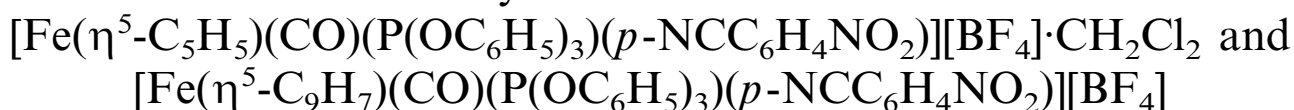# Synthesis of new donor/acceptor η^5-cyclopentadienyl and η^5-indenyliron(II) complexes with p-benzonitrile derivatives. Crystal structures of [Fe(η^5-C$_5$H$_5$)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCC$_6$H$_4$NO$_2$)][BF$_4$]·CH$_2$Cl$_2$ and [Fe(η^5-C$_9$H$_7$)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCC$_6$H$_4$NO$_2$)][BF$_4$]

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On the occasion of the 60th birthday of Professor Alberto Romão Dias

Abstract

New complexes of the type [Fe(η^5-Cp or Ind)(L)(L')(p-NCR)][BF$_4$] (L, L' = CO, P(OC$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_3$; R = C$_6$H$_4$N(CH$_3$)$_2$, C$_6$H$_4$NO$_2$, (E)-C(H)=C(H)C$_6$H$_4$NO$_2$, (E)-C(H)=C(H)C$_6$H$_4$N(CH$_3$)$_2$) have been synthesised and characterised. Spectroscopic data were analysed in order to evaluate the tuning of the electronic density at the metal centre and the extension of the π-delocalisation on the molecule, due to the presence of coligands with different acceptor/donor abilities. The structures of two complexes [Fe(η^5-C$_5$H$_5$)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCC$_6$H$_4$NO$_2$)][BF$_4$] and [Fe(η^5-C$_9$H$_7$)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCC$_6$H$_4$NO$_2$)][BF$_4$] were determined by X-ray crystallographic analysis. The compounds crystallised in the centrosymmetric space groups $P\bar{1}$ and $P2_1/n$, respectively. Bond distances within the nitrile ligand are discussed in order to evaluate the nature of iron–nitrile bonding in these complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron complexes; Benzonitrile derivatives; Cyclopentadienyl; Indenyl; Crystal structures

1. Introduction

Organometallic chemistry has emerged as a promising research area to explore new variables for the engineering of nonlinear optical hyperpolarisabilities and for the development of new materials with potential nonlinear optical (NLO) applications. It is well known that molecular polarisation, due to metal-to-ligand or ligand-to-metal charge transfer bands in the UV–vis spectrum, is responsible for high values of molecular hyperpolarisability β. A further enhancement of molecular polarisation can be introduced, at the design stage, by the use of different metal centres which can be extremely electron-rich or electron-deficient depending on their oxidation states and on their ligand environment [1–3]. In addition, new bonding geometries, interacting with aromatic and nonaromatic coligands, can tune molecular hyperpolarisabilities, since they may change the energies of the occupied and unoccupied metal d orbitals that interact with the π electron orbitals of the conjugated chromophore. Therefore, transition metal compounds are expected to be excellent acceptor or donor partners.

In our earlier studies, we identified the fragments [M(η^5-C$_5$H$_5$)(P_P)]$^+$ (M = Fe(II), Ru(II); P_P =

bidentate phosphine) as good donor groups to built donor-π-system-acceptor molecules for second and third nonlinear optical effects [4–6], where the π-system was a *p*-benzonitrile derivative. Compound [Fe(η^5-C_5H_5)(DPPE)(p-$NCC_6H_4NO_2$)][PF_6] showed a significant molecular hyperpolarisability β of 410×10^{-30} esu [6]. The main structural feature of this family of compounds is the existence of the metal centre in the same plane of the chromophore, thus allowing metal–ligand π-backdonation via the d_{metal}–π^* NC ligand.
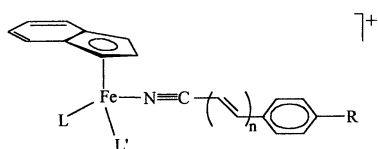
Our continuing interest on the understanding of NLO properties — structural features, prompted us to extend our studies on this type of molecules in order to explore the possibility of fine tuning the NLO properties through some structural changes.

With the aim to modify the electronic richness of the metallic centre, the η^5-cyclopentadienyl ligand was substituted by η^5-indenyl. Also, the bidentate phosphine coligand (DPPE) was replaced by ligands possessing different acceptor/donor abilities, such as CO (good π-acceptor), phosphite (medium π-acceptor) and the monodentate triphenylphosphine (poor π-acceptor).

This work presents an extensive study on the synthesis and characterisation of the family of compounds [Fe(η^5-C_5H_5)(L)(L')(p-NCR)][BF_4] (L, L' = CO, $P(OC_6H_5)_3$, $P(C_6H_5)_3$ with R = $C_6H_4N(CH_3)_2$, $C_6H_4NO_2$, (E)-CH=CHC_6H_4N(CH_3)_2$, (E)-CH=CHC_6H_4NO_2$) and [Fe(η^5-C_9H_7)(L)(L')(p-NCR)][BF_4] (L, L' = CO, $P(OC_6H_5)_3$, and R = $C_6H_4N(CH_3)_2$, $C_6H_4NO_2$, (E)-CH=CHC_6H_4NO_2$) where the organometallic fragment has been systematically enriched or depleted by changing the ligands L and L'. Also, the length of the spacer has been varied in order to maximise the delocalisation on the π-system.

Spectroscopic data were evaluated in order to understand the contribution of all these variables on the donor–acceptor ability of the iron(II) centre and the extension of π-delocalisation on the molecule as well. These studies were complemented with the discussion of the structures, determined by X-ray diffraction, for compounds [Fe(η^5-C_5H_5)(CO)($P(OC_6H_5)_3$)(p-NCC_6H_4-NO_2)][BF_4] (**5**) and [Fe(η^5-C_9H_7)(CO)($P(OC_6H_5)_3$)(p-$NCC_6H_4NO_2$)][BF_4] (**16**).

2. Results and discussion

2.1. Preparation and characterisation of the complexes [Fe(η^5-C_5H_5)(L)(L')(p-NCR)][BF_4] and [Fe(η^5-C_9H_7)(L)(L')(p-NCR)][BF_4]

Treatment of the starting materials [Fe(η^5-C_5H_5)(L)(L')(I)] or [Fe(η^5-C_9H_7)(L)(L')(I)] (L, L' = CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$) with $AgBF_4$ and a slight excess of the appropriate nitrile in dichloromethane or benzene at room temperature afforded the cationic nitrile complexes with different coligands.

After workup, complexes of the type [Fe(η^5-Cp or Ind)(L)(L')(p-NCR)][BF_4] (L, L' = CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$; R = $C_6H_4NO_2$, $C_6H_4N(CH_3)_2$, (E)-CH= CHC_6H_4NO_2$ and (E)-CH=CHC_6H_4N(CH_3)_2$ (**1–18**) (see Fig. 1) were obtained in ca. 30–80% yield. The compounds are fairly stable towards oxidation in air and moisture in both the solid state and solution. The formulation is supported by analytical data, IR and ^1H-, ^{13}C- and ^{31}P-NMR spectra (see Section 4).

The IR spectra of the derivatives reveal the presence of the different coligands: cyclopentadienyl and indenyl groups ($\approx$ 3060 cm^{-1}), the $P(OC_6H_5)_3$ ligand (P–O stretching modes as a clear triplet in the region 1150–1220 cm^{-1}), the CO ligand (in the range 1980–2070 cm^{-1}) and the coordinated nitrile (ν(CN)) (in the range 2230–2270 cm^{-1}).

Analysis of the ν(CN) stretching bands of the new complexes shows a general increase of the ν(CN) upon coordination, this shift being more pronounced for complexes [Fe(η^5-Cp)(CO)$_2$(p-$NCC_6H_4N(CH_3)_2$)]$^+$ (**2**) (+46 cm^{-1}) and [Fe(η^5-Ind)(CO)$_2$(p-NCC_6H_4N-$(CH_3)_2$)]$^+$ (**15**) (+42 cm^{-1}). The extension of this effect is virtually independent of the η^5-group (cyclopentadienyl or indenyl) and seems to be affected by the presence of the carbonyl and/or the phosphorus coligands. For example, in the series [Fe(η^5-Cp)(L)(L')(p-$NCC_6H_4N(CH_3)_2$)]$^+$ (L = L' = $P(OC_6H_5)_3$ (**12**), L = CO, L' = $P(OC_6H_5)_3$ (**6**) and L = L' = CO (**2**), the increasing values of $\Delta\nu$(CN) +21 (**12**), +29 (**6**) and +46 cm^{-1} (**2**) are in agreement with the electronic depletion at the iron centre. This enhancement of ν(CN) seems to be consistent with a nitrile σ-type coordination where the presence of π-backdonation

L = L'= CO; n=0, R = NO$_2$ (**1**), R = N(CH$_3$)$_2$ (**2**); n=1, R = NO$_2$ (**3**), R = N(CH$_3$)$_2$ (**4**)

L = CO, L' = P(OC$_6$H$_5$)$_3$; n=0, R = NO$_2$ (**5**), R = N(CH$_3$)$_2$ (**6**)

L = CO, L' = P(C$_6$H$_5$)$_3$; n=0, R = NO$_2$ (**7**), R = N(CH$_3$)$_2$ (**8**); n=1, R = NO$_2$ (**9**), R = N(CH$_3$)$_2$ (**10**)

L = L'= P(OC$_6$H$_5$)$_3$; n=0, R = NO$_2$ (**11**), R = N(CH$_3$)$_2$ (**12**); n=1, R = N(CH$_3$)$_2$ (**13**)

L = L'= CO; n=0, R = NO$_2$ (**14**), R = N(CH$_3$)$_2$ (**15**)

L = CO, L' = P(OC$_6$H$_5$)$_3$; n=0, R = NO$_2$ (**16**), R = N(CH$_3$)$_2$ (**17**); n=1, R = NO$_2$ (**18**)

Fig. 1. Structural formulae of complexes [Fe(η^5-C_5H_5 or C_9H_7)(L)(L')(p-NCR)][BF_4] (**1–18**).

owing to π-bonding between the metal d orbitals and the π* orbital of the CN group does not contribute essentially to describe the metal nitrile interaction.

