.092 (3H, s, N–$C\mathit{H}_3$), 2.519 (4H, broad m, $Ph_2PC\mathit{H}_2CH_2PPh_2$), 2.029 (4H, broad m, $Ph_2PCH_2C\mathit{H}_2PPh_2$), −11.265 (1H, quintet, $^2J_{P\text{–}H} = 46$ Hz, *H*–Fe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 164.892 (q, *C*NMe), 136.480, 136.034, 133.781, 133.051, 130.670, 130.637, 129.036, 128.422 (phenyl), 34.279 (t, $J_{P\text{–}C} = 12.5$ Hz, $Ph_2P\mathit{C}H_2\mathit{C}H_2PPh_2$) 30.372 (s, N$\mathit{C}H_3$). ^{31}P-NMR ($CDCl_3$): δ 88.544 (d, $^2J_{P\text{–}H} = 46$ Hz). Anal. Calc. for $C_{55}H_{52}NO_3F_3P_4SFe$: C, 63.29; H, 5.02; N, 1.34. Found: C, 63.65; H, 5.37; N, 1.27. M.p. (dec.): 96–98°C. IR (KBr): 2118 (CN) cm^{-1}.

2.12.2. $[FeH(CNH)(dppe)_2][SO_3CF_3]$ (**7b**)

Trifluoromethanesulfonic acid (CF_3SO_3H, 4 μl, 0.045 mmol) was added to 10 ml of CH_2Cl_2 containing **6** (0.04 g, 0.045 mmol) and then the resulting solution was allowed to stir for 3 h. The color of the solution turned from yellow to yellow–green. The solvent was removed under vacuum to give yellow–green solids, which were washed with diethyl ether (2 × 10 ml) and pentane (2 × 10 ml) and then dried under vacuum to give **7b** (0.042 g, 0.041 mmol, 91%). ^{1}H-NMR ($CDCl_3$): δ 7.429–7.034 (40H, m, phenyl, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 2.456 (4H, broad m, $Ph_2PC\mathit{H}_2CH_2PPh_2$), 2.000 (4H, broad m, $Ph_2PCH_2C\mathit{H}_2PPh_2$), 1.858 (1H, s, N–*H*), −11.115 (1H, quintet, $^2J_{P\text{–}H} = 47$ Hz, *H*–Fe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 136.876, 135.906, 133.996, 133.426, 130.489, 130.348, 128.847, 128.203 (phenyl), 34.052 ($Ph_2P\mathit{C}H_2\mathit{C}H_2PPh_2$). ^{31}P-NMR ($CDCl_3$): δ 88.061 (d, $^2J_{P\text{–}H} = 47$ Hz). Anal. Calc. for $C_{54}H_{50}NO_3F_3P_4SFe$: C, 62.98; H, 4.89; N, 1.36. Found: C, 62.67; H, 4.34; N, 1.57. M.p. (dec.): 132–134°C. IR (KBr): 3140 (NH), 1978 (CN) cm^{-1}.

2.13. X-ray structure determination

All X-ray data were collected with use of either a Siemens P4 (**2b** and **7a**) or an Enraf–Nonius CAD4 (**3b**) diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 25–40 reflections in the range $10.0° < 2\theta < 30.0°$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out with use of the SHELX-97 programs [11].

A yellow crystal of **2b**, shaped as a block, of approximate dimensions 0.35 × 0.68 × 0.75 mm^3, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), unambiguously indicated $P2_1/c$ as a space group. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2s, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. The hydride ligand was located in the difference Fourier map and refined isotropically. All the other hydrogen atoms were generated in idealized positions and refined in a riding model.

A yellow crystal of, **3b**·C_6H_{14}, shaped as a block, of approximate dimensions 0.5 × 0.4 × 0.5 mm^3, was used for crystal and intensity data collection. The unit cell parameters indicated a triclinic lattice. A statistical analysis of intensities suggested a centrosymmetric space group and the structural analysis converged only in the space group $P\bar{1}$. The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations of F^2, with anisotropic temperature factors for all non-hydrogen atoms, except for the carbon atoms in the cocrystallized hexane (C81–C86) that exhibited an extreme structural disorder. The best fit for the disordered hexane was obtained by considering the five out of six hexane carbons to be distributed over two positions with the site occupation factors of 0.54:0.46 (C82–C86: C82A–C86A). The hydride ligand was located in the difference Fourier map and refined isotropically. Locating the hydrogen atoms in the disordered hexane was not tried. All the other hydrogen atoms were generated in idealized positions and refined in a riding model.

A yellow crystal of **7a**, shaped as a block, of approximate dimensions 0.60 × 0.42 × 0.40 mm^3, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), unambiguously indicated $P2_1/c$ as a space group. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2, with anisotropic temperature factors for all non-hydrogen atoms except for the counteranion (CF_3SO_3) that exhibited an extreme structural disorder. The atoms in the counteranion were refined isotropically because anisotropic refinements including these atoms were unstable. The best fit was obtained by considering these atoms to be distributed over two positions with site occupation factors (S1:S1A = 0.65:0.35, O1:O1A = 0.42:0.58, O3:O3A = 0.42:0.58 and F3:F3A = 0.36:0.64). The hydride ligand was located in the difference Fourier map and refined isotropically. All the other hydrogen atoms were generated in idealized positions and refined in a riding model.

