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Organometallic compounds for non-linear optics: synthesis, reactivity and electrochemistry of chiral η^5-monocyclopentadienyl(nitrile)iron complexes

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Abstract

A new family of compounds of general formula $[FeCp((+)\text{-DIOP})(p\text{-}NCC_6H_4R')][PF_6]$ (R' = donor or acceptor group) was synthesized and characterized for non-linear optical properties. Spectroscopic (IR and ^1H ^{13}C and ^{31}P NMR) and electrochemical (cyclic voltammetry) studies are consistent with charge-transfer from Fe^{II} to coordinated benzonitrile via d–π^* back donation. One compound of this family, $[FeCp((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][PF_6]$ has an SHG value 38 times greater than that of urea.

1. Introduction

Recent results [1] have shown that organometallic chemistry is an attractive area for the synthesis of new compounds with non-linear optical (NLO) properties, motivated by relevance to optical device technology [2]. The necessary, but not sufficient, criteria for a material to exhibit large second-order optical non-linearity, are that it should consist of polarizable dipolar molecules and that it should crystallize in a non-centrosymmetric space group.

Our aim has been to improve the SHG properties of organic molecules by coordination to a metal centre. Benzene derivatives with electron-donor substituents such as methoxy and amino at one end and electron-acceptor groups such as nitro and cyano at the other [3] are suitable for coordination to our organometallic moieties.

In previous work in this field, we studied complexes $[MCp_2(SR)(p\text{-}NCC_6H_4D)][PF_6]$ ($M = Mo^{IV}$ or W^{IV}; R = alkyl or aryl; D = donor group) and found surprisingly low values for second harmonic generation [4]. Nevertheless, spectroscopic and X-ray structural evidence showed higher π-delocalization in the nitriles after coordination and this encouraged us to study a different organometallic partner, $[FeCp(+)\text{-DIOP}]^+$, where a chiral ligand ensures the crystallization in a non-centrosymmetric space group. Moreover, to understand whether the organometallic moiety is better as a donor or as an acceptor, two different types of nitriles, $p\text{-}NCC_6H_4R'$, were used, where R′ is either a donor group as before [4] or a strong acceptor group such as NO_2. In this last case, the nitrile is quite unusual since both N≡C and NO_2 are acceptors groups, the latter being stronger.

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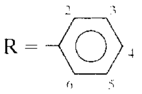
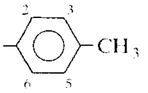
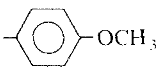
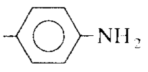
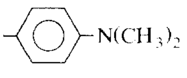
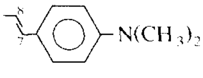
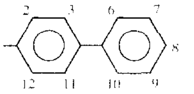
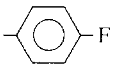
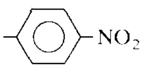
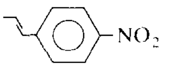
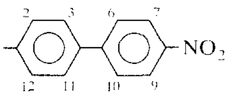
2. Chemical studies

2.1. Preparation of the p-substituted benzonitrile complexes, [FeCp((+)-DIOP)(p-NCC$_6$H$_4$R')][PF$_6$]

Nitrile complexes were prepared by iodide abstraction from the parent neutral complex [FeCp((+)-DIOP)I] by TlPF$_6$ in the presence of a slight excess of nitrile in dichloromethane at room temperature. After work-up, orange or red crystals of [FeCp((+)-DIOP)-(p-NCC$_6$H$_4$R')][PF$_6$] were obtained in *ca.* 80% yield. The compounds are fairly stable towards oxidation in air and to moisture both in the solid state and in solution. The formulation is supported by analytical data, IR and ^{1}H, ^{31}P, ^{13}C NMR spectra (Table 1), as discussed below. The molar conductivities of 10^{-3} M solutions of the complexes in nitromethane, in the range 68–84 Ω^{-1} cm^2 mol^{-1}, are consistent with values reported for 1 : 1 electrolytes [5].

