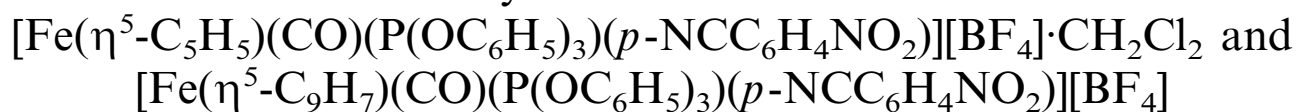


Synthesis of new donor/acceptor η^5 -cyclopentadienyl and η^5 -indenyliron(II) complexes with *p*-benzonitrile derivatives.

Crystal structures of



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

Abstract

New complexes of the type $[\text{Fe}(\eta^5\text{-Cp or Ind})(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ ($\text{L}, \text{L}' = \text{CO}, \text{P}(\text{OC}_6\text{H}_5)_3, \text{P}(\text{C}_6\text{H}_5)_3$; $\text{R} = \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2, \text{C}_6\text{H}_4\text{NO}_2, (E)\text{-C}(\text{H})=\text{C}(\text{H})\text{C}_6\text{H}_4\text{NO}_2, (E)\text{-C}(\text{H})=\text{C}(\text{H})\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$) 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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ and $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ 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 $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{P_P})]^+$ ($\text{M} = \text{Fe}(\text{II}), \text{Ru}(\text{II}); \text{P_P} =$

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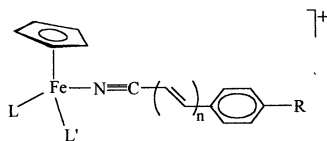
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bidentate phosphine) as good donor groups to built donor- π -system-acceptor molecules for second and third nonlinear optical effects [4–6], where the π -system was a *p*-benzonitrile derivative. Compound $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ 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 $d_{\text{metal}}-\pi^*$ NC ligand.

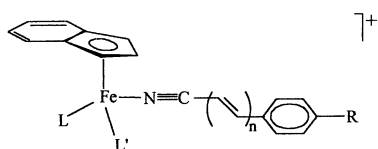
Our continuing interest on the understanding of NLO properties — structural features, prompted us to extend our studies on this type of molecules in order to explore the possibility of fine tuning the NLO properties through some structural changes.

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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ (L, L' = CO, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$ with $\text{R} = \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, $\text{C}_6\text{H}_4\text{NO}_2$, (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{N}(\text{CH}_3)_2$, (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$) and $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ (L, L' = CO, $\text{P}(\text{OC}_6\text{H}_5)_3$, and $\text{R} = \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, $\text{C}_6\text{H}_4\text{NO}_2$, (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$) 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.



- L = L' = CO; n=0, R = NO₂ (1), R = N(CH₃)₂ (2); n=1, R = NO₂ (3), R = N(CH₃)₂ (4)
 L = CO, L' = P(OC₆H₅)₃; n=0, R = NO₂ (5), R = N(CH₃)₂ (6)
 L = CO, L' = P(C₆H₅)₃; n=0, R = NO₂ (7), R = N(CH₃)₂ (8); n=1, R = NO₂ (9),
 R = N(CH₃)₂ (10)
 L = L' = P(OC₆H₅)₃; n=0, R = NO₂ (11), R = N(CH₃)₂ (12); n=1, R = N(CH₃)₂ (13)



- L = L' = CO; n=0, R = NO₂ (14), R = N(CH₃)₂ (15)
 L = CO, L' = P(OC₆H₅)₃; n=0, R = NO₂ (16), R = N(CH₃)₂ (17); n=1, R = NO₂ (18)

Fig. 1. Structural formulae of complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5$ or $\text{C}_9\text{H}_7)(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ (1–18).

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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ (5) and $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ (16).

2. Results and discussion

2.1. Preparation and characterisation of the complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ and $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$

Treatment of the starting materials $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{L}')(\text{I})]$ or $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{L})(\text{L}')(\text{I})]$ (L, L' = CO, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$) 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 $[\text{Fe}(\eta^5\text{-Cp}$ or $\text{Ind})(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ (L, L' = CO, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$; $\text{R} = \text{C}_6\text{H}_4\text{NO}_2$, $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$ and (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{N}(\text{CH}_3)_2$) (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-, ¹³C- and ³¹P-NMR spectra (see Section 4).

The IR spectra of the derivatives reveal the presence of the different coligands: cyclopentadienyl and indenyl groups ($\approx 3060\text{ cm}^{-1}$), the $\text{P}(\text{OC}_6\text{H}_5)_3$ 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 ($\nu(\text{CN})$) (in the range 2230–2270 cm^{-1}).

Analysis of the $\nu(\text{CN})$ stretching bands of the new complexes shows a general increase of the $\nu(\text{CN})$ upon coordination, this shift being more pronounced for complexes $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})_2(p\text{-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)]^+$ (2) (+46 cm^{-1}) and $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})_2(p\text{-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)]^+$ (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 $[\text{Fe}(\eta^5\text{-Cp})(\text{L})(\text{L}')(p\text{-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)]^+$ (L = L' = $\text{P}(\text{OC}_6\text{H}_5)_3$ (12), L = CO, L' = $\text{P}(\text{OC}_6\text{H}_5)_3$ (6) and L = L' = CO (2), the increasing values of $\Delta\nu(\text{CN})$ +21 (12), +29 (6) and +46 cm^{-1} (2) are in agreement with the electronic depletion at the iron centre. This enhancement of $\nu(\text{CN})$ seems to be consistent with a nitrile σ -type coordination where the presence of π -backdonation