The IR spectra of the [Fe(η⁵-Cp or Ind)(CO)(L′)(*p*-NCR)]⁺ (L′ = P(OC₆H₅)₃, P(C₆H₅)₃, R = C₆H₄N-(CH₃)₂, C₆H₄NO₂, etc.) derivatives are also characterised by one strong carbonyl stretching absorption corresponding to the terminal CO group. These ν(CO) bands show lower values than those of the parent dicarbonyl compounds. Regarding the series [Fe(η⁵-Cp)(CO)(L′)(*p*-NCC₆H₄N(CH₃)₂)]⁺, with L′ = P(C₆H₅)₃ (**8**), L′ = P(OC₆H₅)₃ (**6**) and L′ = CO (**2**) we found the values 1993, 2007 and 2015 cm⁻¹, respectively. These differences are consistent with the enhancement of π bonding between the metal and the remaining terminal carbonyl group, due to the replacement of one CO in [Fe(η⁵-Cp or Ind)(CO)₂(*p*-NCR)]⁺ by the more basic and poorer π-acceptor phosphine or phosphite. This effect of phosphorus ligands on the ν(CO) frequency values in these complexes seems to be more pronounced in the η⁵-indenyl derivatives consistent with a stronger donor character of indenyl complexes relative to the corresponding cyclopentadienyl derivatives.

¹H-NMR chemical shifts for the cyclopentadienyl ring in the complexes [Fe(η⁵-Cp)(L)(L′)(*p*-NCR)][BF₄] are in the range usually observed for monocationic iron(II) complexes, and seem to be affected by all the other coligands. In fact, substitution of CO with the more electron donating phosphite or phosphine leads to a shift on Cp resonances upfield owing to the increased electron density at the metal centre. Replacement of the donor group (*p*-N(CH₃)₂) by the acceptor group (*p*-NO₂) on the nitrile benzene ring gives a deshielding effect on the Cp resonance, as it was observed previously for analogous iron(II) complexes [4,7]. The presence of triphenylphosphine and triphenylphosphite are also confirmed by their respective signals in the corresponding ranges of the spectra. However, in contrast to the effect observed for Cp ring, the phosphine and phosphite signals are shown to be relatively insensitive to the nature of the aromatic nitrile.

Our previous studies for complexes [Fe(η⁵-Cp)(P_P)(*p*-NCR)]⁺ (P_P = bidentate phosphines; R = donor and acceptor aromatic nitriles) [4,7] suggested that IR and NMR spectroscopic data could be used as a tool to predict the nonlinear optical behaviour of the compounds in solution. A good correlation was found for the shift of the ν(CN) to lower frequencies and a simultaneous upfield shift in the ¹H-NMR spectra for the *ortho* protons of the nitrile aromatic ring, with high values for molecular hyperpolarisabilities (β) [7]. According to this behaviour, which reflects the donor ability of the [Fe(η⁵-Cp)(P_P)]⁺ fragment, we were able to identify in the present work the role of [Fe(η⁵-Cp)(CO)₂]⁺ and [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)]⁺ as ac-

ceptor groups relative to the same coordinated chromophores. For example, a deshielding of +0.15 ppm (upon coordination) was found for the *ortho* protons relative to NC group of complex [Fe(η⁵-Cp)(CO)₂(*p*-NCC₆H₄N(CH₃)₂)][BF₄] (**2**), and a smaller value of +0.03 ppm for the corresponding [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)]⁺ derivative (**6**). Moreover, in these dimethylamino derivatives this effect is followed by a deshielding of the methyl protons of the amino group (+0.06 ppm for complex **2**), indicating that this group is acting as an electron donor upon coordination to the organometallic centre. Although in most cases the ¹H-NMR shift values might be insignificant, a trend is observed and is consistent with the IR results. Nevertheless, the [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)]⁺ fragment (**7**–**10**) behaves as a weak π-donor group, in spite of the presence of the CO ligand, since small shieldings were observed on the same protons (an effect more prominent for the nitro derivatives). This π-donor behaviour reflects an overall effect of π-backdonation towards the nitrile ligand, due to the presence of the triphenylphosphine coligand.

Comparison of these spectroscopic data with our previous results on [Fe(η⁵-Cp)(P_P)]⁺ (P_P = bidentate phosphines) fragments suggests that the substitution of phosphine by coligands with different acceptor/donor abilities contribute to the tuning of the donor/acceptor capacity of the iron(II) moiety towards the nitrile ligand. Actually, it is possible to classify the studied complexes in two groups:
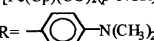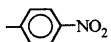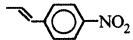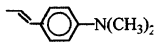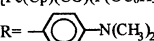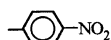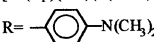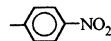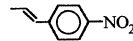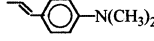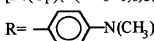
1. organometallic moieties acting as acceptor groups ([Fe(η⁵-Cp)(CO)₂]⁺ and [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)]⁺);
2. organometallic moiety acting as a π-donor group ([Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)]⁺) to be added to the former fragment [Fe(η⁵-Cp)(P_P)]⁺.

Moreover, within each group we can also recognise different strengths on the acceptor ability: [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)]⁺ < [Fe(η⁵-Cp)(CO)₂]⁺ and in the donor capacity: [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)]⁺ < [Fe(η⁵-Cp)(P_P)]⁺.

The ¹³C-NMR spectroscopic data is also valuable in assessing the donor/acceptor properties of the phosphine or phosphite, in the derivatives [Fe(η⁵-Cp)(CO)(L′)(*p*-NCR)]⁺, since the ¹³CO resonance of the carbonyl group in these complexes should reflect these properties. Analysis of the carbonyl chemical shift data for [Fe(η⁵-Cp)(CO)(L′)(*p*-NCR)]⁺ derivatives indicate a net donation of the electron density from L′ to the Fe centre showing the increasing order: CO (209.11) < P(OC₆H₅)₃ (213.50) < P(C₆H₅)₃ (217.09) found for the series [Fe(η⁵-Cp)(CO)(L′)(*p*-NCC₆H₄NO₂)]⁺ (L′ = CO (**1**); P(OC₆H₅)₃ (**5**); P(C₆H₅)₃ (**7**)) and which could be extended for the other nitrile chromophores.

Table 1
Optical spectral data for complexes [Fe(η⁵-L)(L')(L'')(p-NCR)][BF₄] in chloroform solutions at room temperature, concentration ca. 2.0×10^{-5} mol dm⁻³

Compound	λ_{exp} (nm)	$\varepsilon \times 10^4$ (M⁻¹cm⁻¹)
[Fe(η⁵-L)(L')(L'')(p-NCR)][BF₄]		
[Fe(Cp)(CO)₂(p-NCR)]⁺		
R= —(C₆H₄)—N(CH₃)₂	321	3.08
	369	0.21
	447*	0.05
—(C₆H₄)—NO₂	298	1.32
	362 (sh)	
—CH=CH—(C₆H₄)—NO₂	316	4.13
—CH=CH—(C₆H₄)—N(CH₃)₂	322 (sh)	
	364	3.31
	407 (sh)	
[Fe(Cp)(CO)(P(OC₆H₅)₃)(p-NCR)]⁺		
R= —(C₆H₄)—N(CH₃)₂	327	4.13
	475*(sh)	0.04
—(C₆H₄)—NO₂	250	1.89
	353	0.66
	410*	0.16
[Fe(Cp)(CO)(P(C₆H₅)₃)(p-NCR)]⁺		
R= —(C₆H₄)—N(CH₃)₂	332	4.02
	409	0.12
	510* (sh)	
—(C₆H₄)—NO₂	290	0.78
	341	0.55
	393	0.71
—CH=CH—(C₆H₄)—NO₂	290	2.50
	398	1.04
—CH=CH—(C₆H₄)—N(CH₃)₂	253	1.92
	327	0.80
	400	1.92
	519*	0.05
[Fe(Cp)(P(OC₆H₅)₃)₂(p-NCR)]⁺		
R= —(C₆H₄)—N(CH₃)₂	337	5.14
	410	1.24
	461* (sh)	

Compound	λ_{exp} (nm)	$\varepsilon \times 10^4$ (M⁻¹cm⁻¹)
[Fe(η⁵-L)(L')(L'')(p-NCR)][BF₄]		
[Fe(Cp)(P(OC₆H₅)₃)₂(p-NCR)]⁺		
—(C₆H₄)—NO₂	314	0.21
	413	0.77
—CH=CH—(C₆H₄)—N(CH₃)₂	326	0.59
	417	2.14
[Fe(Ind)(CO)(P(OC₆H₅)₃) (p-NCR)]⁺		
R= —(C₆H₄)—N(CH₃)₂	330	3.22
	366	0.48
	519*	0.07
—(C₆H₄)—NO₂	306 (sh)	
	368	0.96
	490	0.09
—CH=CH—(C₆H₄)—NO₂	282	2.89
	371	1.39
	497	0.11

* Only observed in solutions with a concentration ca. 2×10^{-3} mol dm⁻³.