Details on crystal data and intensity data are given in Table 1. The selected bond distances and bond angles for **2b**, **3b** and **7a** are given in Tables 2–4.

3. Results and discussion

3.1. Preparation

Reactions to prepare iron(II)–nitrile complexes in this study are summarized in Scheme 1. Dissolution of *trans*-$FeHCl(dppe)_2$, **1**, in various nitriles under argon leads to the formation of complexes of the type *trans*-$[FeH(NCR)(dppe)_2]Cl$ (**2a** ($R = CH_3$), **3a** ($R = CH_2CH_2OMe$), **4a** ($R = CH_2CH_2CH_2Cl$) and **5a** (R = Ph)) in several hours. Complexes **2a**–**4a** can be further converted to *trans*-$[FeH(NCR)(dppe)_2][BPh_4]$ (**2b**–**4b**) and *trans*-$[FeH(NCR)(dppe)_2][BF_4]$ (**2c**–**4c**) when they are treated with $NaBPh_4$ and $NaBF_4$, respectively. However, the iron(II)–benzonitrile complex **5a** will not proceed further when it is treated with $NaBPh_4$ or $NaBF_4$. In these reactions nitriles behave both as reagents and as solvents. As expected, complexes of **2b**–**4b** and **2c**–**4c** can also be prepared directly (in one step) from **1** with NaX ($X = BPh_4, BF_4$) in the corresponding nitriles. In all of the reactions, there is a color change from red to orange or yellow. In addition, a down-field shift ($\Delta\delta$ 7.6–5.8) of the chemical shift of the hydride in ^1H-NMR spectra is consistent with the formation of a salt, in which the hydride resides in the cationic part of the product.

It has been reported that the reaction of *trans*-$FeHCl(depe)_2$ ($depe = Et_2PCH_2CH_2PEt_2$) with $NaBPh_4$ in acetone under nitrogen leads to the formation of a relatively stable dinitrogen complex, *trans*-$[FeH(N_2)(depe)_2][BPh_4]$ (Eq. (1)) [12]. This methodology has also been employed to prepare a series of cationic iron–hydride complexes of the type *trans*-$[MH(L)(depe)_2][BPh_4]$ (M = Fe, L = CO, *p*-$MeOC_6H_4NC$, Me_3CNC, $P(OPh)_3$, $P(OMe)_3$, N_2, PhCN, or CH_3CN; M = Ru or Os, L = CO, *p*-$MeOC_6H_4NC$, Me_3CNC, $P(OPh)_3$, N_2, or PhCN) [13].

$$\begin{aligned} &trans\text{-}FeHCl(depe)_2 + N_2 + NaBPh_4 \\ &\quad \rightarrow trans\text{-}[FeH(N_2)(depe)_2][BPh_4] + NaCl \qquad (1)\end{aligned}$$

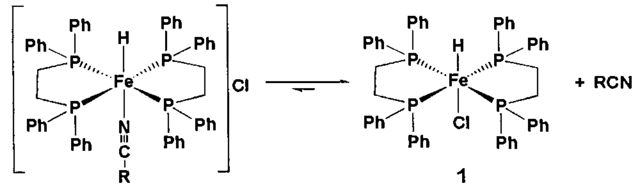
The closely related complex $[FeH(L)(dppe)_2]X$ ($X = BPh_4$ or ClO_4; $L = Me_2CO$, N_2, CO, NH_3, py, MeCN or PhCN) has been prepared by reactions of **1** with NaX under nitrogen in the presence of L [9]. In addition, $[FeH(L)(dppe)_2][BF_4]$ has been prepared by the reaction of *cis*-$FeH_2(dppe)_2$ with $HBF_4 \cdot Et_2O$ in the presence of the strongly coordinating ligand L ($L = CH_3CN$, CO) through H_2 evolution at 26°C [9].

Complexes (**2b**–**4b** and **2c**–**4c**) containing larger counterions (BPh_4^- or BF_4^-) are stable both in solution and in the solid state. On the other hand, complexes (**2a**–**5a**) containing a smaller counterion (Cl^-) are stable in the solid state but unstable in solution. For example, ^1H- and ^{31}P-NMR spectra of **2a**–**5a** could be obtained, but their $^{13}C\{^1H\}$-NMR spectra, which require a longer time, could not be obtained due to the equilibrium shown in Eq. (2). This observation is consistent with the well-known fact that a large counterion can stabilize an ionic lattice of a large organometallic ion [14].