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 $[\text{Fe}(\eta^5\text{-Cp or Ind})(\text{CO})(\text{L}')(\text{p-NCR})]^+$ ($\text{L}' = \text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{R} = \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, $\text{C}_6\text{H}_4\text{NO}_2$, etc.) derivatives are also characterised by one strong carbonyl stretching absorption corresponding to the terminal CO group. These $\nu(\text{CO})$ bands show lower values than those of the parent dicarbonyl compounds. Regarding the series $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{L}')(\text{p-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)]^+$, with $\text{L}' = \text{P}(\text{C}_6\text{H}_5)_3$ (**8**), $\text{L}' = \text{P}(\text{OC}_6\text{H}_5)_3$ (**6**) and $\text{L}' = \text{CO}$ (**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 $[\text{Fe}(\eta^5\text{-Cp or Ind})(\text{CO})_2(\text{p-NCR})]^+$ by the more basic and poorer π -acceptor phosphine or phosphite. This effect of phosphorus ligands on the $\nu(\text{CO})$ frequency values in these complexes seems to be more pronounced in the η^5 -indenyl derivatives consistent with a stronger donor character of indenyl complexes relative to the corresponding cyclopentadienyl derivatives.

$^1\text{H-NMR}$ chemical shifts for the cyclopentadienyl ring in the complexes $[\text{Fe}(\eta^5\text{-Cp})(\text{L})(\text{L}')(\text{p-NCR})][\text{BF}_4]$ 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 ($\text{p-N}(\text{CH}_3)_2$) by the acceptor group (p-NO_2) 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 $[\text{Fe}(\eta^5\text{-Cp})(\text{P-P})(\text{p-NCR})]^+$ ($\text{P-P} = \text{bidentate phosphines}$; $\text{R} = \text{donor and acceptor aromatic nitriles}$) [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 $\nu(\text{CN})$ to lower frequencies and a simultaneous upfield shift in the $^1\text{H-NMR}$ 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 $[\text{Fe}(\eta^5\text{-Cp})(\text{P-P})]^+$ fragment, we were able to identify in the present work the role of $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})_2]^+$ and $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)]^+$ 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 $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})_2(\text{p-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)][\text{BF}_4]$ (**2**), and a smaller value of +0.03 ppm for the corresponding $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)]^+$ 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 $^1\text{H-NMR}$ shift values might be insignificant, a trend is observed and is consistent with the IR results. Nevertheless, the $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)]^+$ 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 $[\text{Fe}(\eta^5\text{-Cp})(\text{P-P})]^+$ ($\text{P-P} = \text{bidentate phosphines}$) 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:

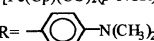
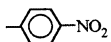
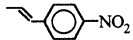
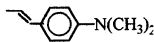
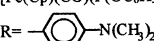
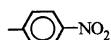
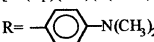
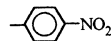
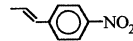
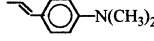
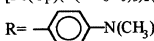
1. organometallic moieties acting as acceptor groups ($[\text{Fe}(\eta^5\text{-Cp})(\text{CO})_2]^+$ and $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)]^+$);
2. organometallic moiety acting as a π -donor group ($[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)]^+$) to be added to the former fragment $[\text{Fe}(\eta^5\text{-Cp})(\text{P-P})]^+$.

Moreover, within each group we can also recognise different strengths on the acceptor ability: $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)]^+ < [\text{Fe}(\eta^5\text{-Cp})(\text{CO})_2]^+$ and in the donor capacity: $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)]^+ < [\text{Fe}(\eta^5\text{-Cp})(\text{P-P})]^+$.

The $^{13}\text{C-NMR}$ spectroscopic data is also valuable in assessing the donor/acceptor properties of the phosphine or phosphite, in the derivatives $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{L}')(\text{p-NCR})]^+$, since the ^{13}CO resonance of the carbonyl group in these complexes should reflect these properties. Analysis of the carbonyl chemical shift data for $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{L}')(\text{p-NCR})]^+$ derivatives indicate a net donation of the electron density from L' to the Fe centre showing the increasing order: CO (209.11) $<$ $\text{P}(\text{OC}_6\text{H}_5)_3$ (213.50) $<$ $\text{P}(\text{C}_6\text{H}_5)_3$ (217.09) found for the series $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{L}')(\text{p-NCC}_6\text{H}_4\text{NO}_2)]^+$ ($\text{L}' = \text{CO}$ (**1**); $\text{P}(\text{OC}_6\text{H}_5)_3$ (**5**); $\text{P}(\text{C}_6\text{H}_5)_3$ (**7**)) and which could be extended for the other nitrile chromophores.

Table 1

Optical spectral data for complexes $[\text{Fe}(\eta^5\text{-L})(\text{L}')(\text{L}'')(p\text{-NCR})][\text{BF}_4]$ in chloroform solutions at room temperature, concentration ca. 2.0×10^{-5} mol dm $^{-3}$

Compound	λ_{exp} (nm)	$\epsilon \times 10^4$ (M $^{-1}$ cm $^{-1}$)
$[\text{Fe}(\eta^5\text{-L})(\text{L}')(\text{L}'')(p\text{-NCR})][\text{BF}_4]$		
$[\text{Fe}(\text{Cp})(\text{CO})_2(p\text{-NCR})]^+$		
R = 	321 369 447*	3.08 0.21 0.05
	298 362 (sh)	1.32
	316	4.13
	322 (sh) 364 407 (sh)	3.31
$[\text{Fe}(\text{Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCR})]^+$		
R = 	327 475*(sh)	4.13 0.04
	250 353 410*	1.89 0.66 0.16
$[\text{Fe}(\text{Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)(p\text{-NCR})]^+$		
R = 	332 409 510* (sh)	4.02 0.12
	290 341 393	0.78 0.55 0.71
	290 398	2.50 1.04
	253 327 400 519*	1.92 0.80 1.92 0.05
$[\text{Fe}(\text{Cp})(\text{P}(\text{OC}_6\text{H}_5)_3)_2(p\text{-NCR})]^+$		
R = 	337 410 461* (sh)	5.14 1.24

indenyl protons H(4–7) give rise to four separate signals of the type AA'BB', or in the case of $[(\eta^5\text{-Ind})\text{Fe}(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)]^+$ (**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 $^1\text{H-NMR}$ patterns were already described in the literature [8] for compounds $[(\eta^5\text{-Ind})\text{Fe}(\text{CO})(\text{L})(\text{CO}_2\text{R})]^+$ (L = phosphines or phosphites; R = CHMe $_2$, Me).