Typical IR bands confirm the presence of the cyclopentadienyl ligand (≈ 3060 cm^{-1}), the [PF$_6$]$^-$ anion (840 and 560 cm^{-1}) and the coordinated nitrile (ν(CN) at ≈ 2200 cm^{-1}). No significant change was observed in ν(CN) upon coordination, except for p-NCC$_6$H$_4$NO$_2$ which showed a shift of 35 cm^{-1} to lower frequency. Such shifts have also been reported for terminal nitrile coordination in benzonitriles and substituted benzonitriles and were explained by a decreased C–N bond order caused by π-bonding between the metal d orbitals and the π^* orbital of the CN group [6]. In contrast, we found a high frequency shift for ν(CN) for p-NCC$_6$H$_4$R' upon coordination to [MCp$_2$L]$^+$ (M = Mo^{IV} or W^{IV}) fragments, where EHMO calculations have shown that back-donation

TABLE 1. ^{1}H NMR data for complexes [FeCp((+)-DIOP)(NCR)][PF$_6$]

Compound [FeCp((+)-DIOP)(p-NCR)]$^+$	δ(ppm), multiplicity, relative integrals, assignment
	4.27 (s, 5H, η^5-C$_5$H$_5$); 7.38 (t, 2H, H$_3$, H$_5$); 7.56 (m, 3H, H$_2$, H$_4$, H$_6$)
	2.42 (s, 3H, CH$_3$); 4.25 (s, 5H, η^5-C$_5$H$_5$); 7.27 (d, 2H, H$_3$, H$_5$); 7.38 (d, 2H, H$_2$, H$_6$)
	3.89 (s, 3H, OCH$_3$); 4.23 (s, 5H, η^5-C$_5$H$_5$); 7.08 (d, 2H, H$_3$, H$_5$); 7.33 (d, 2H, H$_2$, H$_6$)
	4.17 (s, 5H, η^5-C$_5$H$_5$); 5.91 (b, 2H, NH$_2$); 6.68 (d, 2H, H$_3$, H$_5$); 7.14 (d, 2H, H$_2$, H$_6$)
	3.07 (s, 6H, N(CH$_3$)$_2$); 4.18 (s, 5H, η^5-C$_5$H$_5$); 6.73 (d, 2H, H$_3$, H$_5$); 7.14 (d, 2H, H$_2$, H$_6$)
	3.04 (s, 6H, N(CH$_3$)$_2$); 4.13 (s, 5H, η^5-C$_5$H$_5$); 6.04 (d, 1H, H$_8$, ^1J(H, H) = 16.3); 6.56 (d, 1H, H$_7$, ^1J(H, H) = 16.3); 6.69 (d, 2H, H$_3$, H$_5$); 7.28 (d, 2H, H$_2$, H$_6$)
	4.28 (s, 5H, η^5-C$_5$H$_5$); 7.48 (m, 3H, H$_7$, H$_8$, H$_9$); 7.71 (d, 2H, H$_6$, H$_{10}$); 7.85 (d, 4H, H$_2$, H$_3$, H$_{11}$, H$_{12}$)
	4.25 (s, 5H, η^5-C$_5$H$_5$); 7.34 (t, 2H, H$_3$, H$_5$); 7.45 (q, 2H, H$_2$, H$_6$)
	4.32 (s, 5H, η^5-C$_5$H$_5$); 7.65 (d, 2H, H$_2$, H$_6$); 8.35 (d, 2H, H$_3$, H$_5$)
	4.25 (s, 5H, η^5-C$_5$H$_5$); 6.76 (d, 1H, H$_8$, ^1J(H, H) = 16.5); 7.03 (d, 1H, H$_7$, ^1J(H, H) = 16.5); 7.51 (d, 2H, H$_2$, H$_6$); 8.29 (d, 2H, H$_3$, H$_5$)
	4.29 (s, 5H, η^5-C$_5$H$_5$); 7.37 (d, 2H, H$_2$, H$_{12}$); 7.99 (d, 2H, H$_3$, H$_{11}$); 8.01 (d, 2H, H$_6$, H$_{10}$); 8.35 (d, 2H, H$_7$, H$_9$)

from the metal fragment to the coordinated nitrile would be impossible [7].

The ^{1}H, ^{31}P, ^{13}C NMR spectra of the (+)-DIOP ligand did not change with nitrile coligand, although there was a significant difference between the spectra of the free and bound nitrile. For instance, the ^{31}P NMR spectrum of $[FeCp((+)\text{-DIOP})(p\text{-}NCC_6H_4NH_2)][PF_6]$ in $(CD_3)_2CO$ at room temperature displayed two doublets at 56.7 ppm, an AB pattern with $J(P_AP_B) = 48.3$ Hz, showing two inequivalent phosphorus atoms, whereas free (+)-DIOP shows a singlet at 26.6 ppm in the same solvent. The ^{1}H NMR spectrum also showed a significant deshielding of coordinated (+)-DIOP and an obvious inequivalence of CH_2, CH and CH_3 groups. The enhanced deshielding observed for one of the CH_3 groups can be understood if one assumes that the structure of the parent compound [FeCp((−)-DIOP)(I)] is maintained [8] when the iodide is replaced by the substituted *p*-benzonitrile. A molecular model based on tetrahedral geometry at the iron centre and a chair structure for the seven-membered chelate ring of the coordinated phosphine shows two inequivalent methyl groups, one of them close to the benzonitrile ligand current.