Table 1
X-ray data collection and structure refinement for **2b**, **3b** and **6**

	2b	**3b** · C_6H_{14}	**7a**
Formula	$C_{78}H_{72}BNP_4Fe$	$C_{86}H_{90}BNOP_4Fe$	$C_{55}H_{52}NO_3F_3P_4SFe$
FW	1213.91	1344.13	1043.77
Temperature (K)	293	293	294
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	22.508(1)	13.240(1)	12.456(1)
b (Å)	16.120(1)	14.732(2)	21.880(3)
c (Å)	19.257(1)	19.807(1)	19.924(3)
α (°)		75.276(6)	
β (°)	113.86(1)	72.466(6)	108.08(1)
γ (°)		82.033(6)	
V (Å)^3	6389.9(6)	3554.8(6)	5162(1)
Z	4	2	4
D_{calc} (g cm^{-3})	1.262	1.256	1.343
μ (mm^{-1})	0.382	0.350	0.511
T_{min}	0.3966	0.8629	0.3374
T_{max}	0.4263	1.0000	0.3649
F(000)	2552	1424	2168
2θ range (°)	3.5–50	3–52	3.5–50
Scan type	ω	$\omega-2\theta$	ω
Scan speed	Variable	Variable	Variable
No. of reflections measured	13099	14300	9429
No. of reflections unique	11119	13687	9003
No. of reflections with $I>2\sigma(I)$	11119	8671	6287
No. of parameters refined	772	849	622
Max. in $\Delta\rho$ (e Å^{-3})	0.306	0.464	0.896
Min. in $\Delta\rho$ (e Å^{-3})	−0.317	−0.284	−1.026
GOF on F^2	1.065	0.844	1.031
R	0.0361	0.0368	0.0663
wR_2 [a]	0.0882	0.0835	0.1647

[a] $wR_2=\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.



(2)

All of the ionic products exhibit a quintet (δ −19.224 to −21.022) for the hydride ligand in their ^{1}H-NMR spectra and a doublet (δ 83.779–86.555) for the four phosphine ligands in their ^{31}P-NMR spectra. These observations indicate that the hydride ligand couples with the four equivalent phosphorus nuclei in the phosphines occupying the equatorial plane and that the *trans* orientation between the hydride and the nitrile remains intact. The *trans* orientation has been confirmed further by the crystal structure determination (see below) and the substitution reaction (Eq. (3)). When **2b** is treated with excess deuterated acetonitrile (CD_3CN), [FeH($NCCD_3$)(dppe)$_2$][BPh_4] (**2b**–CD_3CN) is formed. In the ^{1}H-NMR spectra of **2b**–CD_3CN, a singlet at δ 0.97 for C*H*$_3$CN in **2b** disappears, but a quintet (δ −20.61 for Fe–*H*) remains intact. This reaction (Eq. (3)) also shows a possibility of the nitrile exchange reaction, through which many nitrile complexes have been prepared [3].

Table 2
Selected bond distances (Å) and bond angles (°) in **2b**

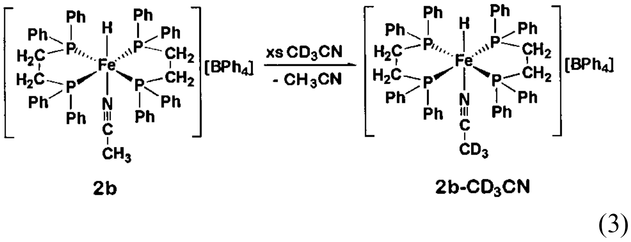
Bond lengths (Å)			
Fe–N1	1.933(2)	P4–C4	1.838(2)
Fe–P4	2.2318(6)	N1–C53	1.141(3)
Fe–P1	2.2739(6)	C1–C2	1.514(3)
Fe–P3	2.2547(6)	C3–C4	1.519(3)
Fe–P2	2.2453(5)	C53–C54	1.454(3)
Fe–H1	1.50(2)	B1–C55	1.643(3)
P1–C1	1.861(2)	B1–C61	1.651(3)
P2–C2	1.837(2)	B1–C67	1.642(4)
P3–C3	1.854(2)	B1–C73	1.642(4)
Bond angles (°)			
N1–Fe–P2	91.35(5)	N1–C53–C54	176.3(3)
P4–Fe–P2	171.09(2)	N1–Fe–H1	175.4(9)
N1–Fe–P3	91.09(5)	P1–Fe–H1	91.9(9)
P4–Fe–P3	84.32(2)	C73–B1–C67	104.8(2)
P2–Fe–P3	95.14(2)	C73–B1–C55	112.5(2)
N1–Fe–P1	89.92(5)	C67–B1–C55	113.9(2)
P4–Fe–P1	96.62(2)	C73–B1–C61	110.1(2)
P2–Fe–P1	83.75(2)	C67–B1–C61	111.7(2)
C53–N1–Fe	174.9(2)	C55–B1–C61	104.0(2)