For [(η⁵-Ind)Fe(CO)(P(OC₆H₅)₃)(p-NCR)]⁺ complexes, ¹H- and ¹³C-NMR spectra show that all the protons and carbons of indenyl ligand are nonequivalent reflecting the asymmetry of the molecule. The four indenyl protons H(4–7) give rise to four separate signals of the type AA'BB', or in the case of [(η⁵-Ind)Fe(CO)(P(OC₆H₅)₃)(p-NCC₆H₄NO₂)]⁺ (16), two doublets for the protons 4, 7 and two triplets for the protons 5, 6; the three protons H(1–3) give rise to three separate multiplets or singlets. These ¹H-NMR patterns were already described in the literature [8] for compounds [(η⁵-Ind)Fe(CO)(L)(CO₂R)]⁺ (L = phosphines or phosphites; R = CHMe₂, Me).

The hapticity of the indenyl ligand can be evaluated spectroscopically by comparing the ¹³C-NMR chemical shifts of the ring junction carbons (C3a, C7a) in the metal complex with those of the sodium indenyl: larger distortions from η⁵ coordination result in larger downfield shifts [9–11]. According to this procedure, the parameter $\Delta\delta$(C-3a,7a) $= \delta$(C-3a,7a (η-indenyl complex)) $- \delta$(C-3a,7a (sodium indenyl)) has been proposed as an indication of the indenyl distortion, having values in the range -20 to -40 ppm for planar η⁵-indenyl, -10 to -20 ppm for a partially slipped η⁵-indenyl and $+5$ to $+30$ ppm for η³-indenyl ligands [12]. For all the indenyl complexes obtained in this work we found upfield shifts, $\Delta\delta$(C-3a,7a) ≈ -21 ppm for the dicarbonyl derivatives 14 and 15 and ≈ -23 ppm for the carbonyltriphenylphosphite complexes 16–18, consistent with a indenyl ligand coordinated in a η⁵ fashion. Analysis of the spectroscopic data of η⁵-indenyl derivatives, when compared with the η⁵-cyclopentadienyl analogues, shows a similar trend and also both fragments [Fe(η⁵-Ind)(CO)₂]⁺ and [Fe(η⁵-Ind)(CO)(P(OC₆H₅)₃)]⁺ behaved as accepting groups relatively to the coordinated chromophores.

Optical absorption spectra of complexes [Fe(η⁵-Cp)(L)(L')(p-NCR)][BF₄] and [Fe(η⁵-Ind)(L)(L')(p-NCR)][BF₄] were recorded in ca. 2.0×10^{-5} mol dm⁻³ in chloroform, in the wavelength range of 230–800 nm (Table 1). For all the complexes, the spectra are characterised by one or two bands in the UV region that could be attributed to electronic transitions on the nitrile ligand. In addition, it was generally found for cyclopentadienyliron or indenyliron derivatives the existence of a very weak CT band in the visible region, with exception for the [Fe(η⁵-Cp or Ind)(CO)₂]⁺ (1), (3), (14) derivatives, containing the p-nitrobenzonitrile ligand, where no CT band was observed.

The solvatochromic response of some complexes of this series was studied, using solvents of different polarity, and results reveal that the position of all the absorption bands remain almost unchanged.

2.2. Crystallographic studies

We were able to obtain good quality crystals, grown from dichloromethane/diethylether solutions, for X-ray diffraction work for the complexes [Fe(η⁵-C₅H₅)(CO)(P(OC₆H₅)₃)(p-NCC₆H₄NO₂)][BF₄] (5) and [Fe(η⁵-

$C_9H_7)(CO)(P(OC_6H_5)_3)(p\text{-}NCC_6H_4NO_2)][BF_4]$ **(16)**. These X-ray structural studies allowed us to obtain structural data about the coordinated metal centre and especially on the geometrical parameters of the nitrile ligand.

The molecular diagrams of the cations $[Fe(\eta^5\text{-}C_5H_5)(CO)(P(OC_6H_5)_3)(p\text{-}N{\equiv}CC_6H_4NO_2)]^+$ and $[Fe(\eta^5\text{-}C_9H_7)(CO)(P(OC_6H_5)_3)(p\text{-}N{\equiv}CC_6H_4NO_2)]^+$ are shown in Figs. 2 and 3, respectively, along with the atomic numbering scheme. Values of selected bond lengths and angles are given in Table 2. The structural studies confirm the presence of the BF_4^- anion and reveal the presence of a CH_2Cl_2 crystallisation solvent molecule in the case of compound **5**.

In both complexes, the metal is coordinated to the η^5-cyclopentadienyl ring, one phosphorus atom of the phosphite ligand, one carbon atom of the carbonyl ligand and to the nitrile nitrogen atom of the p-$NCC_6H_4NO_2$ ligand. The coordination geometry around the iron atom is best described as pseudo-octahedral, three-legged piano stool, on the assumption that the cyclopentadienyl (**5**) and indenyl (**16**) groups take up three coordination sites. This pseudo-octahedral ge-
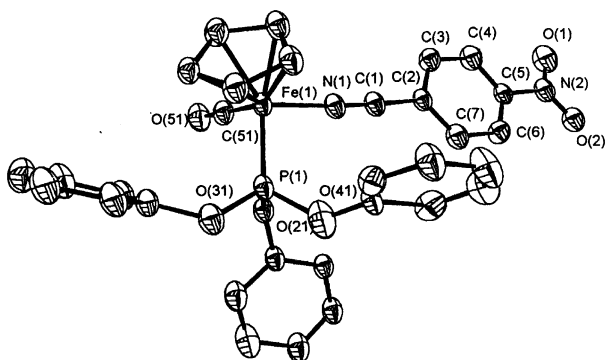
Table 2
Selected bond lengths (Å) and angles (°) for $[Fe(\eta^5\text{-}Cp)(CO)(P(OC_6H_5)_3)(p\text{-}N{\equiv}CC_6H_4NO_2)][BF_4]\cdot CH_2Cl_2$ (**5**) and $[Fe(\eta^5\text{-}Ind)(CO)(P(OC_6H_5)_3)(p\text{-}N{\equiv}CC_6H_4NO_2)][BF_4]$ (**16**)

	5	**16**
Bond lengths		
Fe(1)–N(1)	1.878(10)	1.900(8)
Fe(1)–C(11)	2.074(12)	
Fe(1)–C(12)	2.078(12)	
Fe(1)–C(13)	2.079(12)	
Fe(1)–C(14)	2.113(12)	
Fe(1)–C(15)	2.110(12)	
Fe(1)–C(1′)		2.072(11)
Fe(1)–C(2′)		2.076(12)
Fe(1)–C(3′)		2.086(10)
Fe(1)–C(3′a)		2.193(9)
Fe(1)–C(7′a)		2.193(10)
Fe–Cp or Ind (centroid)	1.718(20)	1.745(20)
Fe(1)–C(51)	1.796(14)	1.793(12)
C(51)–O(51)	1.136(14)	1.133(11)
Fe(1)–P(1)	2.158(3)	2.139(3)
N(1)–C(1)	1.139(14)	1.156(12)
C(1)–C(2)	1.463(16)	1.439(13)
C(2)–C(3)	1.374(15)	1.401(13)
C(3)–C(4)	1.378(16)	1.370(14)
C(4)–C(5)	1.370(16)	1.354(14)
C(5)–C(6)	1.333(16)	1.380(13)
C(6)–C(7)	1.378(17)	1.377(13)
C(5)–N(2)	1.498(15)	1.464(13)
C(7)–C(2)	1.369(15)	1.351(13)
N(2)–O(1)	1.211(13)	1.210(12)
N(2)–O(2)	1.202(13)	1.220(12)
Bond angles		
P(1)–Fe(1)–Cp(centroid)	127.8(6)	120.3(5)
N(1)–Fe(1)–Cp(centroid)	122.6(4)	124.2(6)
C(51)–Fe(1)–Cp(centroid)	120.9(6)	120.5(8)
N(1)–Fe(1)–P(1)	91.6(3)	97.1(2)
N(1)–Fe(1)–C(51)	94.5(5)	98.1(4)
P(1)–Fe(1)–C(51)	90.4(4)	89.5(3)
Fe(1)–N(1)–C(1)	175.0(9)	173.7(8)
N(1)–C(1)–C(2)	178.3(12)	175.3(11)
O(1)–N(2)–O(2)	124.9(13)	122.9(11)
O(1)–N(2)–C(5)	117.2(12)	118.8(12)
O(2)–N(2)–C(5)	117.8(12)	118.3(10)
O(51)–C(51)–Fe(1)	177.1(12)	174.3(9)

Fig. 2. ORTEP diagram for $[Fe(\eta^5\text{-}C_5H_5)(CO)(P(OC_6H_5)_3)(p\text{-}NCC_6H_4NO_2)]^+$, with 20% thermal ellipsoids, showing the atomic labelling scheme. Hydrogen atoms have been omitted for clarity.

Fig. 3. ORTEP diagram for $[Fe(\eta^5\text{-}C_9H_7)(CO)(P(OC_6H_5)_3)(p\text{-}NCC_6H_4NO_2)]^+$, with 20% thermal ellipsoids, showing the atomic labelling scheme. Hydrogen atoms have been omitted for clarity.
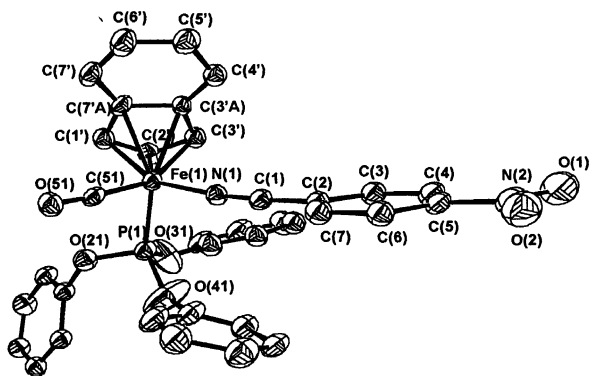
ometry is confirmed by the N–Fe–C, P–Fe–C and N–Fe–P angles around the iron atom, which are all close to 90° to (see Table 2) for both complexes and the remaining C(η^5-centroid)–Fe–X (with X = N, C or P) angles which are 122.6(4), 120.9(6), 127.8(6)° and 120.3(5), 120.5(8), 124.2(6)°, respectively, for complexes **5** and **16**.