Despite the fact that all compounds display sharp signals for the η^5-C_5H_5 ring in the narrow ranges 4.13–4.32 and 80.32–81.91 ppm for the ^{1}H and ^{13}C NMR spectra, respectively, there is a linear correlation between ΔCp (^{13}C NMR) and σ_p Taft parameters (ΔCp = δCp (*p*-substituted benzonitrile) − δCp (benzonitrile)), corresponding to the equation $\Delta(Cp) = -0.056 + 1.017\sigma_p$ (Fig. 1). These results seem to indicate that if the substituting group increases the donating ability of the nitrile, the iron transmits electron density to the Cp ring, and consequently back-donation is diminished.

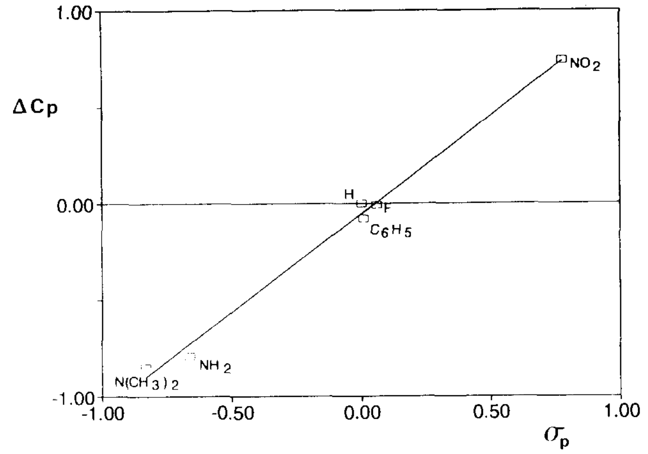
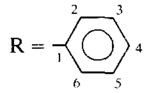
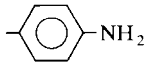
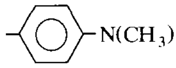
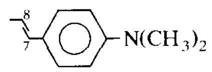
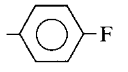
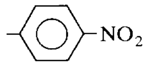
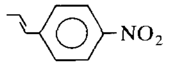
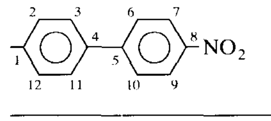


Fig. 1. Plot of $\Delta(C_5H_5)$ *vs.* σ_p for complexes $[FeCp((+)\text{-DIOP})(p\text{-}NCC_6H_4R)][PF_6]$. ($\Delta(C_5H_5) = \delta(C_5H_5)_{R \neq H} - \delta(C_5H_5)_{R-H}$).

TABLE 2. ^{13}C NMR data for complexes $[FeCp((+)\text{-DIOP})(NCR)][PF_6]$

Compound $[FeCp((+)\text{-DIOP})(p\text{-}NCR)]^+$	δ(ppm), assignment
	81.17 (C_5H_5); 111.33 (C1); 129.02 (C3, C5); 130.09 (C2, C6); 132.10 (C4); 136.58 (CN)
	80.38 (C_5H_5); 97.15 (C1); 114.63 (C3, C5); 133.53 (C2, C6); 142.00 (CN); 152.45 (C4)
	39.77 ($N(CH_3)_2$); 80.32 (C_5H_5); 95.21 (C1); 111.57 (C3, C5); 133.09 (C2, C6); 139.10 (CN); 153.02 (C4)
	39.91 ($N(CH_3)_2$); 80.56 (C_5H_5); 88.04 (C8); 111.64 (C3, C5); 120.78 (C1); 129.17 (C2, C6); 138.78 (CN); 152.10 (C7); 152.67 (C4)
	81.16 (C_5H_5); 107.50 (C1); 117.24 (C3, C5, $^{2}J(CF) = 22.8$); 134.14 (C2, C6, $^{3}J(CF) = 11.5$); 135.66 (CN)
	81.91 (C_5H_5); 117.03 (C1); 124.32 (C3, C5); 129.96 (C2, C6); 130.10 (CN); 149.70 (C4)
	81.46 (C_5H_5); 100.87 (C8); 124.20 (C3, C5); 128.41 (C2, C6); 138.95 (C1); 148.21 (C7); 148.91 (C4)
	81.35 (C_5H_5); 111.33 (C1); 119.48 (CN); 124.28 (C7, C9); 128.22 (C3, C11); 128.37 (C6, C10); 132.89 (C2, C12); 143.60 (C4); 144.94 (C5); 147.92 (C8)

This is also consistent with the IR data for ν(CN). Finally, comparison of ^{1}H and ^{13}C NMR data (Tables 1 and 2) for complexes and uncoordinated nitriles (see Experimental section) shows a general trend of shielding of protons H_1 and H_4 after coordination, regardless of whether the substituent is a π-acceptor or a π-donor. The deshielding observed for the carbon of the coordinated N≡C functional group is lower for acceptors; this corroborates the postulated increased back-donation inferred from the IR spectra.