Table 3
Selected bond distances (Å) and bond angles (°) in **3b**

Bond lengths (Å)			
Fe–N1	1.930(2)	O1–C56	1.430(3)
Fe–P4	2.2500(6)	N1–C53	1.149(2)
Fe–P1	2.2569(6)	C1–C2	1.524(3)
Fe–P3	2.2573(6)	C3–C4	1.518(3)
Fe–P2	2.2594(6)	C53–C54	1.458(3)
Fe–H1	1.44(2)	C54–C55	1.518(3)
P1–C1	1.847(2)	B1–C57	1.632(3)
P2–C2	1.861(2)	B1–C75	1.640(3)
P3–C3	1.864(2)	B1–C63	1.651(3)
P4–C4	1.842(2)	B1–C69	1.653(3)
O1–C55	1.399(3)		
Bond angles (°)			
N1–Fe–P4	98.07(5)	N1–Fe–P1	86.76(5)
P4–Fe–P1	175.15(2)	N1–Fe–P3	91.12(5)
P4–Fe–P3	83.68(2)	P1–Fe–P3	95.85(2)
N1–Fe–P2	93.23(5)	P4–Fe–P2	96.77(2)
P1–Fe–P2	83.32(2)	P3–Fe–P2	175.51(2)
N1–Fe–H1	178.1(8)	C55–O1–C56	112.4(2)
C53–N1–Fe	174.3(2)	C1–C2–P2	110.2(1)
C4–C3–P3	109.5(1)	C3–C4–P4	108.3(1)
N1–C53–C54	177.6(2)	C53–C54–C55	112.2(2)
O1–C55–C54	108.7(2)	C57–B1–C75	112.9(2)
C57–B1–C63	111.3(2)	C75–B1–C63	105.6(2)
C57–B1–C69	104.7(2)	C75–B1–C69	110.8(2)
C63–B1–C69	111.7(2)		

Table 4
Selected bond distances (Å) and bond angles (°) in **7a**

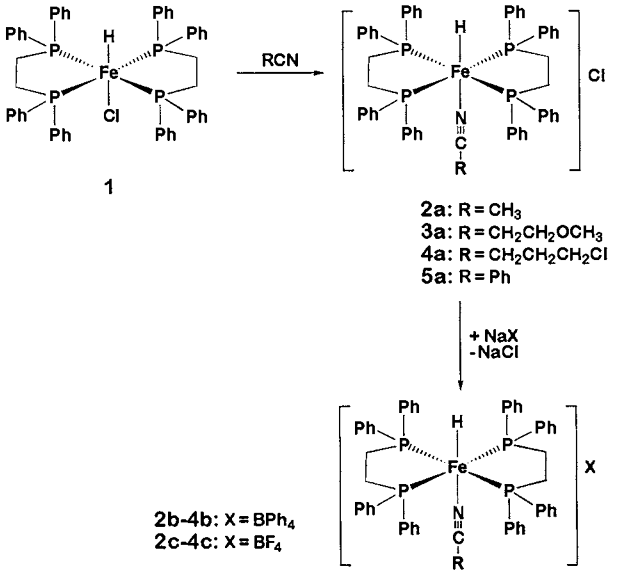
Bond lengths (Å)			
Fe–C53	1.851(5)	P2–C50	1.849(5)
Fe–P1	2.232(1)	P3–C51	1.853(5)
Fe–P4	2.240(1)	P4–C52	1.828(5)
Fe–P3	2.257(1)	N1–C53	1.154(6)
Fe–P2	2.262(1)	N1–C54	1.432(7)
Fe–Hfe	1.52(5)	C49–C50	1.507(7)
P1–C49	1.831(5)	C51–C52	1.505(8)
Bond angles (°)			
C53–Fe–P1	104.0(1)	C53–Fe–P4	89.2(2)
P1–Fe–P4	94.38(5)	C53–Fe–P3	93.7(2)
P1–Fe–P3	162.03(5)	P4–Fe–P3	82.85(5)
C53–Fe–P2	92.0(2)	P1–Fe–P2	85.16(5)
P4–Fe–P2	178.81(5)	P3–Fe–P2	97.25(5)
C53–Fe–Hfe	175(2)	P4–Fe–Hfe	96 (2)
C53–N1–C54	173.0(6)	N1–C53–Fe	177.4(4)



(3)

3.2. Structure

The structure of the cationic part of **2b**, $[FeH(NCCH_3)(dppe)_2]^+$, with the atomic numbering scheme is shown in Fig. 1. The structure of the cationic part of **3b**, $[FeH(NCCH_2CH_2OCH_3)(dppe)_2]^+$, is shown in Fig. 2, in which the extremely disordered cocrystallized hexane molecule is omitted for clarity. The structure of the cationic part of **7a**, $[FeH(CNMe)(dppe)_2]^+$, is shown in Fig. 3, in which the disordered counteranion (O_3SCF_3) is omitted for clarity. The coordination sphere of each Fe metal can be described as an octahedron, with two bidentate dppe ligands at the equatorial



Scheme 1.

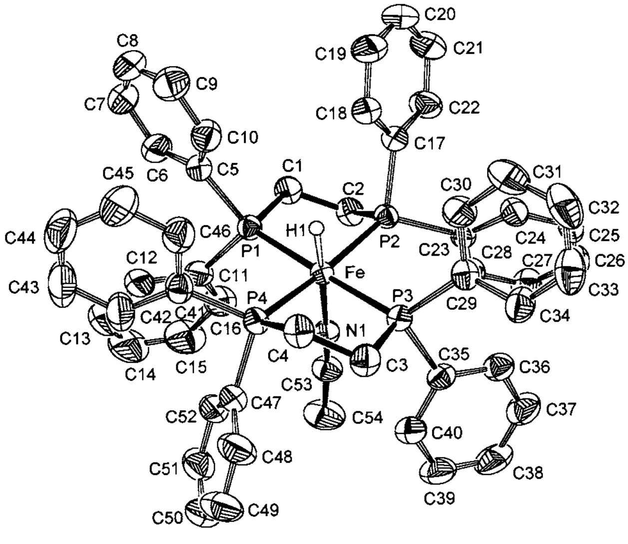


Fig. 1. ORTEP drawing [24] of the cationic part of **2b**, $[FeH(NCCH_3)(dppe)_2]^+$, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