The hapticity of the indenyl ligand can be evaluated spectroscopically by comparing the $^{13}\text{C-NMR}$ chemical shifts of the ring junction carbons (C3a, C7a) in the metal complex with those of the sodium indenyl: larger distortions from η^5 coordination result in larger downfield shifts [9–11]. According to this procedure, the parameter $\Delta\delta(\text{C-3a,7a}) = \delta(\text{C-3a,7a}(\eta\text{-indenyl complex})) - \delta(\text{C-3a,7a}(\text{sodium indenyl}))$ has been proposed as an indication of the indenyl distortion, having values in the range -20 to -40 ppm for planar η^5 -indenyl, -10 to -20 ppm for a partially slipped η^5 -indenyl and $+5$ to $+30$ ppm for η^3 -indenyl ligands [12]. For all the indenyl complexes obtained in this work we found upfield shifts, $\Delta\delta(\text{C-3a,7a}) \approx -21$ 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 η^5 fashion. Analysis of the spectroscopic data of η^5 -indenyl derivatives, when compared with the η^5 -cyclopentadienyl analogues, shows a similar trend and also both fragments $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})_2]^+$ and $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)]^+$ behaved as accepting groups relatively to the coordinated chromophores.

Optical absorption spectra of complexes $[\text{Fe}(\eta^5\text{-Cp})(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ and $[\text{Fe}(\eta^5\text{-Ind})(\text{L})(\text{L}')(p\text{-NCR})][\text{BF}_4]$ 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 $[\text{Fe}(\eta^5\text{-Cp or Ind})(\text{CO})_2]^+$ (**1**), (**3**), (**14**) derivatives, containing the *p*-nitrobenzotrile 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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ (**5**) and $[\text{Fe}(\eta^5\text{-$

For $[(\eta^5\text{-Ind})\text{Fe}(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCR})]^+$ complexes, $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra show that all the protons and carbons of indenyl ligand are nonequivalent reflecting the asymmetry of the molecule. The four

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



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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)]^+$ and $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)]^+$ 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 $p\text{-NCC}_6\text{H}_4\text{NO}_2$ 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-

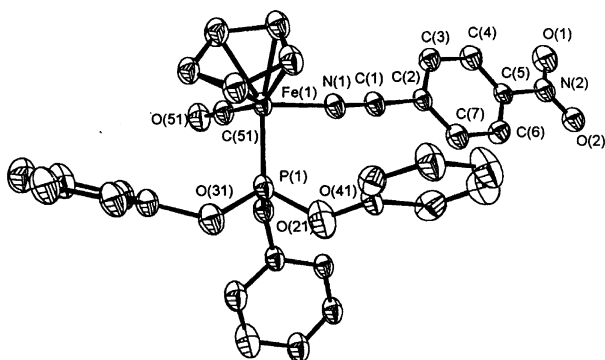


Fig. 2. ORTEP diagram for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)]^+$, with 20% thermal ellipsoids, showing the atomic labelling scheme. Hydrogen atoms have been omitted for clarity.

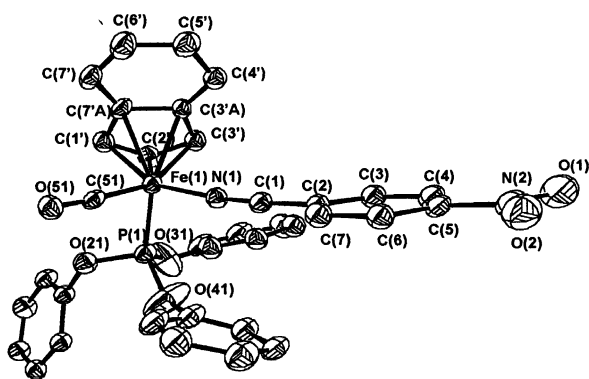


Fig. 3. ORTEP diagram for $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)]^+$, with 20% thermal ellipsoids, showing the atomic labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) for $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ (**5**) and $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ (**16**)

	5	16
<i>Bond lengths</i>		
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)
<i>Bond angles</i>		
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)

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 $122.6(4)$, $120.9(6)$, $127.8(6)^\circ$ and $120.3(5)$, $120.5(8)$, $124.2(6)^\circ$, 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 \AA . 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 ₆ H 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 ₆ H ₅) ₃]- (NCCH(COOH) ^t Bu) [BF ₄]	2.070–2.132	2.235	1.772	1.911	1.116	1.480	174.329		[14c]
[Fe(Cp)(DPPE)- (<i>p</i> -NCC ₆ H ₄ NO 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 ₆ H ₅) ₃)- (<i>p</i> -NCC ₆ H ₄ NO 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 ₆ H ₅) ₃)- (<i>p</i> -NCC ₆ H ₄ NO ₂)] [BF ₄]	2.072–2.193	2.139	1.793	1.900	1.156	1.439	173.7	175.3	This work
<i>p</i> -NCC ₆ H ₄ NO 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 η⁵-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 η⁵-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(η⁵-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(η⁵-Cp)(DPPE)(*p*-NCC₆H₄NO₂)] [PF₆]. This feature is associated with N≡C bond lengths in the same range of the corresponding length on the free *p*-NCC₆H₄NO₂ 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(η⁵-Cp or Ind)(CO)₂]⁺ and [Fe(η⁵-Cp or Ind)(CO)(P(OC₆H₅)₃)]⁺ as acceptor groups relative to the coordinated benzonitrile derivatives. Conversely, [Fe(η⁵-Cp)(CO)-(P(C₆H₅)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(η⁵-Cp)(P_P)]⁺ was identified as a good π-donor group, these results show that it can also behave 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(η⁵-