3. Electrochemical studies

The electrochemistry of each compound was studied by cyclic voltammetry in dichloromethane and acetonitrile between the limits imposed by the solvents, *i.e. ca.* −1.5 and 1.6 V (Table 3). Tetrabutylammonium hexafluorophosphate was the supporting electrolyte.

The electrochemical behaviour of the family of compounds [FeCp((+)-DIOP)(NCC$_6$H$_4$R)]$^+$ is characterized by a reversible redox wave attributed to Fe^{II} → Fe^{III} oxidation, in the range 0.75–0.91 V, exemplified in Fig. 2.

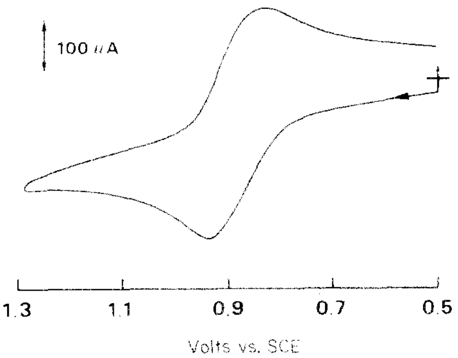


Fig. 2. Cyclic voltammogram of [FeCp((+)-DIOP)(p-NCC$_6$H$_4$C$_6$H$_5$)][PF$_6$] in CH$_3$CN containing 0.1 M ^{n}Bu$_4$NPF$_6$ (sweep rate = 200 mV/s).

However, where R = NH$_2$ and N(CH$_3$)$_2$ the electrochemistry was considerably more complex and, in spite of many experiments, we understand it only partially. [FeCp((+)-DIOP)(p-NCC$_6$H$_4$NH$_2$)]$^+$ showed anodic processes at E_{p_a} = 1.310 V (B) and 1.400 V (C) without corresponding cathodic peaks in addition to the reversible wave at $E_{p/2}$ = 0.810 V (A), attributed to Fe^{II} → Fe^{III} oxidation. In the very first sweep, peak B appeared as a shoulder on wave C, but 3 h later, a voltammogram of the same solution obtained in the same experimental conditions showed B as a very intense anodic wave instead of the original shoulder, and wave C (E_{p_a} = 1.400 V) had almost disappeared, while the oxidation wave Fe^{II} → Fe^{III} ($E_{p/2}$ = 0.810 V) was unaffected.

In the case of [FeCp((+)-DIOP)(p-NCC$_6$H$_4$N(CH$_3$)$_2$]$^+$, the behaviour was quite similar, but the two additional waves, B and C, at $E_{p/2}$ = 1.150 and 1.390 V, respectively, were reversible (see Table 3). One hour after the very first cycle, the cyclic voltammogram showed clearly that wave C had almost gone, while B was very intense and the first (Fe^{II} → Fe^{III}) remained unchanged. The reversibility of this system encouraged us to undertake several chemical oxidation experiments, in order to reproduce the reactions occurring in the electrochemical cell. The product obtained after oxidation with sulphuric acid, showed a cyclic voltam-

TABLE 3. Electrochemical data [a]

Compound	E_{pa} (V)	E_{pc} (V)	$E_{p/2}$ (V)	$E_{pc} - E_{pa}$ (mV)	$\frac{I_c}{I_a}$
[FeCp((+)-DIOP)(NC-ϕ)]$^+$	0.94	0.85	0.90	90	
[FeCp((+)-DIOP)(p-NC-ϕ-CH$_3$)]$^+$	0.90	0.80	0.85	100	1.0
[FeCp((+)-DIOP)(p-NC-ϕ-OCH$_3$)]$^+$	0.93	0.82	0.88	110	1.1
[FeCp((+)-DIOP)(p-NC-ϕ − NH$_2$)]$^+$	0.85	0.76	0.81	90	1.0(5)
	1.31	–		–	
	1.40	–	–	–	
[FeCp((+)-DIOP)(p-NC-ϕ-N(CH$_3$)$_2$)]$^+$	0.81	0.74	0.78	70	1.0(4)
	1.18	1.12	1.15	60	
	1.43	1.35	1.39	80	0.9(5)
[FeCp((+)-DIOP)(p-NC–CH=CH-ϕ-N(CH$_3$)$_2$)]$^+$	0.80	0.71	0.75	90	0.9(5)
	1.10	1.02	1.06	80	1.2
[FeCp((+)-DIOP)(p-NC-ϕ-ϕ)]$^+$	0.94	0.86	0.90	80	0.9(6)
[FeCp((+)-DIOP)(p-NC-ϕ-F]$^+$	0.84	0.74	0.79	100	1.0
[FeCp((+)-DIOP)(p-NC-ϕ-NO$_2$)]$^+$	0.95	0.87	0.91	80	1.1