The slip-fold distortion of the indenyl ligand can be described by the following parameters: the slip parameter, Δ, and both the 'fold' angle (FA) and 'hinge' angle (HA), representing the bending of the indenyl ligand at C(1), C(3) and C(3a), C(7a), respectively [12,13]. Accordingly, indenyl complexes are considered to be η^5-coordinated with an HA lower than 10° and Δ less than 0.25 Å. For complex **16**, we found the values FA =

Table 3
Structural data for Fe derivatives containing nitrile, phosphine or carbonyl groups

Compound	Fe–C [a] (Å)	Fe–P (Å)	Fe–C (Å)	Fe–N (Å)	N≡C (Å)	NC–C (Å)	Fe–N–C (°)	N≡C–C (°)	Refs.
$[Fe(Cp)(CO)_2(NCCH_3)][BF_4]$	2.030–2.112		1.746–1.770	1.914	1.200	1.494	175.676	175.045	14a
$[Fe(Cp)(CO)(PC_6H_5)_3)$-$(NCCH_3)][BF_4]$	2.061–2.124	2.227	1.762	1.916	1.137	1.457	179.791	178.592	[14b]
$[Fe(Cp)(CO)(PC_6H_5)_3)$-$(NCCH(COOH)^tBu)][BF_4]$	2.070–2.132	2.235	1.772	1.911	1.116	1.480	174.329		[14c]
$[Fe(Cp)(DPPE)$-$(p$-$NCC_6H_4NO_2)][PF_6]$	2.063–2.090	2.209		1.874	1.129	1.42	176.6	177.4	[7]
$[Fe(Cp)(CO)(P(OC_6H_5)_3)$-$(p$-$NCC_6H_4NO_2)][BF_4]$	2.074–2.113	2.158	1.796	1.878	1.139	1.463	175.0	178.3	This work
$[Fe(Ind)(CO)(P(OC_6H_5)_3)$-$(p$-$NCC_6H_4NO_2)][BF_4]$	2.072–2.193	2.139	1.793	1.900	1.156	1.439	173.7	175.3	This work
p-$NCC_6H_4NO_2$					1.155	1.438		179.2	[14d]

[a] Fe–C (Cp, Ind) range.

5.1(1)°; HA = 5.4(1)°; Δ = 0.11(1) Å, consistent with an η^5-indenyl coordination.

In Table 3, we present a comparison between the coordination geometry about the Fe atom for the reported structures as well as other related complexes with an iron nitrile bonding. The Fe–C (of the Cp ring) distances obtained in both structures are within the expected values for Fe(II) compounds of this type (2.072–2.193 Å range), even for the indenyl derivative **16**, which also indicates an η^5-coordination for the indenyl ligand. The phosphite geometric data are similar to the other compounds containing the phosphite ligand [15]. The well-known contraction of the Fe–P bond, due to the presence of the oxygen as α-atom of the pendent groups on triphenylphosphite, when compared with analogous triphenylphosphine derivatives, is also observed in these complexes.

Our previous studies [7] on complexes of the type $[Fe(\eta^5$-$Cp)(P\_P)]$ (P_P = bidentate phosphine) containing the *p*-nitrobenzonitrile chromophore showed that the remarkable structural features found in X-ray diffraction studies, namely Fe–N and N≡C bond lengths and the retention of aromaticity on the benzonitrile ring, did not corroborate the existence of π-backdonation from the metal to the nitrile ligand, in the solid state, although this effect was found in solution from IR and NMR spectroscopic data.

For the reported compounds (**5** and **16**), the Fe–N bond lengths (1.878(10) and 1.900(8) Å, respectively), are relatively shorter (within crystallographic errors) than the corresponding distance found in iron(II) complexes with the acetonitrile ligand and similar to the Fe–N bond length of the $[Fe(\eta^5$-$Cp)(DPPE)(p$-$NCC_6H_4NO_2)][PF_6]$. This feature is associated with N≡C bond lengths in the same range of the corresponding length on the free *p*-$NCC_6H_4NO_2$ ligand, particularly in the case of **16**, and the retention of aromaticity on the benzonitrile ring. These observations altogether suggest that the metal-to-nitrile back-donation does not

contribute to describe the Fe–N≡C bond in the solid state, although this effect could be supported by the almost linear geometry of nitrile ligand in both compounds (see Table 2). These results are in agreement with IR spectroscopic studies which show an increase in nitrile stretching frequency upon coordination, indicating that the N–C bond is apparently strengthened rather than weakened.

3. Concluding remarks

IR and NMR spectroscopic data for this family of complexes, also supported by the X-ray structural studies, indicate that coordination of nitrile ligand to the metal centre has essentially a σ-type character, the metal–ligand π-backdonation being less significant. These data identify the fragments $[Fe(\eta^5$-Cp or $Ind)(CO)_2]^+$ and $[Fe(\eta^5$-Cp or $Ind)(CO)(P(OC_6H_5)_3)]^+$ as acceptor groups relative to the coordinated benzonitrile derivatives. Conversely, $[Fe(\eta^5$-$Cp)(CO)$-$(P(C_6H_5)_3)]^+$ acts as a weak π donor group, reflecting an overall effect of π-backdonation towards the nitrile ligand.

In addition to our previous work where the iron(II) centre $[Fe(\eta^5$-$Cp)(P\_P)]^+$ was identified as a good π-donor group, these results show that it can also behaves as an acceptor or a weak π-donor group towards the coordinated *p*-substituted benzonitrile, depending on the coligands environment.

4. Experimental

4.1. General procedures

All experiments were carried out under dinitrogen by use of standard Schlenk techniques. Solvents were dried according to the usual published methods [16]. $[Fe(\eta^5$-

Cp)(CO)$_2$(I)] [17], [Fe(η^5-Cp)(CO)(P(OC$_6$H$_5$)$_3$)(I)], [Fe(η^5-Cp)(CO)(P(C$_6$H$_5$)$_3$)(I)] and [Fe(η^5-Cp)(P(OC$_6$-H$_5$)$_3$)$_2$(I)] [18] were prepared using different irradiation times following the literature procedures. (E)-p-NCCH=CHC$_6$H$_4$NO$_2$ [19], [Fe(η^5-Ind)(CO)$_2$]$_2$ [20], [Fe(η^5-Ind)(CO)$_2$(I)] [21] and [Fe(η^5-Ind)(CO)-(P(OC$_6$H$_5$)$_3$)(I)] [17] were prepared according to the procedures described in the literature. All the other starting materials were used as purchased from Aldrich Chemical Co.

Solid state IR spectra were recorded on a Perkin–Elmer Paragon 1000 PC FTIR spectrophotometer in KBr pellets; only significant bands are cited in the text. ^{1}H-, ^{13}C- and the ^{31}P-NMR spectra were recorded on a Varian Unity 300 spectrometer at probe temperature using acetone-d_6 as solvent. The ^{1}H and ^{13}C chemical shifts are reported in parts per million downfield from internal Me$_4$Si and the ^{31}P-NMR spectra are reported in parts per million downfield from external 85% H$_3$PO$_4$ standard. Spectral assignments follow the numbering scheme shown in Fig. 4.

The UV–vis spectra were recorded on Hitachi U-2001 and Shimadzu 1603 spectrophotometers. Microanalyses were performed in our laboratories using a Fisons Instruments EA1108 system with data acquisition, integration and handling performed using a PC with the EAGER-200 software package (Carlo Erba Instruments). Melting points were obtained on a Leica Galen III instrument and are not corrected.

4.2. Preparation of [Fe(η^5-Cp)(CO)$_2$(p-NCR)][BF$_4$]

All the complexes were prepared by the process described below. The appropriate nitrile p-NCR (R = C$_6$H$_4$NO$_2$, (E)-CH=CHC$_6$H$_4$NO$_2$, C$_6$H$_4$N(CH$_3$)$_2$, (E)-CH=CHC$_6$H$_4$N(CH$_3$)$_2$) (1.3 mmol) was added to a solution of [Fe(η^5-Cp)(CO)$_2$(I)] (1 mmol) and one equivalent of AgBF$_4$ in CH$_2$Cl$_2$ (40 ml) at room temperature (r.t.) and the mixture was stirred overnight. A change was observed from dark brown to light orange with simultaneous precipitation of AgI. The orange solution was filtered, evaporated under vacuum to dryness and washed several times with Et$_2$O. The residue

Fig. 4. Numbering scheme for NMR spectral assignments.

was recrystallised from Me$_2$CO–Et$_2$O or CH$_2$Cl$_2$–Et$_2$O.

4.2.1. [Fe(η^5-Cp)(CO)$_2$(p-NCC$_6$H$_4$NO$_2$)][BF$_4$] (1)
Yellow crystals; 72% yield, m.p. 156.3–156.4 °C. Anal. Found: C, 40.99; H, 2.15; N, 6.64. Calc. for C$_{14}$H$_9$N$_2$O$_4$FeBF$_4$: C, 40.83; H, 2.20; N, 6.80%. IR (KBr, cm^{-1}): ν(CO) 2072 and 2017, ν(N≡C) 2267, ν(NO$_2$) 1524 and 1346. ^{1}H-NMR ((CD$_3$)$_2$CO): 5.81 (s, 5H, η^5-C$_5$H$_5$); 8.26 (d, 2H, J_{HH} = 9.0 Hz, H$_2$, H$_6$); 8.44 (d, J_{HH} = 9.0 Hz, 2H, H$_3$, H$_5$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 88.42 (η^5-C$_5$H$_5$); 117.32 (C1); 125.02 (C3, C5); 134.15 (NC); 136.16 (C2, C6); 151.89 (C4); 209.11 (CO).

