

Synthesis and electrochemical studies of organometallic cobalt(III) complexes with substituted benzonitrile chromophores: NMR spectroscopic data as a probe on the second-order non-linear optical properties

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Abstract

The family of organometallic Co(III) benzonitrile derivatives of general formula $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$ ($\text{R} = \text{C}_6\text{H}_4\text{NMe}_2$, $\text{C}_6\text{H}_4\text{NH}_2$, $\text{C}_6\text{H}_4\text{OMe}$, $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$, C_6H_5 , $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$, and $\text{C}_6\text{H}_4\text{NO}_2$) have been synthesized. Spectroscopic and electrochemical data were analyzed in order to evaluate the extent of electronic coupling between the organometallic fragment and the nitrile ligands. An attempt of correlation between NMR spectroscopic data and the second-order non-linear optical properties is presented, based on this work and available published data for related η^5 -monocyclopentadienyliron, ruthenium and nickel complexes.

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1. Introduction

The search for new organometallic materials with non-linear optical (NLO) properties is currently the subject of considerable interest due to their potential technological applications in the area of integrated optics [1–6]. It is well known that organometallic complexes can possess low energy, sometimes intense, electronic metal-to-ligand or ligand-to-metal charge transfer excitations which can be responsible for high values of molecular first hyperpolarizability β . The value of these systems is that the energy of the charge transfer excitation can be tuned by variation of the metal itself and its oxidation state, ligand environment and coordination geometries to optimize the second-order NLO response.

The main studies have been made in push-pull systems in which the metal center, bonded to a polarizable organic conjugated backbone (chromophore), acts as an electron releasing or withdrawing group.

Among the organometallic compounds presenting this donor– π -system–acceptor interaction, the family of η^5 -monocyclopentadienylmetal derivatives revealed significant second-order optical non-linearities, especially those of iron and ruthenium complexes coordinated to *p*-nitrobenzonitriles, *p*-nitrobenzoacetylides and *p*-nitrothienylnitriles [7–15]. Compared with the metallocene systems, which were the first organometallic compounds to be studied for their NLO properties, the main structural feature of this family of compounds is the existence of the metal center in the same plane of the chromophore, thus allowing a better coupling between the organometallic fragment and the conjugated chromophores. In fact, the existence of metal–ligand

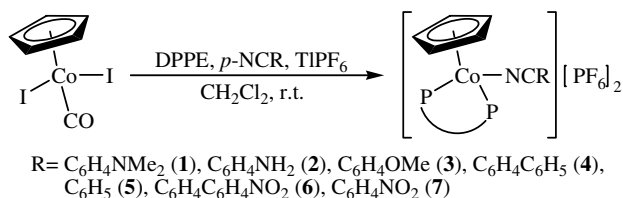
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π -backdonation through $d_{\text{metal}}-\pi^*_{\text{ligand}}$ interaction was found to play an important role on the second-order NLO response of this family of compounds, where the driving force is the presence of the strong acceptor NO_2 group on the end of the π -system of the chromophore [16]. In our earlier studies on systematic variation of the metal ion in η^5 -monocyclopentadienylmetal complexes with *p*-substituted benzonitrile chromophores, the first hyperpolarizability was found to increase along the sequence Co, Ni, Ru, Fe, where the high values found for Ru and Fe complexes were attributed to the occurrence of π -backdonation, clearly supported by IR and NMR spectroscopic data [16]. Therefore, spectroscopic IR and NMR data, besides the employment of the UV–Vis spectra to probe electronic metal-to-ligand or ligand-to-metal charge transfer excitations, can be used to give an insight on the molecular electronic factors that may be responsible for the second-order non-linear optical responses.