[a] The electrochemical studies were carried out with CH$_3$CN solutions containing 0.1 M Bu$_4$NPF$_6$. Potentials are referenced to a calomel electrode containing saturated KCl solution. Sweep rates of 200 mV/s were used and the temperature was 20 ± 2°C. The solute concentration was generally about 1 mM.

mogram quite similar to that obtained from the solution 1 h after the first cycle, but some problems arose in its characterization. This is still under investigation. However, we hope eventually to understand the overall oxidations, which probably occur on the coordinated nitrile.

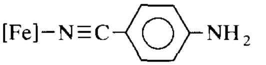
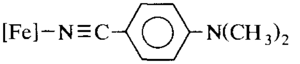
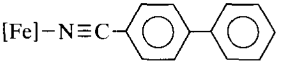
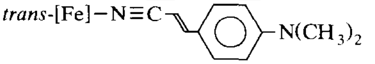
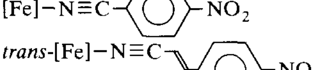
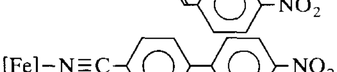
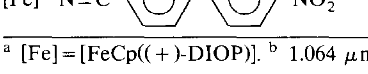
The oxidative electrochemistry of [FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$NO$_2$)]$^+$ showed the highest potential observed for the redox pair Fe^{II} → Fe^{III} in the entire family ($E_{p/2} = 0.910$ V). This is in good agreement with IR and ^{13}C NMR spectroscopic data above, because release of electron density from the iron(II) centre to the nitrile group via π back-donation should increase the oxidation potential.

4. SHG studies

We have tested for second-harmonic generation of some of the compounds synthesized in this work. The experiments were done with powder samples obtained as described in the Experimental section, without any further grinding, using the Kurtz powder technique. Since all the compounds are red, light from an Nd:YAG laser operating at 1.064 μm was Raman shifted to 1.907 μm with a high pressure hydrogen-gas cell. The relative efficiencies of second-harmonic generation (SHG) are summarized in Table 4.

The compound [FeCp((+)-DIOP)(*p*-NCC(H)=C(H)C$_6$H$_4$N(CH$_3$)$_2$)][PF$_6$] exhibits the highest SHG efficiency, possibly due to the ethenyl group in the nitrile substituent which gives this molecule the most extensive π-delocalization in the series of amine-substituted organometallics.

TABLE 4. Evaluation of SHG

Complex [a]	SHG signal (error ±10%) (urea = 1.0)
	0.0 [b]
	0.2
	4.2
	3.3
	38.0
	0.0 [b]
	0.0

[a] [Fe] = [FeCp((+)-DIOP)]. [b] 1.064 μm.

The best value of SHG was obtained for [FeCp((+)-DIOP)(NCC$_6$H$_4$NO$_2$)][PF$_6$], which is 38 times more efficient than urea. This suggests that the [FeCp((+)-DIOP)] fragment, acting as a π donor *via* d–π*(NC) orbitals towards the NO$_2$ acceptor group, enhances the hyperpolarizability of the coordinated nitrile giving rise to a large molecular second order hyperpolarizability, which is related to non-linear optical properties.

In contrast to the amine-substituted compounds, the incorporation of the *trans*-ethenyl group in the *p*-nitrobenzonitrile ligand leads to a vanishingly small non-linearity in the compound [FeCp((+)-DIOP)(*p*-NCC(H)=C(H)C$_6$H$_4$NO$_2$)][PF$_6$]. As reported before [9], we also found that neither the certainty of non-centrosymmetry, nor the enhanced hyperpolarizability of the chiral molecule guarantees large values of non-linearity. This suggests that solid state factors related to crystal symmetry and molecular orientation could be at the origin of small SHG signals.

Crystals are now being grown in order to study the crystallographic structures. This, we believe, may contribute to a better understanding of our system.