4.2.2. [Fe(η^5-Cp)(CO)$_2$(p-NCC$_6$H$_4$N(CH$_3$)$_2$)][BF$_4$] (2)
Golden crystals; 60% yield, m.p. 142.7–143.3 °C. Anal. Found: C, 46.33; H, 3.69; N, 6.53. Calc. for C$_{16}$H$_{15}$N$_2$O$_2$FeBF$_4$: C, 46.88; H, 3.69; N, 6.83%. IR (KBr, cm^{-1}): ν(CO) 2065 and 2015, ν(N≡C) 2256. ^{1}H-NMR ((CD$_3$)$_2$CO): 3.09 (s, 6H, N(CH$_3$)$_2$); 5.73 (s, 5H, η^5-C$_5$H$_5$); 6.79 (d, 2H, J_{HH} = 9.3 Hz, H$_3$, H$_5$); 7.61 (d, 2H, J_{HH} = 9.0 Hz, H$_2$, H$_6$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 39.87 (N(CH$_3$)$_2$); 87.98 (η^5-C$_5$H$_5$); 94.76 (C1); 112.21 (C3, C5); 135.29 (C2, C6); 138.62 (NC); 154.66 (C4); 209.81 (CO).

4.2.3. [Fe(η^5-Cp)(CO)$_2$((E)-p-NCCH=CHC$_6$H$_4$NO$_2$)]-[BF$_4$] (3)
Yellow crystals; 58% yield, m.p. 129.7–131.0 °C. Anal. Found: C, 43.65; H, 2.45; N, 6.34. Calc. for C$_{16}$H$_{11}$N$_2$O$_4$FeBF$_4$: C, 43.88; H, 2.53; N, 6.40%. IR (KBr, cm^{-1}): ν(CO) 2079 and 2022, ν(N≡C) 2262, ν(NO$_2$) 1518 and 1343. ^{1}H-NMR ((CD$_3$)$_2$CO): 5.77 (s, 5H, η^5-C$_5$H$_5$); 6.77 (d, 1H, J_{HH} = 16.5 Hz, H$_8$); 7.95 (d, 2H, J_{HH} = 8.7 Hz, H$_2$, H$_6$); 7.98 (d, 1H, J_{HH} = 16.5 Hz, H$_7$); 8.32 (d, 2H, J_{HH} = 8.7 Hz, H$_3$, H$_5$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 88.24 (η^5-C$_5$H$_5$); 100.65 (C8); 124.96 (C3, C5); 130.15 (C2, C6); 135.45 (C1); 139.86 (NC); 150.35 (C4); 153.51 (C7); 209.30 (CO).

4.2.4. [Fe(η^5-Cp)(CO)$_2$((E)-p-NCCH=CHC$_6$H$_4$N-(CH$_3$)$_2$)][BF$_4$] (4)
Yellow crystals; 81% yield, m.p. 149.4–151.3 °C. Anal. Found: C, 48.77; H, 4.31; N, 5.82. Calc. for C$_{18}$H$_{17}$N$_2$O$_2$FeBF$_4$: C, 49.59; H, 3.93; N, 6.43%. IR (KBr, cm^{-1}): ν(CO) 2077, 2037 and 1989 (sh), ν(N≡C) 2250. ^{1}H-NMR ((CD$_3$)$_2$CO): 3.08 (s, 6H, N(CH$_3$)$_2$); 5.71 (s, 5H, η^5-C$_5$H$_5$); 6.07 (d, 1H, J_{HH} = 16.5 Hz, H$_8$); 6.79 (d, 2H, J_{HH} = 8.4 Hz, H$_3$, H$_5$); 7.49 (d, 2H, J_{HH} = 9.3 Hz, H$_2$, H$_6$); 7.65 (d, 1H, J_{HH} = 16.5 Hz, H$_7$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 40.40 (N(CH$_3$)$_2$); 87.01 (C8); 88.06 (η^5-C$_5$H$_5$); 113.00 (C3, C5); 122.35 (C1); 131.08 (C2, C6); 138.30 (NC); 153.80 (C4); 156.31 (C7); 209.77 (CO).
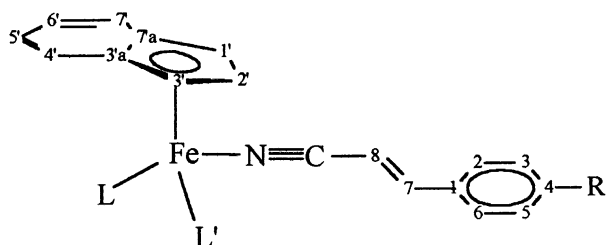
4.3. Preparation of [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)-(p-NCR)][BF₄]

All the complexes were prepared by the process described below. The appropriate nitrile *p*-NCR (R = C₆H₄NO₂, C₆H₄N(CH₃)₂) (1.3 mmol) was added to a solution of [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)(I)] (1 mmol) and AgBF₄ (1 mmol) in C₆H₆ or CH₂Cl₂ (40 ml) at r.t. The mixture was stirred overnight at r.t. A change of colour was observed from dark brown to orange with simultaneous precipitation of AgI. After filtration, the solution was evaporated under vacuum to dryness and washed several times with Et₂O to remove the excess of nitrile. The residue was recrystallised from CH₂Cl₂–Et₂O.

4.3.1. [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)(p-NCC₆H₄NO₂)]-[BF₄] (5)

Golden crystals; 34% yield, m.p. 135.9–136.9 °C. Anal. Found: C, 53.62; H, 3.40; N, 3.89. Calc. for C₃₁H₂₄N₂O₆FePBF₄: C, 53.64; H, 3.48; N, 4.04%. IR (KBr, cm⁻¹): ν(CO) 2012, ν(N≡C) 2257, ν(NO₂) 1528 and 1347. ¹H-NMR ((CD₃)₂CO): 5.12 (s, 5H, η⁵-C₅H₅); 7.30–7.35 and 7.46–7.53 (m, 15H, OPh); 8.10 (d, 2H, J_{HH} = 9.3 Hz, H₂, H₆); 8.45 (d, 2H, J_{HH} = 9.3 Hz, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)₂CO): 85.93 (η⁵-C₅H₅); 117.14 (C1); 121.94 (d, $^4J_{CP}$ = 4.4 Hz, OPh, C-*meta*); 125.06 (C3, C5); 127.13 (OPh, C-*para*); 131.40 (OPh, C-*ortho*); 134.36 (NC); 135.09 (C2, C6); 151.50 and 151.62 (C4 and OPh, C-*ipso*), 213.50 (d, $^2J_{CP}$ = 43.1 Hz, CO). ³¹P{¹H}-NMR ((CD₃)₂CO): 164.83.

4.3.2. [Fe(η⁵-Cp)(CO)(P(OC₆H₅)₃)(p-NCC₆H₄N-(CH₃)₂)][BF₄] (6)

Orange solid; 33% yield, m.p. 125.4–127.1 °C. Anal. Found: C, 56.57; H, 4.48; N, 3.67. Calc. for C₃₃H₃₀N₂O₄FePBF₄: C, 56.27; H, 4.37; N, 4.05%. IR (KBr, cm⁻¹): ν(CO) 2007, ν(N≡C) 2242. ¹H-NMR ((CD₃)₂CO): 3.11 (s, 6H, N(CH₃)₂); 4.97 (s, 5H, η⁵-C₅H₅); 6.81 (d, 2H, J_{HH} = 8.1 Hz, H₃, H₅); 7.34–7.50 (m, 15H, OPh)); 7.49 (d, 2H, H₂, H₆).[1] ¹³C{¹H}-NMR ((CD₃)₂CO): 39.92 (N(CH₃)₂); 85.25 (η⁵-C₅H₅); 95.07 (C1); 112.37 (C3, C5); 121.97 (d, $^4J_{CP}$ = 3.38 Hz, OPh, C-*meta*); 127.06 (OPh, C-*para*); 131.33 (OPh, C-*ortho*); 135.05 (C2, C6); 138.90 (NC); 151.56 (d, $^2J_{CP}$ = 8.0 Hz, OPh, C-*ipso*); 154.58 (C4); 214.45 (d, $^2J_{CP}$ = 40.2 Hz, CO). ³¹P{¹H}-NMR ((CD₃)₂CO): 166.68 (s).

4.4. Preparation of [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)(p-NCR)][BF₄]

All the complexes were prepared by the process described below. The appropriate nitrile *p*-NCR (R =

C₆H₄NO₂, (*E*)-CH=CHC₆H₄NO₂, C₆H₄N(CH₃)₂, (*E*)-CH=CHC₆H₄N(CH₃)₂) (1.3 mmol) was added to a solution of [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)(I)] (1 mmol) and one equivalent of AgBF₄ in CH₂Cl₂ (40 ml) at r.t. and the mixture was stirred for 6 h. A change of colour was observed from dark green to deep red with simultaneous precipitation of AgI. The deep red solution was filtered, evaporated under vacuum to dryness and washed several times with Et₂O. The residue was recrystallised from CH₂Cl₂–Et₂O.