Cp)(CO)₂(I)] [17], [Fe(η^5 -Cp)(CO)(P(OC₆H₅)₃)(I)], [Fe(η^5 -Cp)(CO)(P(C₆H₅)₃)(I)] and [Fe(η^5 -Cp)(P(OC₆-H₅)₃)₂(I)] [18] were prepared using different irradiation times following the literature procedures. (*E*)-*p*-NCCH=CHC₆H₄NO₂ [19], [Fe(η^5 -Ind)(CO)₂]₂ [20], [Fe(η^5 -Ind)(CO)₂(I)] [21] and [Fe(η^5 -Ind)(CO)-(P(OC₆H₅)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. ¹H-, ¹³C- and the ³¹P-NMR spectra were recorded on a Varian Unity 300 spectrometer at probe temperature using acetone-*d*₆ as solvent. The ¹H and ¹³C chemical shifts are reported in parts per million downfield from internal Me₄Si and the ³¹P-NMR spectra are reported in parts per million downfield from external 85% H₃PO₄ 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)][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(η^5 -Cp)(CO)₂(I)] (1 mmol) and one equivalent of AgBF₄ in CH₂Cl₂ (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 Et₂O. The residue

was recrystallised from Me₂CO–Et₂O or CH₂Cl₂–Et₂O.

4.2.1. [Fe(η^5 -Cp)(CO)₂(*p*-NCC₆H₄NO₂)] [BF₄] (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 C₁₄H₉N₂O₄FeBF₄: C, 40.83; H, 2.20; N, 6.80%. IR (KBr, cm⁻¹): ν (CO) 2072 and 2017, ν (N≡C) 2267, ν (NO₂) 1524 and 1346. ¹H-NMR ((CD₃)₂CO): 5.81 (s, 5H, η^5 -C₅H₅); 8.26 (d, 2H, *J*_{HH} = 9.0 Hz, H₂, H₆); 8.44 (d, *J*_{HH} = 9.0 Hz, 2H, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)₂CO): 88.42 (η^5 -C₅H₅); 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*-NCC₆H₄N(CH₃)₂)] [BF₄] (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 C₁₆H₁₅N₂O₂FeBF₄: C, 46.88; H, 3.69; N, 6.83%. IR (KBr, cm⁻¹): ν (CO) 2065 and 2015, ν (N≡C) 2256. ¹H-NMR ((CD₃)₂CO): 3.09 (s, 6H, N(CH₃)₂); 5.73 (s, 5H, η^5 -C₅H₅); 6.79 (d, 2H, *J*_{HH} = 9.3 Hz, H₃, H₅); 7.61 (d, 2H, *J*_{HH} = 9.0 Hz, H₂, H₆). ¹³C{¹H}-NMR ((CD₃)₂CO): 39.87 (N(CH₃)₂); 87.98 (η^5 -C₅H₅); 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=CHC₆H₄NO₂]-[BF₄] (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 C₁₆H₁₁N₂O₄FeBF₄: C, 43.88; H, 2.53; N, 6.40%. IR (KBr, cm⁻¹): ν (CO) 2079 and 2022, ν (N≡C) 2262, ν (NO₂) 1518 and 1343. ¹H-NMR ((CD₃)₂CO): 5.77 (s, 5H, η^5 -C₅H₅); 6.77 (d, 1H, *J*_{HH} = 16.5 Hz, H₈); 7.95 (d, 2H, *J*_{HH} = 8.7 Hz, H₂, H₆); 7.98 (d, 1H, *J*_{HH} = 16.5 Hz, H₇); 8.32 (d, 2H, *J*_{HH} = 8.7 Hz, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)₂CO): 88.24 (η^5 -C₅H₅); 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=CHC₆H₄N(CH₃)₂][BF₄] (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 C₁₈H₁₇N₂O₂FeBF₄: C, 49.59; H, 3.93; N, 6.43%. IR (KBr, cm⁻¹): ν (CO) 2077, 2037 and 1989 (sh), ν (N≡C) 2250. ¹H-NMR ((CD₃)₂CO): 3.08 (s, 6H, N(CH₃)₂); 5.71 (s, 5H, η^5 -C₅H₅); 6.07 (d, 1H, *J*_{HH} = 16.5 Hz, H₈); 6.79 (d, 2H, *J*_{HH} = 8.4 Hz, H₃, H₅); 7.49 (d, 2H, *J*_{HH} = 9.3 Hz, H₂, H₆); 7.65 (d, 1H, *J*_{HH} = 16.5 Hz, H₇). ¹³C{¹H}-NMR ((CD₃)₂CO): 40.40 (N(CH₃)₂); 87.01 (C8); 88.06 (η^5 -C₅H₅); 113.00 (C3, C5); 122.35 (C1); 131.08 (C2, C6); 138.30 (NC); 153.80 (C4); 156.31 (C7); 209.77 (CO).