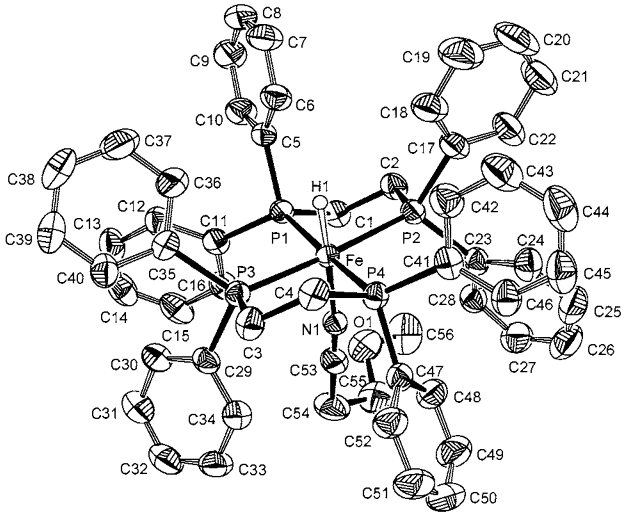


Fig. 2. ORTEP drawing [24] of the cationic part of **3b**, $[FeH(NCCH_2CH_2OCH_3)(dppe)_2]^+$, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

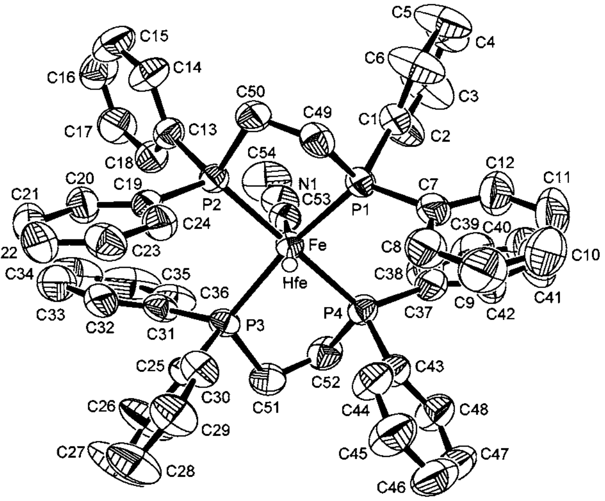


Fig. 3. ORTEP drawing [24] of the cationic part of **7a**, $[FeH(CNMe)(dppe)_2]^+$, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

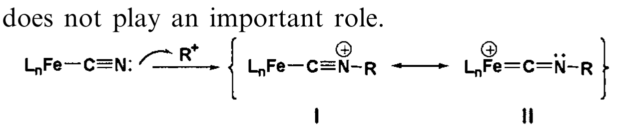
sites and the hydride and nitrile ($NCCH_3$ for **2b** and $NCCH_2CH_2OCH_3$ for **3b**) or methyl isocyanide (for **7a**) ligands at the axial sites. The anions $[BPh_4]^-$ in **2b** and **3b** and $[SO_3CF_3]^-$ in **7a** are not bonded to the Fe metal and act as counteranions to retain electroneutrality. The bond distances and angles around the B atom in **2b** and **3b** indicate that the boron atom in $[BPh_4]^-$ in both compounds is sp^3-hybridized (Tables 2 and 3).

The equatorial plane in **2b**, defined by the four dppe phosphorus atoms (P1–P4) and Fe, is nearly planar with an average atomic displacement of 0.0786 Å. On the other hand, the equatorial plane in **3b**, defined by the four dppe phosphorus atoms (P1–P4), is essentially planar with an average atomic displacement of 0.0001 Å. The Fe metal in **3b** lies 0.095 Å above the equatorial plane. The $-CH_2CH_2OCH_3$ moiety of the nitrile in **3b** is directed toward the open space between the two phenyl rings (C29–C34 and C47–C52), probably due to steric congestion. In addition, the equatorial plane in **7a**, defined by the four dppe phosphorus atoms (P1–P4) and iron atom (Fe), is roughly planar with an average atomic displacement of 0.1627 Å.