4.4.1. [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)(p-NCC₆H₄NO₂)][BF₄] (7)

Red crystals; 63% yield, m.p. 176.8–178.6 °C. Anal. Found: C, 57.61; H, 3.82; N, 4.25. Calc. for C₃₁H₂₄N₂O₃FePBF₄: C, 57.62; H, 3.74; N, 4.34%. IR (KBr, cm⁻¹): ν(CO) 1974, ν(N≡C) 2247, ν(NO₂) 1528 and 1347. ¹H-NMR ((CD₃)₂CO): 5.25 (s, 5H, η⁵-C₅H₅); 7.51–7.62 (m, 15H, PPh₃); 7.67 (d, 2H, J_{HH} = 9.0 Hz, H₂, H₆); 8.33 (d, 2H, J_{HH} = 9.0 Hz, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)₂CO): 86.52 (η⁵-C₅H₅); 117.32 (C1); 124.88 (C3, C5); 130.25 (d, $^3J_{CP}$ = 9.8 Hz, PPh₃,C-*meta*), 132.42 (PPh₃, C-*para*); 133.15 (NC); 134.19 (d, $^2J_{CP}$ = 9.8 Hz, PPh₃, C-*ortho*); 135.32 (C2, C6); 151.42 (C4); 217.09 (d, $^2J_{CP}$ = 28.1 Hz, CO). ³¹P{¹H}-NMR ((CD₃)₂CO): 67.80 (s).

4.4.2. [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)(p-NCC₆H₄N-(CH₃)₂)][BF₄] (8)

Deep red crystals; 72% yield, m.p. 193.0–193.6 °C. Anal. Found: C, 61.01; H, 5.02; N, 4.08. Calc. for C₃₃H₃₀N₂OFePBF₄: C, 61.52; H, 4.69, N, 4.35%. IR (KBr, cm⁻¹): ν(CO) 1993, ν(N≡C) 2249. ¹H-NMR ((CD₃)₂CO): 3.04 (s, 6H, N(CH₃)₂); 5.12 (d, 5H, J_{CP} = 1.2 Hz, η⁵-C₅H₅); 6.66 (d, 2H, J_{HH} = 9.0 Hz, H₃, H₅); 7.06 (d, 2H, J_{HH} = 9.0 Hz, H₂, H₆); 7.49–7.60 (m, 15H, PPh₃). ¹³C{¹H}-NMR ((CD₃)₂CO): 39.82 (N(CH₃)₂); 85.88 (η⁵-C₅H₅); 95.38 (C1); 112.03 (C3, C5); 130.04 (d, $^3J_{CP}$ = 9.7 Hz, PPh₃, C-*meta*); 132.16 (d, $^4J_{CP}$ = 1.2 Hz, PPh₃, C-*para*); 133.25 (d, $^1J_{CP}$ = 46.1 Hz, PPh₃, C-*ipso*); 134.01 (d, $^2J_{CP}$ = 9.7 Hz, PPh₃, C-*ortho*); 134.61 (C2, C6); 138.99 (NC); 154.27 (C4); 217.87 (d, $^2J_{CP}$ = 29.2 Hz, CO). ³¹P{¹H}-NMR ((CD₃)₂CO): 67.88 (s).

4.4.3. [Fe(η⁵-Cp)(CO)(P(C₆H₅)₃)((E)-p-NCCH= CHC₆H₄NO₂)][BF₄] (9)

Red crystals; 75% yield, m.p. 161.9–163.1 °C. Anal. Found: C, 58.85; H, 3.99; N, 4.14. Calc. for C₃₃H₂₆N₂O₃FePBF₄: C, 58.96; H, 3.90; N, 4.17%. IR (KBr, cm⁻¹): ν(CO) 1993, ν(N≡C) 2243, ν(NO₂) 1523 and 1345. ¹H-NMR ((CD₃)₂CO): 5.16 (s, 5H, η⁵-C₅H₅); 6.46 (d, 1H, J_{HH} = 16.5 Hz, H₈); 7.19 (d, 1H, J_{HH} = 16.5 Hz, H₇); 7.51–7.64 (m, 15H, PPh₃); 7.81 (d, 2H, J_{HH} = 8.4 Hz, H₂, H₆); 8.26 (d, 2H, J_{HH} = 8.1 Hz, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)₂CO): 86.27 (η⁵-C₅H₅); 100.75 (C8); 124.96 (C3, C5); 129.88 (C2, C6); 130.19

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[1] Signal obscured by the aromatic protons of triphenylphosphite.

(d, $^3J_{CP} = 10.0$ Hz, PPh$_3$, C-*meta*); 132.32 (PPh$_3$, C-*para*); 132.96 (d, $^1J_{CP} = 46.4$ Hz, PPh$_3$, C-*ipso*); 134.15 (d, $^2J_{CP} = 10.0$ Hz, PPh$_3$, C-*ortho*); 135.79 (C1); 139.80 (NC); 150.20 (C4); 151.60 (C7); 217.36 (d, $^2J_{CP} = 27.8$ Hz, CO). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO): 67.30 (s).

4.4.4. [Fe(η^5-Cp)(CO)(P(C$_6$H$_5$)$_3$)((E)-p-NCCH=CHC$_6$H$_4$N(CH$_3$)$_2$)][BF$_4$] (10)

Red crystals; 51% yield, m.p. 180.7–182.6 °C. Anal. Found: C, 62.50; H, 4.89; N, 4.08. Calc. for C$_{35}$H$_{32}$N$_2$OFePBF$_4$: C, 62.72; H, 4.81; N, 4.18%. IR (KBr, cm^{-1}): ν(CO) 1983, ν(N≡C) 2248. ^{1}H-NMR ((CD$_3$)$_2$CO): 3.04 (s, 6H, N(CH$_3$)$_2$); 5.09 (s, 5H, η^5-C$_5$H$_5$); 5.78 (d, 1H, $J_{HH} = 16.5$ Hz, C$_8$); 6.72 (d, 2H, $J_{HH} = 8.7$ Hz, H$_3$, H$_5$); 6.81 (d, 1H, $J_{HH} = 16.5$ Hz, C$_7$); 7.34 (d, 2H, $J_{HH} = 8.4$ Hz, H$_2$, H$_6$); 7.48–7.66 (m, 15H, PPh$_3$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 40.16 (N(CH$_3$)$_2$); 85.91 (η^5-C$_5$H$_5$); 88.03 (C8); 112.66 (C3, C5); 121.76 (C1); 130.72 (C2, C6); 130.81 (d, $^3J_{CP} = 9.7$ Hz, PPh$_3$, C-*meta*); 132.20 (PPh$_3$, C-*para*), 133.23 (d, $^1J_{CP} = 46.1$ Hz, PPh$_3$, C-*ipso*); 134.11 (d, $^2J_{CP} = 9.7$ Hz, PPh$_3$, C-*ortho*); 138.62 (NC); 153.79 (C4); 154.58 (C7); 217.82 (d, $^2J_{CP} = 28.0$ Hz, CO). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO): 67.82 (s).

4.5. Preparation of [Fe(η^5-Cp)(P(OC$_6$H$_5$)$_3$)$_2$(p-NCR)][BF$_4$]

All the complexes were prepared by the process described below. The appropriate nitrile p-NCR (R = C$_6$H$_4$NO$_2$, C$_6$H$_4$N(CH$_3$)$_2$, (E)-CH=CHC$_6$H$_4$N(CH$_3$)$_2$) (1.3 mmol) was added to a solution of [Fe(η^5-Cp)(P(OC$_6$H$_5$)$_3$)$_2$(I)] (1 mmol) and AgBF$_4$ (1 mmol) in C$_6$H$_6$ (40 ml) at r.t. The mixture was stirred at r.t. for 2 days. A change of colour was observed from dark brown to orange with simultaneous precipitation of AgI. After filtration, the solution was evaporated under vacuum to dryness and washed several times with Et$_2$O to remove the excess of nitrile. The residue was recrystallised from CH$_2$Cl$_2$ or Me$_2$CO–Et$_2$O.

4.5.1. [Fe(η^5-Cp)(P(OC$_6$H$_5$)$_3$)$_2$(p-NCC$_6$H$_4$NO$_2$)][BF$_4$] (11)

Orange crystals; 63% yield, m.p. 104.0–105.5 °C. Anal. Found: C, 58.90; H, 4.01; N, 2.88. Calc. for C$_{48}$H$_{39}$N$_2$O$_8$FeP$_2$BF$_4$: C, 59.04; H, 4.03; N, 2.87%. IR (KBr, cm^{-1}): ν(N≡C) 2238, ν(NO$_2$) 1525 and 1345. ^{1}H-NMR ((CD$_3$)$_2$CO): 4.60 (s, 5H, η^5-C$_5$H$_5$); 7.20–7.25 (m, 6H, OPh), 7.34–7.41 (m, 24H, OPh); 8.01 (d, 2H, $J_{HH} = 9.0$ Hz, H$_2$, H$_6$); 8.45 (d, 2H, $J_{HH} = 8.7$ Hz, H$_3$, H$_5$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 82.58 (η^5-C$_5$H$_5$); 117.63 (C1); 121.95 (OPh, C-*meta*); 125.38 (C3, C5); 126.47 (OPh, C-*para*); 131.03 (OPh, C-*ortho*); 134.30 (NC); 135.24 (C2, C6); 151.26 (C4); 152.30 (OPh, C-*ipso*). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO): 163.19 (s).

4.5.2. [Fe(η^5-Cp)(P(OC$_6$H$_5$)$_3$)$_2$(p-NCC$_6$H$_4$N-(CH$_3$)$_2$)][BF$_4$] (12)

Orange crystals; 57% yield, m.p. 120.1–121.6 °C. Anal. Found: C, 61.92; H, 4.85; N, 2.79. Calc. for C$_{50}$H$_{45}$N$_2$O$_6$FeP$_2$BF$_4$: C, 61.63; H, 4.65; N, 2.87%. IR (KBr, cm^{-1}): ν(N≡C) 2231. ^{1}H-NMR ((CD$_3$)$_2$CO): 3.12 (s, 6H, N(CH$_3$)$_2$); 4.39 (s, 5H, η^5-C$_5$H$_5$); 6.86 (d, 2H, $J_{HH} = 9.3$ Hz, H$_3$, H$_5$); 7.25–7.41 (m, 30H, OPh); 7.48 (d, 2H, $J_{HH} = 9.3$ Hz, H$_2$, H$_6$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 40.35 (N(CH$_3$)$_2$); 81.54 (η^5-C$_5$H$_5$); 97.07 (C1); 113.24 (C3, C5); 122.03 (OPh, C-*meta*); 126.35 (OPh, C-*para*); 130.93 (OPh, C-*ortho*); 134.64 (C2, C6); 138.73 (NC); 152.33 (OPh, C-*ipso*); 153.96 (C4). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO): 164.84 (s).