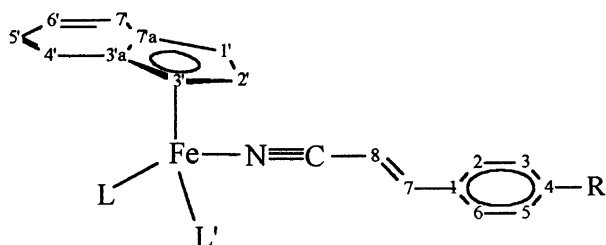


Fig. 4. Numbering scheme for NMR spectral assignments.

4.3. Preparation of $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCR})][\text{BF}_4]$

All the complexes were prepared by the process described below. The appropriate nitrile $p\text{-NCR}$ ($\text{R} = \text{C}_6\text{H}_4\text{NO}_2$, $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$) (1.3 mmol) was added to a solution of $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(\text{I})]$ (1 mmol) and AgBF_4 (1 mmol) in C_6H_6 or CH_2Cl_2 (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 Et_2O to remove the excess of nitrile. The residue was recrystallised from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$.

4.3.1. $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)]\text{-}[\text{BF}_4]$ (**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 $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_6\text{FePBF}_4$: C, 53.64; H, 3.48; N, 4.04%. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 2012, $\nu(\text{N}\equiv\text{C})$ 2257, $\nu(\text{NO}_2)$ 1528 and 1347. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 5.12 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 7.30–7.35 and 7.46–7.53 (m, 15H, OPh); 8.10 (d, 2H, $J_{\text{HH}} = 9.3$ Hz, H_2 , H_6); 8.45 (d, 2H, $J_{\text{HH}} = 9.3$ Hz, H_3 , H_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 85.93 ($\eta^5\text{-C}_5\text{H}_5$); 117.14 (C1); 121.94 (d, $^4J_{\text{CP}} = 4.4$ 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, $^2J_{\text{CP}} = 43.1$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 164.83.

4.3.2. $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)]\text{-}[\text{BF}_4]$ (**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 $\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_4\text{FePBF}_4$: C, 56.27; H, 4.37; N, 4.05%. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 2007, $\nu(\text{N}\equiv\text{C})$ 2242. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 3.11 (s, 6H, $\text{N}(\text{CH}_3)_2$); 4.97 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 6.81 (d, 2H, $J_{\text{HH}} = 8.1$ Hz, H_3 , H_5); 7.34–7.50 (m, 15H, OPh); 7.49 (d, 2H, H_2 , H_6). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 39.92 ($\text{N}(\text{CH}_3)_2$); 85.25 ($\eta^5\text{-C}_5\text{H}_5$); 95.07 (C1); 112.37 (C3, C5); 121.97 (d, $^4J_{\text{CP}} = 3.38$ Hz, OPh, *C-meta*); 127.06 (OPh, *C-para*); 131.33 (OPh, *C-ortho*); 135.05 (C2, C6); 138.90 (NC); 151.56 (d, $^2J_{\text{CP}} = 8.0$ Hz, OPh, *C-ipso*); 154.58 (C4); 214.45 (d, $^2J_{\text{CP}} = 40.2$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 166.68 (s).

4.4. Preparation of

$[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)(p\text{-NCR})][\text{BF}_4]$

All the complexes were prepared by the process described below. The appropriate nitrile $p\text{-NCR}$ ($\text{R} =$

$\text{C}_6\text{H}_4\text{NO}_2$, (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$, $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, (*E*)- $\text{CH}=\text{CHC}_6\text{H}_4\text{N}(\text{CH}_3)_2$) (1.3 mmol) was added to a solution of $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)(\text{I})]$ (1 mmol) and one equivalent of AgBF_4 in CH_2Cl_2 (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 Et_2O . The residue was recrystallised from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$.

4.4.1. $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{NO}_2)]\text{-}[\text{BF}_4]$ (**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 $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_3\text{FePBF}_4$: C, 57.62; H, 3.74; N, 4.34%. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1974, $\nu(\text{N}\equiv\text{C})$ 2247, $\nu(\text{NO}_2)$ 1528 and 1347. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 5.25 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 7.51–7.62 (m, 15H, PPh_3); 7.67 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, H_2 , H_6); 8.33 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, H_3 , H_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 86.52 ($\eta^5\text{-C}_5\text{H}_5$); 117.32 (C1); 124.88 (C3, C5); 130.25 (d, $^3J_{\text{CP}} = 9.8$ Hz, PPh_3 , *C-meta*), 132.42 (PPh_3 , *C-para*); 133.15 (NC), 134.19 (d, $^2J_{\text{CP}} = 9.8$ Hz, PPh_3 , *C-ortho*); 135.32 (C2, C6); 151.42 (C4); 217.09 (d, $^2J_{\text{CP}} = 28.1$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 67.80 (s).

4.4.2. $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)(p\text{-NCC}_6\text{H}_4\text{N}(\text{CH}_3)_2)]\text{-}[\text{BF}_4]$ (**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 $\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_4\text{FePBF}_4$: C, 61.52; H, 4.69; N, 4.35%. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1993, $\nu(\text{N}\equiv\text{C})$ 2249. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 3.04 (s, 6H, $\text{N}(\text{CH}_3)_2$); 5.12 (d, 5H, $J_{\text{CP}} = 1.2$ Hz, $\eta^5\text{-C}_5\text{H}_5$); 6.66 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, H_3 , H_5); 7.06 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, H_2 , H_6); 7.49–7.60 (m, 15H, PPh_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 39.82 ($\text{N}(\text{CH}_3)_2$); 85.88 ($\eta^5\text{-C}_5\text{H}_5$); 95.38 (C1); 112.03 (C3, C5); 130.04 (d, $^3J_{\text{CP}} = 9.7$ Hz, PPh_3 , *C-meta*); 132.16 (d, $^4J_{\text{CP}} = 1.2$ Hz, PPh_3 , *C-para*); 133.25 (d, $^1J_{\text{CP}} = 46.1$ Hz, PPh_3 , *C-ipso*); 134.01 (d, $^2J_{\text{CP}} = 9.7$ Hz, PPh_3 , *C-ortho*); 134.61 (C2, C6); 138.99 (NC); 154.27 (C4); 217.87 (d, $^2J_{\text{CP}} = 29.2$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 67.88 (s).