The hydride ligands (H1 for **2b** and **3b** and Hfe for **7a**) for these three compounds could be located and reasonably refined with an isotropic thermal parameter and the distances of Fe–H (1.50(2) Å for **2b**, 1.44(2) Å for **3b** and 1.52(5) Å for **7a**) appear to be fairly reliable. In the closely related complex, *trans*-$[FeH(\eta^2\text{-}H_2)(dppe)_2][BF_4]$, which has been prepared by protonation of $FeH_2(dppe)_2$ with $HBF_4{\cdot}Et_2O$ and structurally characterized by X-ray diffraction, the bond distance of Fe–H (terminal) is 1.28(8) Å [15]. In another related complex, *trans*-$[FeH(\eta^2\text{-}H_2)(dppe)_2][BPh_4]$, which was prepared by counterion exchange of *trans*-$[FeH(\eta^2\text{-}H_2)(dppe)_2][BF_4]$ with $NaBPh_4$ and structurally characterized both by X-ray diffraction and by neutron diffraction, the bond distances of Fe–H (terminal) are 1.30(3) Å (X-ray diffraction) and 1.535(12) Å (neutron diffraction), respectively [16]. The mean values of transition metal–hydride (M–H) bond distances determined by neutron diffraction have been summarized by Bau and Drabnis and the average distance of a terminal Fe–H bond is 1.575(17) Å and that of a bridging Fe–H–Fe bond is 1.664(11) Å [17].

The Fe–N1 bond distances (1.933(2) Å for **2b** and 1.930(2) Å for **3b**) indicate an Fe–N single bond, because a metal–nitrogen single bond is expected to lie within 1.95–2.15 Å [18]. The C53–N1–Fe bond angle of 174.9(2)° in **2b** and the C53–N1–Fe bond angle of 174.3(2)° in **3b** are fairly typical of nitrile ligands (168–178°) and indicate an ‘end-on’ coordination of these ligands [2]. The bond distances of N1–C53 (1.141(3) Å for **2b** and 1.149(2) Å for **3b**) parallel the known fact that the N≡C bond distances in nitrile ligands usually shorten on coordination. The N≡C bond distances (in nitrile ligands) of 1.11–1.15 Å are most frequently found, compared to 1.16 Å in the free CH_3CN [3].

In **7a**, the Fe–C53 bond distance of 1.851(5) Å belongs to the lower limit of the range (1.923–1.850 Å) of the Fe–C bond distance found for Fe–CN (terminal) complexes [19]. The C53–N1 bond distance of 1.154(6) Å indicates a C≡N triple bond and the N1–C54 bond distance of 1.432(7) Å indicates an N–C single bond. In addition, the Fe–C53–N1 and C53–N1–C54 bonds are almost linear with the angles of 177.4(4) and 173.0(6)°. These bonding parameters suggest that resonance form **I** is a major contribution in which Fe → C π-back bonding does not play an important role.



$$\mathrm{L_nFe{-}C{\equiv}N{:}} \xrightarrow{R^+} \left\{ \underset{\textbf{I}}{\mathrm{L_nFe{-}C{\equiv}\overset{\oplus}{N}{-}R}} \longleftrightarrow \underset{\textbf{II}}{\mathrm{L_n\overset{\oplus}{Fe}{=}C{=}\ddot{N}{-}R}} \right\}$$

All the structurally characterized compounds in this study have a pseudo four-fold rotation axis that passes through the Fe, N1 and H1 atoms (for **2b** and **3b**) or Fe, C53 and Hfe atoms (for **7a**) and is perpendicular to the equatorial plane, implying that the four phosphorus nuclei are equivalent. These crystal structures explain the NMR spectra of the compounds that show a quintet for the H ligand (δ −20.793 for **2b**, δ −20.355 for **3b** and δ −11.265 ppm for **7a**) in their ^{1}H-NMR and a doublet for the four P atoms (δ 85.468 for **2b**, δ 84.985 for **3b** and δ 88.544 for **7a**) in their ^{31}P-NMR spectra. The results of the X-ray crystal structures and NMR spectral data indicate that these molecules have the same structure both in solution and in the solid state.

3.3. Properties

As mentioned in Section 1, nitrile complexes are known to provide an example of activation because the electrophilicity of the nitrile α-carbon is enhanced upon coordination. On the contrary to this expectation, compounds **2b**, **2c**, **3b**, **3c**, **4b** and **4c** react with KCN or NaCN to give [FeH(CN)(dppe)$_2$] (**6**), which is a substitution product, not a nucleophilic addition product ([FeH(NC(CN)R)(dppe)$_2$]) (Eq. (4)). In other words, the nucleophile CN$^-$ attacked directly at the Fe metal, not at the nitrile α-carbon. This pattern of substitution for metal–nitrile complexes has often been observed. For example, a cationic rhenocene–nitrile adduct [Cp$_2$Re(NCCH$_3$)][BF$_4$] (Cp = C$_5$H$_5$) has a labile acetonitrile ligand that can be readily replaced by other ligands L (L = PPh$_3$, CN^{t}Bu, or HC≡CPh) [20]. The geometry of **6** can be readily deduced from NMR data (a quintet for hydride in ^{1}H-NMR and a doublet for phosphorus in ^{31}P-NMR) and elemental analysis data. The IR spectra of **6** show the C≡N band at 2050 cm^{-1}, whereas the starting materials show that band at 2232–2248 cm^{-1}. In addition, the ^{1}H-NMR spectra of **6** do not show any peak assignable to nitrile ligand protons.