5. Experimental details

All experiments were carried out under dinitrogen or argon by use of standard Schlenk techniques. Solvents were purified according to the usual methods [10]. Solid state IR spectra were taken on a Perkin-Elmer 457 spectrophotometer with KBr pellets; only significant bands are cited in the text. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker CXP 300 spectrometer, and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer at probe temperature. Microanalyses were performed in our laboratories. Melting points were obtained on a Reichert Thermovar.

The ^{1}H (acetone-d_6) and ^{13}C (chloroform-*d*) 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$_4$.

(+)-DIOP ^{1}H and ^{13}C NMR data are quite similar for all the complexes: ^{1}H: 0.95 (s, 3H, CH$_3$); 1.21 (s, 3H, CH$_3$); 2.51 (m, 4H, CH$_2$); 3.32 (m, 2H, CH); 7.56 (m, 10H, C$_6$H$_5$); 7.71 (m, 4H, C$_6$H$_5$); 7.84 (t, 4H, C$_6$H$_5$); 8.29 (t, 2H, C$_6$H$_5$). ^{13}C: 26.42 (CH$_3$); 26.82 (CH$_3$); 28.20 (CH$_2$, ^1J(C, P) = 20.4); 31.16 (CH$_2$, ^1J(C, P) = 23.2); 74.87 (CH,^2J(C, P) = 12.34); 78.20 (CH, ^2J(C, P) = 12.34); 108.84 (*C*(CH$_3$)$_2$); 128.92–134.10 (aryl CH); 138.67 (*C*-*ipso*, aryl CH); 141.77 (*C*-*ipso*, aryl CH).

[FeCp((+)-DIOP)I] was prepared following the procedure described previously [11].

5.1. Preparation of [FeCp((+)-DIOP)(NCR)][PF$_6$]

All the complexes were prepared by the process described below. To a solution of [FeCp((+)-DIOP)I] (1 mmol) and the appropriate nitrile NCC$_6$H$_4$R (2 mmol) in dichloromethane (40 ml) was added TlPF$_6$ (1 mmol) at room temperature with stirring. The mixture was stirred at room temperature for 12 h. A change was observed from dark-violet to orange with simultaneous precipitation of thallium iodide. After filtration, the solution was evaporated under vacuum to dryness and washed several times with ether to remove the excess nitrile. The residue was recrystallized from dichloromethane/ether.

[FeCp((+)-DIOP)(NCC$_6$H$_5$)][PF$_6$]: 60% yield, m.p. 188°C (dec.). IR (KBr): ν(CN) 2210 cm^{-1}. Anal. Found: C, 59.60; H, 4.70; N, 1.90. C$_{43}$H$_{42}$F$_6$FeNO$_2$P$_3$. calcd.: C, 59.53; H, 4.88; N, 1.61%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$CH$_3$)][PF$_6$]: 90% yield, m.p. 187°C (dec.). IR (KBr): ν(CN) 2220 cm^{-1}. Anal. Found: C, 59.40; H, 5.35; N, 1.62. C$_{44}$H$_{44}$F$_6$FeNO$_2$P$_3$. calcd.: C, 59.94; H, 5.03; N, 1.59%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$OCH$_3$)][PF$_6$]: 70% yield, m.p. 160–163°C. IR (KBr): ν(CN) 2220, (OCH$_3$) 1265 cm^{-1}. Anal. Found: C, 58.48; H, 5.38; N, 2.20. C$_{44}$H$_{44}$F$_6$FeNO$_3$P$_3$. calcd.: C, 58.87; H, 4.94; N, 1.56%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$NH$_2$)][PF$_6$]: 60% yield, m.p. 157–159°C. IR (KBr): (NH$_2$) 3490, 3400, ν(CN) 2210 cm^{-1}. Anal. Found: C, 58.30; H, 5.06; N, 3.28. C$_{43}$H$_{43}$F$_6$FeN$_2$O$_2$P$_3$. calcd.: C, 58.52; H, 4.91; N, 3.17%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$N(CH$_3$)$_2$)][PF$_6$]: 95% yield, m.p. 182°C (dec.). IR (KBr): (N(CH$_3$)$_2$) 2960, ν(CN) 2210 cm^{-1}. Anal. Found.: C, 59.39; H, 5.40; N, 3.31. C$_{45}$H$_{47}$F$_6$FeN$_2$O$_2$P$_3$. calcd.: C, 59.35; H, 5.20; N, 3.07%.