4.4.3. $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)((E)\text{-}p\text{-NCCH}=\text{CHC}_6\text{H}_4\text{NO}_2)]\text{-}[\text{BF}_4]$ (**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 $\text{C}_{33}\text{H}_{26}\text{N}_2\text{O}_3\text{FePBF}_4$: C, 58.96; H, 3.90; N, 4.17%. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1993, $\nu(\text{N}\equiv\text{C})$ 2243, $\nu(\text{NO}_2)$ 1523 and 1345. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 5.16 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 6.46 (d, 1H, $J_{\text{HH}} = 16.5$ Hz, H_8); 7.19 (d, 1H, $J_{\text{HH}} = 16.5$ Hz, H_7); 7.51–7.64 (m, 15H, PPh_3); 7.81 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, H_2 , H_6); 8.26 (d, 2H, $J_{\text{HH}} = 8.1$ Hz, H_3 , H_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 86.27 ($\eta^5\text{-C}_5\text{H}_5$); 100.75 (C8); 124.96 (C3, C5); 129.88 (C2, C6); 130.19

¹ Signal obscured by the aromatic protons of triphenylphosphite.

(d, $^3J_{CP} = 10.0$ Hz, PPh₃, C-*meta*); 132.32 (PPh₃, C-*para*); 132.96 (d, $^1J_{CP} = 46.4$ Hz, PPh₃, C-*ipso*); 134.15 (d, $^2J_{CP} = 10.0$ Hz, PPh₃, C-*ortho*); 135.79 (C1); 139.80 (NC); 150.20 (C4); 151.60 (C7); 217.36 (d, $^2J_{CP} = 27.8$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 67.30 (s).

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

Red crystals; 51% yield, m.p. 180.7–182.6 °C. Anal. Found: C, 62.50; H, 4.89; N, 4.08. Calc. for C₃₅H₃₂N₂O₆FeP₂BF₄: C, 62.72; H, 4.81; N, 4.18%. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1983, $\nu(\text{N}\equiv\text{C})$ 2248. ^1H -NMR ((CD₃)₂CO): 3.04 (s, 6H, N(CH₃)₂); 5.09 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 5.78 (d, 1H, $J_{\text{HH}} = 16.5$ Hz, C₈); 6.72 (d, 2H, $J_{\text{HH}} = 8.7$ Hz, H₃, H₅); 6.81 (d, 1H, $J_{\text{HH}} = 16.5$ Hz, C₇); 7.34 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, H₂, H₆); 7.48–7.66 (m, 15H, PPh₃). $^{13}\text{C}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 40.16 (N(CH₃)₂); 85.91 ($\eta^5\text{-C}_5\text{H}_5$); 88.03 (C8); 112.66 (C3, C5); 121.76 (C1); 130.72 (C2, C6); 130.81 (d, $^3J_{CP} = 9.7$ Hz, PPh₃, C-*meta*); 132.20 (PPh₃, C-*para*), 133.23 (d, $^1J_{CP} = 46.1$ Hz, PPh₃, C-*ipso*); 134.11 (d, $^2J_{CP} = 9.7$ Hz, PPh₃, C-*ortho*); 138.62 (NC); 153.79 (C4); 154.58 (C7); 217.82 (d, $^2J_{CP} = 28.0$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 67.82 (s).

4.5. Preparation of

$[\text{Fe}(\eta^5\text{-Cp})(\text{P}(\text{OC}_6\text{H}_5)_3)_2(p\text{-NCR})]\text{[BF}_4\text{]}$

All the complexes were prepared by the process described below. The appropriate nitrile *p*-NCR (R = C₆H₄NO₂, C₆H₄N(CH₃)₂, (E)-CH=CHC₆H₄N(CH₃)₂) (1.3 mmol) was added to a solution of [Fe($\eta^5\text{-Cp})(\text{P}(\text{OC}_6\text{H}_5)_3)_2(\text{I})$] (1 mmol) and AgBF₄ (1 mmol) in C₆H₆ (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 Et₂O to remove the excess of nitrile. The residue was recrystallised from CH₂Cl₂ or Me₂CO–Et₂O.

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

Orange crystals; 63% yield, m.p. 104.0–105.5 °C. Anal. Found: C, 58.90; H, 4.01; N, 2.88. Calc. for C₄₈H₃₉N₂O₈FeP₂BF₄: C, 59.04; H, 4.03; N, 2.87%. IR (KBr, cm⁻¹): $\nu(\text{N}\equiv\text{C})$ 2238, $\nu(\text{NO}_2)$ 1525 and 1345. ^1H -NMR ((CD₃)₂CO): 4.60 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 7.20–7.25 (m, 6H, OPh), 7.34–7.41 (m, 24H, OPh); 8.01 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, H₂, H₆); 8.45 (d, 2H, $J_{\text{HH}} = 8.7$ Hz, H₃, H₅). $^{13}\text{C}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 82.58 ($\eta^5\text{-C}_5\text{H}_5$); 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*). $^{31}\text{P}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 163.19 (s).