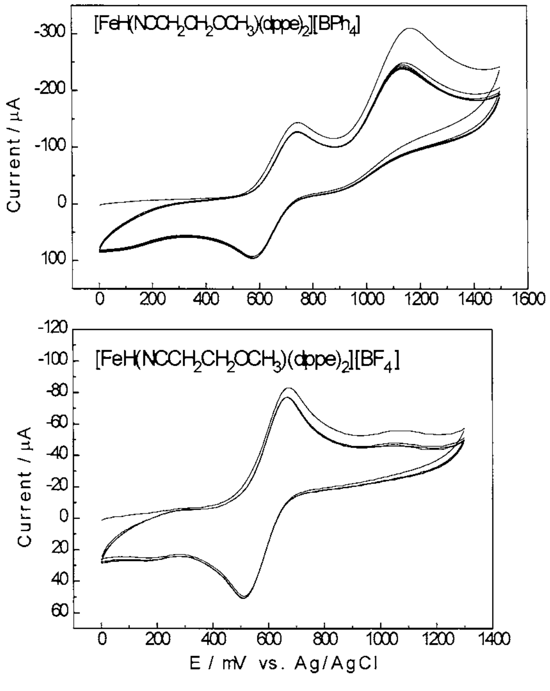
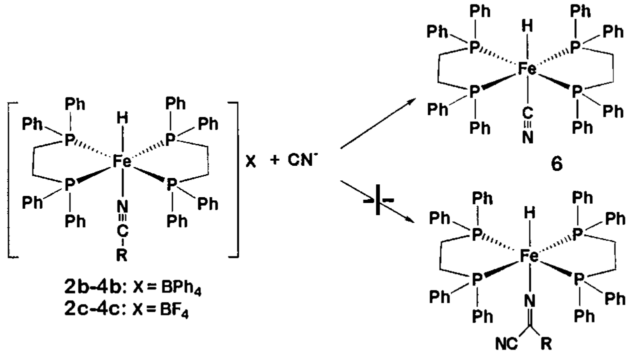


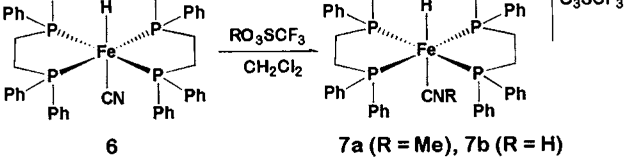
Fig. 4. Cyclic voltammograms (300 mV/s) in 0.1 M [^{n}Bu$_4$N][BF$_4$]–CH$_2$Cl$_2$ solutions of **3b** (top) and **3c** (bottom).



(4)

There are no signs of reactions of compounds **2b**, **2c**, **3b**, **3c**, **4b** and **4c** with phosphines (PMe$_3$, PEt$_3$, or PPh$_3$), amines (^{t}BuNH$_2$, NEt$_2$H, or 4-*tert*-butylpyridine), or unsaturated organic molecules (H$_2$C=CH$_2$ or HC≡CPh). These compounds, however, react with NaN$_3$ to give several products that cannot be identified.

Electrophilic attack at the cyanide nitrogen in **6** with MeOTf or HOTf (OTf = O$_3$SCF$_3$) generates a methyl isocyanide (**7a**) or a hydrogen isocyanide (**7b**) complex (Eq. (5)). In ^{13}C{^{1}H}-NMR spectra of **7b**, the peak corresponding to the hydrogen isocyanide carbon (–*C*NH) does not appear. The IR spectra of **7b**, however, show a band assingable to the N–H bond in the hydrogen isocyanide ligand at 3140 cm^{-1}. A 68 cm^{-1} increase in ν(C≡N) accompanies methylation but a 72 cm^{-1} decrease accompanies protonation. This type of reactivity, electrophilic addition to the cyanide ligand, has often been observed [21]. The structure of **7a** has been confirmed further by X-ray diffraction study (see Section 3.2).



(5)

As shown in Fig. 4 and in Table 5, complexes **2b**, **3b** and **4b**, which possess a larger counteranion BPh$_4^-$, display one reversible oxidation (0.649 V for **2b**, 0.660 V for **3b** and 0.635 V for **4b**) and one irreversible oxidation (1.322 V for **2b**, 1.164 V for **3b** and 1.272 V for **4b**) in their cyclic voltammograms.

Table 5
Electrochemical data from cyclic voltammetry studies at 300 mV s^{-1}

Compound	Scan rate (mV s^{-1})	$E°$	I_{pc}/I_{pa}	E_{pa} (V)	E_{pc} (V)
2b	300	0.649	1.019	0.796 1.322	0.502
3b	300	0.660	0.864	0.741 1.164	0.579
4b	300	0.635	0.894	0.784 1.272	0.486
2c	200	0.660	0.999	0.725	0.594
	300	0.654	1.005	0.730	0.578
	500	0.648	0.915	0.758	0.538
	1000	0.592	0.989	0.660	0.523
3c	300	0.593	0.935	0.672	0.514
4c	300	0.677	0.895	0.740	0.614