trans-[FeCp((+)-DIOP)(*p*-NCC(H)=C(H)C$_6$H$_4$N(CH$_3$)$_2$)][PF$_6$]: 85% yield, m.p. 207–209°C. IR (KBr): (N(CH$_3$)$_2$) 2960, ν(CN) 2205, 1610 (CH=CH) cm^{-1}. Anal. Found.: C, 60.82; H, 5.45; N, 3.12. C$_{47}$H$_{49}$F$_6$FeN$_2$O$_2$P$_3$. calcd.: C, 60.27; H, 5.27; N, 2.99%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$C$_6$H$_5$)][PF$_6$]: 85% yield, m.p. 168–171°C. IR (KBr): ν(CN) 2220 cm^{-1}. Anal. Found.: C, 60.74; H, 5.06; N, 1.97. C$_{49}$H$_{46}$F$_6$FeNO$_2$P$_3$. calc.: C, 62.37; H, 4.91; N, 1.48%. (The sample loses weight during the manipulations)

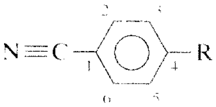
[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$F)][PF$_6$]: 50% yield, m.p. 152°C (dec.). IR (KBr): ν(CN) 2210 cm^{-1}. Anal. Found.: C, 54.50; H, 4.99; N, 1.41. C$_{43}$H$_{37}$F$_7$FeNO$_2$P$_3$. CH$_2$Cl$_2$ calcd.: C, 54.45; H, 4.46; N, 1.44%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$NO$_2$)][PF$_6$]: 65% yield, m.p. 173°C (dec.). IR (KBr): ν(CN) 2205, (NO$_2$) 1525, 1340 cm^{-1}. Anal. Found.: C, 56.30; H, 4.72; N, 3.16. C$_{43}$H$_{41}$F$_6$FeN$_2$O$_4$P$_3$. calcd.: C, 56.59; H, 4.53; N, 3.07%.

trans-[FeCp((+)-DIOP)(*p*-NCC(H)=C(H)C$_6$H$_4$-NO$_2$)][PF$_6$]: 65% yield, m.p. 167–169°C. IR (KBr): ν(CN) 2210, 1625 (CH=CH), (NO$_2$) 1520, 1340 cm^{-1}. Anal. Found.: C, 57.96; H, 4.88; N, 2.93. C$_{45}$H$_{43}$F$_6$FeN$_2$O$_4$P$_3$. calcd.: C, 57.58; H, 4.62; N, 2.99%.

[FeCp((+)-DIOP)(*p*-NCC$_6$H$_4$C$_6$H$_4$NO$_2$)][PF$_6$]: 80% yield, m.p. 190–192°C. IR (KBr): ν(CN) 2210, (NO$_2$) 1515, 1345 cm^{-1}. Anal. Found.: C, 59.68; H, 4.76; N, 3.09. C$_{49}$H$_{45}$F$_6$FeN$_2$O$_4$P$_3$. calcd.: C, 59.53; H, 4.59; N, 2.83%.

5.2. ^{1}H and ^{13}C NMR data for uncoordinated nitriles



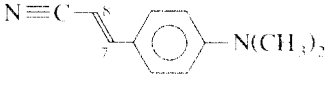
NCC$_6$H$_5$ (^{1}H): 7.53 (t, 2H, H$_3$, H$_5$); 7.70 (m, 3H, H$_2$, H$_4$, H$_6$). ^{13}C: 111.97 (C1); 118.39 (CN); 128.75 (C3, C5); 131.66 (C2, C6); 132.41 (C4).

p-NCC$_6$H$_4$CH$_3$ (^{1}H): 2.40 (s, 3H, CH$_3$); 7.37 (d, 2H, H$_3$, H$_5$); 7.62 (d, 2H, H$_2$, H$_6$).

p-NCC$_6$H$_4$OCH$_3$ (^{1}H): 3.89 (s, 3H, OCH$_3$); 7.08 (d, 2H, H$_3$, H$_5$); 7.68 (d, 2H, H$_2$, H$_6$).

p-NCC$_6$H$_4$NH$_2$ (^{1}H): 5.55 (b, 2H, NH$_2$); 6.72 (d, 2H, H$_3$, H$_5$); 7.36 (d, 2H, H$_2$, H$_6$). ^{13}C: 98.88 (C1); 114.07 (C3, C5); 120.22 (CN); 133.38 (C2, C6); 150.67 (C4).

p-NCC$_6$H$_4$N(CH$_3$)$_2$ (^{1}H): 3.03 (s, 6H, N(CH$_3$)$_2$); 6.75 (d, 2H, H$_3$, H$_5$); 7.46 (d, 2H, H$_2$, H$_6$). ^{13}C: 39.60 (N(CH$_3$)$_2$); 96.84 (C1); 111.16 (C3, C5); 120.48 (CN); 133.01 (C2, C6); 152.23 (C4).