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

Orange crystals; 57% yield, m.p. 120.1–121.6 °C. Anal. Found: C, 61.92; H, 4.85; N, 2.79. Calc. for C₅₀H₄₅N₂O₆FeP₂BF₄: C, 61.63; H, 4.65; N, 2.87%. IR (KBr, cm⁻¹): $\nu(\text{N}\equiv\text{C})$ 2231. ^1H -NMR ((CD₃)₂CO): 3.12 (s, 6H, N(CH₃)₂); 4.39 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 6.86 (d, 2H, $J_{\text{HH}} = 9.3$ Hz, H₃, H₅); 7.25–7.41 (m, 30H, OPh); 7.48 (d, 2H, $J_{\text{HH}} = 9.3$ Hz, H₂, H₆). $^{13}\text{C}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 40.35 (N(CH₃)₂); 81.54 ($\eta^5\text{-C}_5\text{H}_5$); 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). $^{31}\text{P}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 164.84 (s).

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

Orange crystals; 60% yield, m.p. 81.6–83.0 °C. Anal. Found: C, 62.35; H, 4.77; N, 2.78. Calc. for C₅₂H₄₇N₂O₆FeP₂BF₄: C, 62.42; H, 4.73; N, 2.80%. IR (KBr, cm⁻¹): $\nu(\text{N}\equiv\text{C})$ 2223. ^1H -NMR ((CD₃)₂CO): 3.09 (s, 6H, N(CH₃)₂); 4.37 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 6.15 (d, 1H, $J_{\text{HH}} = 16.2$ Hz, H₈); 6.80 (d, 2H, $J_{\text{HH}} = 8.7$ Hz, H₃, H₅); 7.24–7.44 (m, 31H, H₇ and OPh); 7.49 (d, 2H, $J_{\text{HH}} = 9.0$ Hz, H₂, H₆). $^{13}\text{C}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 40.48 (N(CH₃)₂); 81.62 ($\eta^5\text{-C}_5\text{H}_5$); 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. $^{31}\text{P}\{^1\text{H}\}$ -NMR ((CD₃)₂CO): 164.78 (s).

4.6. Preparation of $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})_2(p\text{-NCR})]\text{[BF}_4\text{]}$

All the complexes were prepared by the following process: the appropriate nitrile *p*-NCR (R = C₆H₄NO₂, C₆H₄N(CH₃)₂) (1.3 mmol) was added to a solution of [Fe($\eta^5\text{-Ind})(\text{CO})_2(\text{I})$] (1 mmol) and one equivalent of AgBF₄ in CH₂Cl₂ (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 Et₂O. The residue was recrystallised from CH₂Cl₂–Et₂O.

4.6.1. $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})_2(p\text{-NCC}_6\text{H}_4\text{NO}_2)]\text{[BF}_4\text{]} (14)$

Red crystals; 29% yield, m.p. (dec.) 130.0 °C. Anal. Found: C, 46.88; H, 2.32; N, 6.12. Calc. for C₁₈H₁₁N₂O₄FeBF₄: C, 46.80; H, 2.40; N, 6.06%. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 2038 and 1986, $\nu(\text{N}\equiv\text{C})$ 2274, $\nu(\text{NO}_2)$ 1528 and 1350. ^1H -NMR ((CD₃)₂CO): 5.96 (s, 1H, Ind:H₂); 6.14 (d, 2H, $J_{\text{HH}} = 2.4$ Hz, Ind:H₁,H₃);

² Signal obscured by the aromatic carbons of triphenylphosphite.

7.82–7.85 (m, A₂B₂, 2H, Ind:H₄,H₇); 8.06–8.09 (m, A₂B₂, 2H, Ind:H₅,H₆); 8.20 (d, 2H, J_{HH} = 8.7 Hz, H₂, H₆); 8.44 (d, 2H, J_{HH} = 8.7 Hz, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)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(η⁵-Ind)(CO)₂(p-NCC₆H₄N(CH₃)₂)] [BF₄] (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 C₂₀H₁₇N₂O₂FeBF₄: C, 52.22; H, 3.72; N, 6.09%. IR (KBr, cm⁻¹): ν(CO) 2067, 2031 and 1988, ν(N≡C) 2252. ¹H-NMR ((CD₃)₂CO): 3.09 (s, 6H, N(CH₃)₂); 5.84 (t, 1H, J_{HH} = 2.4 Hz, Ind:H₂); 6.07 (d, 2H, J_{HH} = 2.4 Hz, Ind:H₁,H₃); 6.78 (d, 2H, J_{HH} = 9.0 Hz, H₃, H₅); 7.53 (d, 2H, J_{HH} = 8.4 Hz, H₂, H₆); 7.77–7.81 (m, A₂B₂, 2H, Ind:H₄,H₇), 7.98–8.02 (m, A₂B₂, 2H, Ind:H₅,H₆). ¹³C{¹H}-NMR ((CD₃)₂CO): 39.82 (N(CH₃)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(η⁵-Ind)(CO)(P(OC₆H₅)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-Ind)(CO)(P(OC₆H₅)₃)(I)] (1 mmol) and AgBF₄ (1 mmol) in CH₂Cl₂ (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 Et₂O to remove the excess of nitrile. The residue was recrystallised from CH₂Cl₂–Et₂O.

4.7.1. [Fe(η⁵-Ind)(CO)(P(OC₆H₅)₃)(p-NCC₆H₄NO₂)] [BF₄] (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 C₃₅H₂₆N₂O₆FePBF₄: C, 56.49; H, 3.52; N 3.76%. IR (KBr, cm⁻¹): ν(CO) 1997, ν(N≡C) 2254, ν(NO₂) 1523 and 1346. ¹H-NMR ((CD₃)₂CO): 4.35 (bs, 1H, Ind:H₁ or H₃); 5.62 (dt, J_{HH} = ≈ 3.0 Hz; 1H, Ind:H₂); 5.81 (bs, 1H, Ind:H₁ or H₃); 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:H₅ and H₆); 7.78 (d, 1H, J_{HH} = 8.7 Hz, Ind:H₄ or H₇); 7.86 (d, 1H, J_{HH} = 8.4 Hz, Ind:H₄ or H₇); 8.05 (dt, J_{HH} = 8.4 and 2.1 Hz, 2H, H₂, H₆); 8.42 (dt, J_{HH} = 8.4 and 2.1 Hz, 2H, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)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). ³¹P{¹H}-NMR ((CD₃)₂CO): 166.62 (s).