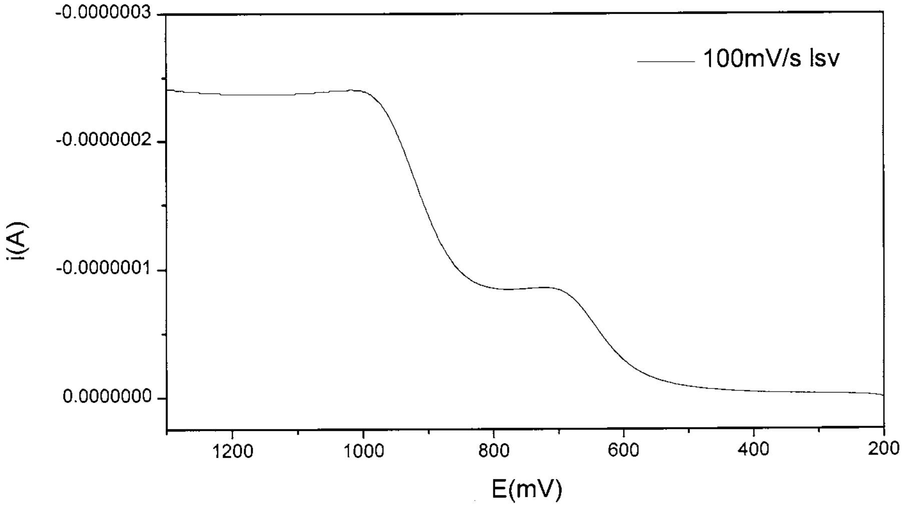


Fig. 5. Linear sweep voltammogram (100 mV/s) in 0.1 M [^{n}Bu$_4$N][BF$_4$]–CH$_2$Cl$_2$ solution of **3b**.

The one-electron character of the oxidation waves has been confirmed by microelectrode linear sweep voltammetry (LSV). When the limiting current flows, the number of electrons transferred per molecule, *n*, can be estimated from Eq. (6) [22]. Linear sweep voltammtry has been carried out in a 3 ml solution of compound **3b** with a 100 μm microdisc electrode, where two-step steady-state currents have been obtained (Fig. 5). A plot of E versus $\log[(i_l - i)/i]$ for each step shows a straight line with a slope of 59 and 61 mV, respectively. These slopes mean one-electron transfer at each step.

$$E = E_{1/2} + (59.1\ \text{mV}/n)\log[(i_l - i)/i] \quad \text{at } 25°\text{C} \qquad (6)$$

The electrochemical data suggest that the first cation **2b**$^{+}$–**4b**$^{+}$ containing Fe(III) is stable on the cyclic voltammetry time scale and the second cation **2b**$^{2+}$–**4b**$^{2+}$ containing Fe(IV) is unstable, assuming that oxidation occurs at the Fe metal center. On the contrary, complexes **2c**, **3c** and **4c**, which possess a smaller counteranion BF_4^-, display only one chemically reversible oxidation (0.654 V for **2c**, 0.593 V for **3c** and 0.677 V for **4c**). At various scan rates (Table 5), the oxidation of **2c** remains constant, which suggests that the cation radical of **2c** ([FeH(NCCH$_2$CH$_2$OMe)(dppe)$_2$][BF$_4$]$^{+\bullet}$) is stable.

On the basis of the inductive effect (H for **2b** and **2c**, CH$_2$OMe for **3b** and **3c** and CH$_2$CH$_2$Cl for **4b** and **4c**), the oxidation potential is expected to be in the order **3b** < **2b** < **4b** and **3c** < **2c** < **4c**. However, the ease of oxidation has turned out to be **4b** < **2b** < **3b** and **3c** < **2c** < **4c**, which suggests that the induction effect does not play an important role in the redox property for these complexes.

In related complexes of the type *trans*-[FeH(CNR)(dppe)$_2$][A] (R = Me, Et, ^{t}Bu, C$_6$H$_4$Me-4, C$_6$H$_4$NO$_2$-4, C$_6$H$_4$OMe-4; A = BPh$_4$, BF$_4$), the alkylisocyanide complexes show a first quasi-reversible anodic (oxidation) wave and a second reversible anodic wave. In contrast, the arylisocyanide complexes show a first irreversible anodic wave and a second quasi-reversible anodic wave [23].

In summary, we have prepared several Fe(II)–nitrile complexes of the type $[FeH(NCR)(dppe)_2]^+X^-$ ($R = CH_3$, $CH_2CH_2OCH_3$, $CH_2CH_2CH_2Cl$, C_6H_5: $X = Cl$, BPh_4, BF_4). The stability and electrochemical properties of these complexes appear to depend mainly on their counteranions. Compounds $[FeH(NCR)(dppe)_2]^+X^-$ ($R = CH_3$, $CH_2CH_2OCH_3$, $CH_2CH_2CH_2Cl$: $X = BPh_4$, BF_4) react with KCN or NaCN to give $[FeH(CN)(dppe)_2]$. In these reactions, the nucleophile CN^- has attacked directly at the Fe metal, not at the nitrile α-carbon. The compound $[FeH(CN)(dppe)_2]$ undergoes electrophilic addition at the cyano nitrogen by RO_3SCF_3 ($R = Me$ or H) to give $[FeH(CNR)(dppe)_2][SO_3CF_3]$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 131473 for **2b**, CCDC no. 131471 for **3b** and CCDC no. 131472 for **7a**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit-@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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