In this work, spectroscopic data were used on the family of compounds $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$ ($\text{R} = \text{C}_6\text{H}_4\text{NMe}_2$, $\text{C}_6\text{H}_4\text{NH}_2$, $\text{C}_6\text{H}_4\text{OMe}$, $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$, C_6H_5 , $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$, and $\text{C}_6\text{H}_4\text{NO}_2$) in order to evaluate the role played by the organometallic fragment on their second-order NLO response. Published data for related iron, ruthenium and nickel complexes were also included in an attempt to correlate NMR spectroscopic data with the corresponding second-order non-linear optical properties. Electrochemical studies by cyclic voltammetry were performed in all the complexes to complement these studies.

2. Results and discussion

The complexes were prepared by the reaction of $[\text{CoCpI}_2\text{CO}]$ with a mixture of DPPE, TIPF_6 and excess of the appropriate *p*-benzonitrile derivative in dichloromethane at room temperature (Scheme 1). After work-up, orange-red crystals of $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$ ($\text{R} = \text{C}_6\text{H}_4\text{NMe}_2$ (1) [16], $\text{C}_6\text{H}_4\text{NH}_2$ (2), $\text{C}_6\text{H}_4\text{OMe}$ (3), $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$ (4) [16], C_6H_5 (5), $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$ (6), and $\text{C}_6\text{H}_4\text{NO}_2$ (7)) were obtained with yield in the range of 62–87%. The synthesis of the complexes involves the formation of $[\text{CoCp}(\text{dppe})\text{I}]^+$ in situ, followed by iodide abstraction by TIPF_6 and coordination of the different *p*-benzonitrile ligands. The compounds are quite stable



Scheme 1. Reaction scheme for the synthesis of cobalt complexes.

towards oxidation in air and to moisture both in the solid state and in solution. Formulation of the new compounds was supported by analytical data, IR and ^1H , ^{13}C and ^{31}P NMR spectra. The molar conductivities of ca. 10^{-3} M solutions of the complexes in nitromethane, in the range $165\text{--}204 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, are consistent with values reported for 2:1 type electrolytes [17].

Typical IR bands confirm the presence of the cyclopentadienyl ligand (ca. $3050\text{--}3080 \text{cm}^{-1}$), the PF_6^- anion (840 and 550cm^{-1}) and the coordinated nitrile ($2235\text{--}2275 \text{cm}^{-1}$) in all complexes. A positive shift of (CN) upon coordination was observed in the range $15\text{--}55 \text{cm}^{-1}$. This means a σ -coordinated nitrile in which the overall $\text{N}\equiv\text{C}$ bond is strengthened upon coordination. The same behavior was found previously on $[\text{NiCpPPh}_3(p\text{-NCR})][\text{PF}_6]$ derivatives [18] and seems to indicate the absence of π backdonation in these cobalt complexes, in opposite of that was found for the previously reported Fe(II) and Ru(II) analogs [7–10]. Accordingly, recent density functional theory (DFT) calculations on some of these cobalt complexes confirm that the ligand–metal interaction are π mainly and have no evidence of π back donation contribution [19].

^1H NMR chemical shifts for the cyclopentadienyl ring are in the range usually observed for dicationic cobalt(III) complexes and seems to be only slightly affected by the nature of the coordinated nitrile. In fact, as the electron donor character of the *p*-substituent in benzonitrile ligands increases, the Cp ring resonance shifts upfield, consistent with an increased electronic density on the Cp ring due to the increased electron density at the metal center. This effect was observed in similar nickel [18], iron [7,8] and ruthenium [9,20] complexes. In contrast to the effect observed for Cp ring, the phosphine signals are relatively insensitive to the nature of the aromatic nitrile. For benzene ring protons of the nitrile ligands, a shielding effect upon coordination was observed. This shielding was found to be in the range of $0.73\text{--}0.87$ ppm for *ortho* (relative to the NC group) protons and $0.08\text{--}0.31$ ppm for *meta* protons. A shielding effect on these protons upon coordination was already found in similar Ru(II) and Fe(II) complexes and was explained by the occurrence of π -backdonation from the organometallic fragment to the coordinated nitrile ligand [7–10]. In the present Co(III) complexes no evidence of π -backdonation was found, as mentioned above. Thus, this shielding effect should be due to other factors. The origin of the observed upfield shifts could be an effect of the change of the $\text{N}\equiv\text{C}$ anisotropy upon coordination. Moreover, an additional explanation can be found by assuming an electronic interaction of the protons with the counter ion, as observed before on Ru(II) [9] and Ni(II) [18] compounds.