4.5.3. [Fe(η^5-Cp)(P(OC$_6$H$_5$)$_3$)$_2$((E)-p-NCCH=CHC$_6$H$_4$N(CH$_3$)$_2$)][BF$_4$] (13)

Orange crystals; 60% yield, m.p. 81.6–83.0 °C. Anal. Found: C, 62.35; H, 4.77; N, 2.78. Calc. for C$_{52}$H$_{47}$N$_2$O$_6$FeP$_2$BF$_4$: C, 62.42; H, 4.73; N, 2.80%. IR (KBr, cm^{-1}): ν(N≡C) 2223. ^{1}H-NMR ((CD$_3$)$_2$CO): 3.09 (s, 6H, N(CH$_3$)$_2$); 4.37 (s, 5H, η^5-C$_5$H$_5$); 6.15 (d, 1H, $J_{HH} = 16.2$ Hz, H$_8$); 6.80 (d, 2H, $J_{HH} = 8.7$ Hz, H$_3$, H$_5$); 7.24–7.44 (m, 31H, H$_7$ and OPh); 7.49 (d, 2H, $J_{HH} = 9.0$ Hz, H$_2$, H$_6$). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO): 40.48 (N(CH$_3$)$_2$); 81.62 (η^5-C$_5$H$_5$); 89.27 (C8); 113.09 (C3, C5); 122.13 (OPh, C-*meta*); 126.37 (OPh, C-*para*); 130.18 (C1); 130.90 (C2, C6); 130.96 (OPh, C-*ortho*); 138.52 (NC); 154.35 (t, $J = 5.7$ Hz, OPh, C-*ipso*); 154.29 (C7); (C4)[2]. ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO): 164.78 (s).

4.6. Preparation of [Fe(η^5-Ind)(CO)$_2$(p-NCR)][BF$_4$]

All the complexes were prepared by the following process: the appropriate nitrile p-NCR (R = C$_6$H$_4$NO$_2$, C$_6$H$_4$N(CH$_3$)$_2$) (1.3 mmol) was added to a solution of [Fe(η^5-Ind)(CO)$_2$(I)] (1 mmol) and one equivalent of AgBF$_4$ in CH$_2$Cl$_2$ (40 ml) at r.t. and the mixture was stirred overnight. A change of colour was observed from reddish brown to red with simultaneous precipitation of AgI. The red solution was filtered, evaporated under vacuum to dryness and washed several times with Et$_2$O. The residue was recrystallised from CH$_2$Cl$_2$–Et$_2$O.

4.6.1. [Fe(η^5-Ind)(CO)$_2$(p-NCC$_6$H$_4$NO$_2$)][BF$_4$] (14)

Red crystals; 29% yield, m.p. (dec.) 130.0 °C. Anal. Found: C, 46.88; H, 2.32; N, 6.12. Calc. for C$_{18}$H$_{11}$N$_2$O$_4$FeBF$_4$: C, 46.80; H, 2.40; N, 6.06%. IR (KBr, cm^{-1}): ν(CO) 2038 and 1986, ν(N≡C) 2274, ν(NO$_2$) 1528 and 1350. ^{1}H-NMR ((CD$_3$)$_2$CO): 5.96 (s, 1H, Ind:H$_{2'}$); 6.14 (d, 2H, $J_{HH} = 2.4$ Hz, Ind:H$_{1'}$,H$_{3'}$);

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[2] Signal obscured by the aromatic carbons of triphenylphosphite.

7.82–7.85 (m, A_2B_2, 2H, Ind:$H_{4'}$,$H_{7'}$); 8.06–8.09 (m, A_2B_2, 2H, Ind:$H_{5'}$,$H_{6'}$); 8.20 (d, 2H, J_{HH} = 8.7 Hz, H_2, H_6); 8.44 (d, 2H, J_{HH} = 8.7 Hz, H_3, H_5). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): 73.66 (Ind:$C1'$,$C3'$); 90.40 (Ind:$C2'$); 109.00 (Ind:$C3'a$,$C7'a$); 116.91 (C1), 124.99 (C3, C5); 127.41 (Ind:$C4'$,$C7'$); 132.87 (NC); 134.83 (Ind:$C5'$,$C6'$); 136.02 (C2, C6); 151.79 (C4); 209.52 (CO).

4.6.2. [Fe(η^5-Ind)(CO)$_2$(p-NCC$_6$H$_4$N(CH$_3$)$_2$)][BF$_4$] (15)

Deep red crystals; 70% yield, m.p. (dec.) 121.0 °C. Anal. Found: C, 52.24; H, 3.84; N, 6.09. Calc. for $C_{20}H_{17}N_2O_2FeBF_4$: C, 52.22; H, 3.72; N, 6.09%. IR (KBr, cm^{-1}): v(CO) 2067, 2031 and 1988, v(N≡C) 2252. ^{1}H-NMR ($(CD_3)_2CO$): 3.09 (s, 6H, N(CH$_3$)$_2$); 5.84 (t, 1H, J_{HH} = 2.4 Hz, Ind:$H_{2'}$); 6.07 (d, 2H, J_{HH} = 2.4 Hz, Ind:$H_{1'}$,$H_{3'}$); 6.78 (d, 2H, J_{HH} = 9.0 Hz, H_3, H_5); 7.53 (d, 2H, J_{HH} = 8.4 Hz, H_2, H_6); 7.77–7.81 (m, A_2B_2, 2H, Ind:$H_{4'}$,$H_{7'}$), 7.98–8.02 (m, A_2B_2, 2H, Ind:$H_{5'}$,$H_{6'}$). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): 39.82 (N(CH$_3$)$_2$); 73.20 (Ind:$C1'$,$C3'$); 89.54 (Ind:$C2'$); 94.45 (C1); 109.26 (Ind:$C3'a$,$C7'a$); 112.21 (C3, C5); 127.35 (Ind:$C4'$,$C7'$); 133.94 (Ind:$C5'$,$C6'$); 135.14 (C2, C6), 137.45 (NC); 154.60 (C4), 210.35 (CO).

4.7. Preparation of [Fe(η^5-Ind)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCR)][BF$_4$]

All the complexes were prepared by the process described below. The appropriate nitrile p-NCR (R = C$_6$H$_4$NO$_2$, (E)-CH=CHC$_6$H$_4$NO$_2$, C$_6$H$_4$N(CH$_3$)$_2$, (E)-CH=CHC$_6$H$_4$N(CH$_3$)$_2$) (1.3 mmol) was added to a solution of [Fe(η^5-Ind)(CO)(P(OC$_6$H$_5$)$_3$)(I)] (1 mmol) and AgBF$_4$ (1 mmol) in CH$_2$Cl$_2$ (40 ml) at r.t. The mixture was stirred overnight at r.t. A change in colour was observed from dark brown to red with simultaneous precipitation of AgI. After filtration, the solution was evaporated under vacuum to dryness and washed several times with Et$_2$O to remove the excess of nitrile. The residue was recrystallised from CH$_2$Cl$_2$–Et$_2$O.

4.7.1. [Fe(η^5-Ind)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCC$_6$H$_4$NO$_2$)][BF$_4$] (16)

Red crystals; 51% yield, m.p. 143.4–144.6 °C. Anal. Found: C, 56.65; H, 3.58; N, 3.70. Calc. for $C_{35}H_{26}N_2O_6FePBF_4$: C, 56.49; H, 3.52; N 3.76%. IR (KBr, cm^{-1}): v(CO) 1997, v(N≡C) 2254, v(NO$_2$) 1523 and 1346. ^{1}H-NMR ($(CD_3)_2CO$): 4.35 (bs, 1H, Ind:$H_{1'}$ or $H_{3'}$); 5.62 (dt, J_{HH} = ≈3.0 Hz; 1H, Ind:$H_{2'}$); 5.81 (bs, 1H, Ind:$H_{1'}$ or $H_{3'}$); 7.31–7.36 (m, 3H, OPh); 7.44–7.54 (m, 12H, OPh); 7.60, 7.69 (t, J_{HH} = 7.35 Hz, 1H, Ind:$H_{5'}$ and $H_{6'}$); 7.78 (d, 1H, J_{HH} = 8.7 Hz, Ind:$H_{4'}$ or $H_{7'}$); 7.86 (d, 1H, J_{HH} = 8.4 Hz, Ind:$H_{4'}$ or $H_{7'}$); 8.05 (dt, J_{HH} = 8.4 and 2.1 Hz, 2H, H_2, H_6); 8.42 (dt, J_{HH} = 8.4 and 2.1 Hz, 2H, H_3, H_5) $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): 64.45, 77.98 (Ind:$C1'$ and $C3'$); 88.75 (Ind:$C2'$); 104.62, 110.65 (Ind:$C3'a$, $C7'a$); 116.76 (C1);

121.87 (OPh, C-*meta*); 125.14 (C3, C5); 126.38, 127.67 (Ind:$C4'$, $C7'$); 127.17 (OPh, C-*para*); 131.40 (OPh, C-*ortho*); 132.46, 133.49 (Ind:$C5'$, $C6'$); 133.19 (NC); 135.81 (C2, C6); 151.44 (d, $^2J_{CP}$ = 8.6 Hz, OPh, C-*ipso*); 151.61 (C4), 213.45 (d, $^2J_{CP}$ = 40.95 Hz, CO). $^{31}P\{^1H\}$-NMR ($(CD_3)_2CO$): 166.62 (s).