4.7.2. [Fe(η⁵-Ind)(CO)(P(OC₆H₅)₃)(p-NCC₆H₄N(CH₃)₂)] [BF₄] (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 C₃₇H₃₂N₂O₄FePBF₄: C, 59.87; H, 4.35; N, 3.77%. IR (KBr, cm⁻¹): ν(CO) 1993, ν(N≡C) 2239. ¹H-NMR ((CD₃)₂CO): 3.11 (s, 6H, N(CH₃)₂); 4.15 (s, 1H, Ind:H₁ or H₃); 5.50 (m, J_{HH} = 3.0 Hz, 1H, Ind:H₂); 5.59 (s, 1H, Ind:H₁ or H₃); 6.79 (d, 2H, J_{HH} = 9.0 Hz, H₃, H₅); 7.33–7.62 (m, 19H, Ind:H₄–H₇ and OPh); 7.41 (d, 2H, H₂, H₆)³. ¹³C{¹H}-NMR ((CD₃)₂CO): 39.95 (N(CH₃)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). ³¹P{¹H}-NMR ((CD₃)₂CO): 168.77 (s).

4.7.3. [Fe(η⁵-Ind)(CO)(P(OC₆H₅)₃)(E)-p-NCCH=CHC₆H₄NO₂)] [BF₄] (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 C₃₇H₂₈N₂O₆FePBF₄: C, 57.70; H, 3.66; N, 3.64%. IR (KBr, cm⁻¹): ν(CO) 2010, ν(N≡C) 2243, ν(NO₂) 1519 and 1341. ¹H-NMR ((CD₃)₂CO): 4.21 (s, 1H, Ind:H₁ or H₃); 5.56 (m, J_{HH} = 3.0 Hz, 1H, Ind:H₂); 5.63 (s, 1H, Ind:H₁ or H₃); 6.68 (d, 1H, J_{HH} = 16.8 Hz, H₈), 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:H₄ or H₇); 7.71 (d, 1H, J_{HH} = 8.7 Hz, Ind:H₄ or H₇); 7.76 (d, 1H, J_{HH} = 16.8 Hz, H₇), 7.83 (d, 2H, J_{HH} = 8.1 Hz, Ind:H₅,H₆); 7.96 (d, 2H, J_{HH} = 8.1 Hz, H₂, H₆); 8.31 (d, 2H, J_{HH} = 8.1 Hz, H₃, H₅). ¹³C{¹H}-NMR ((CD₃)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). ³¹P{¹H}-NMR ((CD₃)₂CO): 167.74 (s).

³ Signal obscured by the aromatic protons of triphenylphosphite.

4.8. X-ray structures of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{OC}_6\text{H}_5)_3)(\text{CO})(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ and $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{P}(\text{OC}_6\text{H}_5)_3)(\text{CO})(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$

Diffraction data for $[\text{Fe}(\eta^5\text{-Cp})(\text{POPh}_3)(\text{CO})(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ (**5**) and $[\text{Fe}(\eta^5\text{-Ind})(\text{POPh}_3)(\text{CO})(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ (**16**) were collected at 293(2) K on an Enraf–Nonius TURBOCAD4 diffractometer with Cu–K α radiation. The unit cell dimensions and orientation matrix was obtained by least-squares refinement of 25 centred reflections with $15.37 < \theta < 23.92^\circ$ for **5** and by least-squares refinement of 23 centred reflections with $15.99 < \theta < 23.15^\circ$ 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 $[\text{Fe}(\eta^5\text{-Cp})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ (**5**) and $[\text{Fe}(\eta^5\text{-Ind})(\text{CO})(\text{P}(\text{OC}_6\text{H}_5)_3)(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{BF}_4]$ (**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	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions		
<i>a</i> (Å)	9.7881(7)	10.000(2)
<i>b</i> (Å)	10.6358(9)	11.500(1)
<i>c</i> (Å)	18.640(3)	29.362(3)
α (°)	94.603(9)	
β (°)	96.51(1)	95.70(2)
γ (°)	115.420(6)	
<i>V</i> (Å ³)	1723.3(3)	3359.9(9)
<i>Z</i>	2	4
<i>D</i> _{calc} (Mg m ^{−3})	1.521	1.471
Absorption coefficient (mm ^{−1})	5.982	4.672
<i>F</i> (000)	800	1520
Index ranges	−1 ≤ <i>h</i> ≤ 10; −11 ≤ <i>k</i> ≤ 11; −20 ≤ <i>l</i> ≤ 20	−11 ≤ <i>h</i> ≤ 1; −13 ≤ <i>k</i> ≤ 1; −35 ≤ <i>l</i> ≤ 35
Reflections collected	6048	7841
Independent reflections	5006 [<i>R</i> _{int} = 0.1141]	5979 [<i>R</i> _{int} = 0.0723]
Reflections observed (>2 σ)	2898	2648
Data/restraints/parameters	5006/27/432	5979/0/452
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1105	<i>R</i> ₁ = 0.1036
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1739	<i>R</i> ₁ = 0.2020
Goodness-of-fit on <i>F</i> 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 × those of the carbon atoms to which they are bonded. The solvent molecule, CH₂Cl₂, 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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