^{13}C NMR data of this family of compounds confirm the evidence found for proton spectra. The Cp ring chemical shifts are in the range usually observed for

dicationic Co(III) complexes and is slightly affected by the nature of substituent at the end of the coordinated nitrile. In spite of the fact that the Cp ring displays signals in a narrow range, there is a linear correlation between ΔC_p ($\Delta C_p = \delta_{C_p}(p\text{-substituted benzonitrile}) - \delta_{C_p}(\text{benzonitrile})$) and σ_p Hammett parameters [21] of the substituents (Fig. 1). This linear relationship was already observed in the analogous iron(II) systems [7]. These results indicate that as the donating ability of the substituents increases, the metal center transmits electron density to the Cp ring, moving their resonance chemical shifts upfield. The slope of this linear correlation could give an insight of the electronic communication between the nitrile ligands and the organometallic cobalt fragment. An interesting relationship between Cp-shifts and strength of donor–acceptor interaction on sesquifulvalene complexes was also reported recently by other authors [22]. The slope of the straight line (0.476) is lower than the observed for Fe(II) compounds [7] and seems to indicate a poorer communicability between the nitrile ligands and the organometallic cobalt fragment. For the nitrile ligand carbons, an expected deshielding on the carbon of the $N\equiv C$ functional group upon coordination was observed, and for the aromatic carbons an also expected more significant changes was observed for the carbon C1, next to the coordination place.

^{31}P NMR data of the complexes showed an expected deshielding upon coordination of the phosphine, in accordance with its donor character, and no significant changes on phosphorous electron density were observed by the presence of different coordinated nitriles.

The optical absorption spectra of all complexes were recorded as 5.0×10^{-5} M solutions in dichloromethane (Table 1). The spectra for the compound $[\text{CoCp}(\text{DPPE})(p\text{-NCC}_6\text{H}_4\text{NMe}_2)][\text{PF}_6]_2$ (1) typify the electronic spectra of this family of compounds, obtained in dichloromethane solution (Fig. 2). The spectra are characterized by the presence of two weak bands in the visible region, where *d-d* transitions are expected to occur,

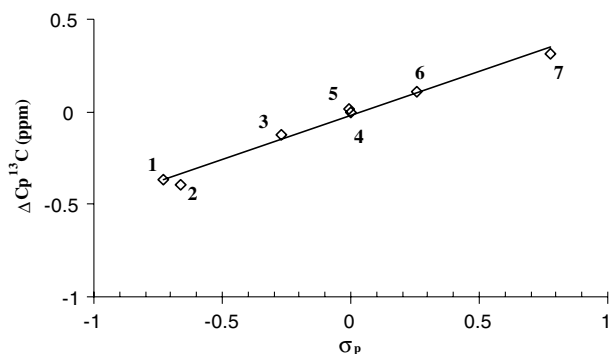


Fig. 1. Plot of ΔC_p vs. σ_p for complexes $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$. ($\Delta C_p = \delta_{C_p}(Y \neq H) - C_p(Y = H)$; σ_p : Hammett parameters; R = $\text{C}_6\text{H}_4\text{NMe}_2$ (1), $\text{C}_6\text{H}_4\text{NH}_2$ (2), $\text{C}_6\text{H}_4\text{OMe}$ (3), $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$ (4), C_6H_5 (5), $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$ (6), and $\text{C}_6\text{H}_4\text{NO}_2$ (7)).