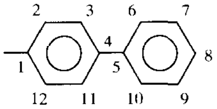
trans-*p*-NCC(H)=C(H)C$_6$H$_4$N(CH$_3$)$_2$ (^{1}H): 3.01 (s, 6H, N(CH$_3$)$_2$); 5.85 (d, 1H, H$_8$, ^1J(H$_7$, H$_8$) = 17.0); 6.72 (d, 2H, H$_3$, H$_5$); 7.35 (d, 1H, H$_7$, ^1J(H$_7$, H$_8$) = 17.0); 7.44 (d, 2H, H$_2$, H$_6$). ^{13}C: 39.70 (N(CH$_3$)$_2$); 88.94 (C8); 111.34 (C3, C5); 119.41 (CN); 121.00 (C1); 128.69 (C2, C6); 150.18 (C7); 151.85 (C4).

p-NCC$_6$H$_4$F (^{1}H): 7.35 (t, 2H, H$_3$, H$_5$); 7.86 (q, 2H, H$_2$, H$_6$). ^{13}C: 108.15 (C1); 116.37 (C3, C5, ^2J(C, F) = 22.8); 117.59 (CN); 134.33 (C2, C6, ^3J(C, F) = 9.1); 164.56 (C4, ^1J(C, F) = −255.5).

p-NCC$_6$H$_4$NO$_2$ (^{1}H): 8.13 (d, 2H, H$_2$, H$_6$); 8.43 (d, 2H, H$_3$, H$_5$). ^{13}C: 116.69 (CN); 118.13 (C1); 124.13 (C3, C5); 133.38 (C2, C6); 149.88 (C4).

trans-*p*-NCC(H)=C(H)C$_6$H$_4$NO$_2$ (^{1}H): 6.59 (d, 1H, H$_8$, ^1J(H$_7$, H$_8$) = 16.9); 7.76 (d, 1H, H$_7$, ^1J(H$_7$, H$_8$) = 16.9); 7.97 (d, 2H, H$_2$, H$_6$); 8.32 (d, 2H, H$_3$, H$_5$). ^{13}C:

100.94 (C8); 116.96 (CN); 124.33 (C3, C5); 128.09 (C2, C6); 139.11 (C1); 147.72 (C7); 148.97 (C4).



p-$NCC_6H_4C_6H_5$ (^1H): 7.48 (m, 3H, H_7, H_8, H_9); 7.69 (d, 2H, H_6, H_{10}); 7.83 (s, 4H, H_2, H_3, H_{11}, H_{12}).

p-$NCC_6H_4C_6H_4NO_2$ (^1H): 7.93 (d, 2H, H_2, H_{12}); 7.99 (d, 2H, H_3, H_{11}); 8.16 (d, 2H H_6, H_{10}); 8.35 (d, 2H, H_7, H_9). ^{13}C: 112.65 (C1); 118.28 (CN); 124.30 (C7, C9); 128.08 (C3, C6, C10, C11); 132.85 (C2, C12); 143.08 (C4); 145.33 (C5); 147.88 (C8).

5.3. Electrochemical apparatus

The electrochemical instrumentation consisted of a Princeton Applied Research Model 173 potentiometer, a Model 175 voltage programmer, a Model 179 digital coulometer and a Omnigraph 2000 X–Y recorder of Houston Instruments. Potentials were referenced to a calomel electrode containing a saturated solution of potassium chloride. The reference electrode was calibrated using a 1.0×10^{-3} M solution of ferrocene in acetonitrile containing 0.10 M $LiClO_4$ for which the ferricinium/ferrocene potential was in agreement with the literature value [12]. The working electrode was a 2-mm piece of platinum wire for voltammetry and a platinum gauze for the coulometry experiments. The secondary electrode was a platinum wire coil. Cyclic voltammetry experiments were performed at room temperature in a PAR polarographic cell or in a three-compartment cell equipped with medium porosity glass frits. Solutions studied were 1 mM in solute and 0.1 M in tetrabutylammonium hexafluorophosphate as supporting electrolyte.

The electrolyte was prepared from Bu_4NBr and KPF_6 (both purchased from Aldrich Chemical Co.), recrystallized from acetone/ethanol, washed with diethyl ether, and dried *in vacuo* at room temperature for 24 h. Reagent grade acetonitrile and dichloromethane, were dried over P_2O_5 and CaH_2, respectively, and distilled before use under an argon atmosphere. A dinitrogen atmosphere was maintained over the solution during the experiment.

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