4.7.2. [Fe(η^5-Ind)(CO)(P(OC$_6$H$_5$)$_3$)(p-NCC$_6$H$_4$N-(CH$_3$)$_2$)][BF$_4$] (17)

Deep red crystals; 54% yield, m.p. 106.7–108.5 °C. Anal. Found: C, 59.75; H, 4.48; N, 3.68. Calc. for $C_{37}H_{32}N_2O_4FePBF_4$: C, 59.87; H, 4.35; N, 3.77%. IR (KBr, cm^{-1}): v(CO) 1993, v(N≡C) 2239. ^{1}H-NMR ($(CD_3)_2CO$): 3.11 (s, 6H, N(CH$_3$)$_2$); 4.15 (s, 1H, Ind:$H_{1'}$ or $H_{3'}$); 5.50 (m, J_{HH} = 3.0 Hz, 1H, Ind:$H_{2'}$); 5.59 (s, 1H, Ind:$H_{1'}$ or $H_{3'}$); 6.79 (d, 2H, J_{HH} = 9.0 Hz, H_3, H_5); 7.33–7.62 (m, 19H, Ind:$H_{4'}$–$H_{7'}$ and OPh); 7.41 (d, 2H, H_2, H_6)[3]. $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): 39.95 (N(CH$_3$)$_2$); 63.46 and 77.40 (Ind:C1,C3); 88.17 (Ind:$C2'$); 94.92 (C1); 104.27, 111,16 (Ind:$C3'a$,$C7'a$); 112.43 (C3, C5); 121.93 (d, $^4J_{CP}$ = 4.6 Hz, OPh, C-*meta*); 126.15, 127.84 (Ind:$C4'$,$C7'$); 127.15 (OPh, C-*para*); 131.35 (OPh, C-*ortho*); 132.01, 133.059 (Ind:$C5'$ and $C6'$); 133.94 (NC); 134.98 (C2, C6); 151.54 (d, $^2J_{CP}$ = 8.7 Hz, OPh, C-*ipso*); 154.64 (C4), 214.31 (d, $^2J_{CP}$ = 43.5 Hz, CO). $^{31}P\{^1H\}$-NMR ($(CD_3)_2CO$): 168.77 (s).

4.7.3. [Fe(η^5-Ind)(CO)(P(OC$_6$H$_5$)$_3$)((E)-p-NCCH=CHC$_6$H$_4$NO$_2$)][BF$_4$] (18)

Orange crystals; 36% yield, m.p. 149.0–149.5 °C. Anal. Found: C, 57.55; H, 3.73; N, 3.56. Calc. for $C_{37}H_{28}N_2O_6FePBF_4$: C, 57.70; H, 3.66; N, 3.64%. IR (KBr, cm^{-1}): v(CO) 2010, v(N≡C) 2243, v(NO$_2$) 1519 and 1341. ^{1}H-NMR ($(CD_3)_2CO$): 4.21 (s, 1H, Ind:$H_{1'}$ or $H_{3'}$); 5.56 (m, J_{HH} = 3.0 Hz, 1H, Ind:$H_{2'}$); 5.63 (s, 1H, Ind:$H_{1'}$ or $H_{3'}$); 6.68 (d, 1H, J_{HH} = 16.8 Hz, H_8), 7.38 (t, 3H, J_{HH} = 7.2 Hz, OPh, C-*para*); 7.47 (d, 6H, J_{HH} = 7.8 Hz, OPh, C-*ortho*); 7.55 (t, 6H, J_{HH} = 7.8 Hz, OPh, C-*meta*); 7.67 (d, 1H, J_{HH} = 8.7 Hz, Ind:$H_{4'}$ or $H_{7'}$); 7.71 (d, 1H, J_{HH} = 8.7 Hz, Ind:$H_{4'}$ or $H_{7'}$); 7.76 (d, 1H, J_{HH} = 16.8 Hz, H_7); 7.83 (d, 2H, J_{HH} = 8.1 Hz, Ind:$H_{5'}$,$H_{6'}$); 7.96 (d, 2H, J_{HH} = 8.1 Hz, H_2, H_6); 8.31 (d, 2H, J_{HH} = 8.1 Hz, H_3, H_5). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): 63.83, 77.92 (Ind:$C1'$,$C3'$); 88.68 (Ind:$C2'$); 100.59 (C8); 104.53, 110.69 (Ind:$C3'a$, $C7'a$); 122.99 (d, $^4J_{CP}$ = 4.1 Hz, OPh, C-*meta*); 124.93 (C3, C5); 126.41, 127.62 (Ind:$C4'$,$C7'$); 127.21 (OPh, C-*para*); 129.08 (C1); 130.22 (C2, C6); 131.43 (OPh, C-*ortho*); 132.32, 133.36 (Ind:$C5'$,$C6'$); 134.48 (NC); 150.34 (C4); 151.50 (d, $^2J_{CP}$ = 8.7 Hz, OPh, C-*ipso*); 152.79 (C7); 213.79 (d, $^2J_{CP}$ = 40.5 Hz, CO). $^{31}P\{^1H\}$-NMR ($(CD_3)_2CO$): 167.74 (s).

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[3] Signal obscured by the aromatic protons of triphenylphosphite.

4.8. X-ray structures of [Fe(η^5-C$_5$H$_5$)(P(OC$_6$H$_5$)$_3$)-(CO)(p-N≡CC$_6$H$_4$NO$_2$)][BF$_4$]·CH$_2$Cl$_2$ and [Fe(η^5-C$_9$H$_7$)(P(OC$_6$H$_5$)$_3$)(CO)(p-N≡CC$_6$H$_4$NO$_2$)][BF$_4$]

Diffraction data for [Fe(η^5-Cp)(POPh$_3$)(CO)(p-N≡CC$_6$H$_4$NO$_2$)][BF$_4$]·CH$_2$Cl$_2$ (**5**) and [Fe(η^5-Ind)-(POPh$_3$)(CO)(p-N≡CC$_6$H$_4$NO$_2$)][BF$_4$] (**16**) were collected at 293(2) K on an Enraf–Nonius TURBOCAD4 diffractometer with Cu–K$_\alpha$ radiation. The unit cell dimensions and orientation matrix was obtained by least-squares refinement of 25 centred reflections with $15.37 < \theta < 23.92°$ for **5** and by least-squares refinement of 23 centred reflections with $15.99 < \theta < 23.15°$ for **16**. Using the CAD4 software [22], data were corrected for Lorentz and polarisation effects and using Ψ-scans for absorption. Intensities of 6048 reflections for **5** and 8225 reflections for **16** were measured by the ω–2θ scan

Table 4
Crystal data and structure refinement for complexes [Fe(η^5-Cp)(CO)(P(OC$_6$H$_5$)(p-N≡CC$_6$H$_4$NO$_2$)][BF$_4$]·CH$_2$Cl$_2$ (**5**) and [Fe(η^5-Ind)(CO)(P(OC$_6$H$_5$)(p-N≡CC$_6$H$_4$NO$_2$)][BF$_4$] (**16**)

Complex	5	16
Empirical formula	C$_{32}$H$_{24}$BCl$_2$F$_4$FeN$_2$O$_6$P	C$_{35}$H$_{26}$BF$_4$FeN$_2$O$_6$P
Formula weight	777.95	744.21
Temperature (K)	293(2)	293(2)
Wavelength (Å)	1.54184	1.54184
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
a (Å)	9.7881(7)	10.000(2)
b (Å)	10.6358(9)	11.500(1)
c (Å)	18.640(3)	29.362(3)
α (°)	94.603(9)	
β (°)	96.51(1)	95.70(2)
γ (°)	115.420(6)	
V (Å^3)	1723.3(3)	3359.9(9)
Z	2	4
D_{calc} (Mg m^{-3})	1.521	1.471
Absorption coefficient (mm^{-1})	5.982	4.672
$F(000)$	800	1520
Index ranges	$-1 \leq h \leq 10$; $-11 \leq k \leq 11$; $-20 \leq l \leq 20$	$-11 \leq h \leq 1$; $-13 \leq k \leq 1$; $-35 \leq l \leq 35$
Reflections collected	6048	7841
Independent reflections	5006 [$R_{int} = 0.1141$]	5979 [$R_{int} = 0.0723$]
Reflections observed ($>2\sigma$)	2898	2648
Data/restraints/parameters	5006/27/432	5979/0/452
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1105$	$R_1 = 0.1036$
R indices (all data)	$R_1 = 0.1739$	$R_1 = 0.2020$
Goodness-of-fit on F^2	1.043	1.031
Largest difference peak and hole (e Å^{-3})	1.069 and -0.974	0.809 and -0.782

mode. The structures were solved by direct methods with SHELXS-97 [23] and refined by the full-matrix least-squares method with SHELXL-97 [24].

Nonhydrogen atoms were anisotropically refined, except for the atoms of the solvent molecule in compound **5**. All hydrogen atoms were inserted in calculated positions and refined isotropically with a thermal parameter equal to $1.2 \times$ those of the carbon atoms to which they are bonded. The solvent molecule, CH$_2$Cl$_2$, was found to be disordered over two positions. The occupation factors refined to 0.50 and 0.50, in the last cycle of refinement. In the disorder model the C–Cl distances were restrained to 1.75 Å. The thermal parameters of the O31 and O41 of the phosphite ligand in complex **5** were also refined with ISOR (estimated S.D. of 0.01). The thermal parameters of the oxygen atoms of the nitrile ligand in the same complex were also restrained (estimated S.D. 0.01). The accuracy of the data allows comparison of the structural parameters; although the relatively high estimated S.D., due to the poor diffraction power of the crystals, preclude some conclusions when interpreting the data. The illustrations were drawn with program ORTEP-III [25] implemented in OSCAIL8 [26]. The atomic scattering factors and anomalous scattering terms were taken from *International Tables* [27]. Other details of data collection and refinement are given in Table 4.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 157903 and 157904 for compounds **5** and **16**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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