Table 1
Optical spectral data for complexes $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$ in dichloromethane solution (ca. 5.0×10^{-5} M)

Compound $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$	λ (nm)	$\epsilon \times 10^4$ ($\text{M}^{-1}\text{cm}^{-1}$)
R = $\text{C}_6\text{H}_4\text{NMe}_2$ (1)	233	2.19
	336	4.50
	413	0.20
	495	0.15
R = $\text{C}_6\text{H}_4\text{NH}_2$ (2)	233	1.30
	308	3.30
	420 (sh)	
	495	0.10
R = $\text{C}_6\text{H}_4\text{OCH}_3$ (3)	234	1.54
	287	3.80
	325 (sh)	
	420	0.03
	495	0.07
R = $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$ (4)	234	1.88
	306	3.60
	415	0.04
	495	0.08
R = C_6H_5 (5)	234	1.66
	245 (sh)	
	275 (sh)	
	316	1.11
	415	0.06
	495	0.07
R = $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$ (6)	233	0.97
	307	2.19
	415	0.02
	495	0.05
R = $\text{C}_6\text{H}_4\text{NO}_2$ (7)	233	2.30
	270 (sh)	
	307	1.98
	415	0.02
	495	0.07

and another two intense absorption bands in the UV region, attributed to electronic transitions occurring both in the organometallic fragment $\{[\text{CoCp}(\text{DPPE})]^{2+}\}$ ($\lambda \sim 235$ nm) and coordinated nitrile chromophores ($\lambda \sim 280\text{--}340$ nm). No bands attributed to any nitrile-metal charge transfer were clearly identified, despite

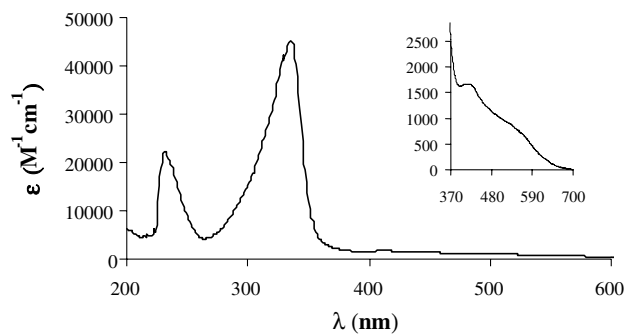


Fig. 2. UV-Vis absorption spectra of $[\text{CoCp}(\text{DPPE})(p\text{-NCC}_6\text{H}_4\text{NMe}_2)][\text{PF}_6]_2$ recorded in CH_2Cl_2 (5.0×10^{-5} M).

the fact that the presence of small shoulders in the UV region for all the complexes does not exclude this possibility. Solvatochromic studies were performed to verify this hypothesis but the results reveal that the position of all the absorption bands remain almost unchanged. The solvents used (chloroform, mixtures of dichloromethane/*n*-hexane and methanol) were chosen considering the stability of the compounds. DFT calculations performed in some of these complexes [19] showed that this possible electronic transition will be a ligand to metal charge transfer (LMCT) instead of MLCT found in related iron and ruthenium complexes [8,10].

The electrochemistry of this family of compounds was studied by cyclic voltammetry both in dichloromethane and acetonitrile between the limits imposed by the solvents (Tables 2 and 3).

In dichloromethane, the electrochemical behavior of the compounds is characterized by the presence of two redox processes, exemplified in Fig. 3. The first (A) is an irreversible process, presenting one single cathodic wave in the range from -0.01 to 0.09 V without the anodic counterpart, and the second (B) is a quasi-reversible process with $E_{p/2} = 0.55$ V, independent of the coordinated nitrile. For complexes **1**, **2**, **6** and **7** additional redox waves were observed and attributed to redox processes occurring on the coordinated nitrile ligands. The changes

Table 2
Electrochemical data for [CoCp(dppe)(*p*-NCR)][PF₆]₂ in dichloromethane^{a,b}

Compound [CoCp(dppe)(<i>p</i> -NCR)][PF ₆] ₂	E_c (V)	E_a (V)	$E_{p/2}$ (V)	ΔE^c (mV)	i_a/i_c
R = C ₆ H ₄ NMe ₂ (1)	-0.01	–	–	–	–
	-0.58	-0.52	-0.55	60	0.8
	1.34	1.44	1.39	100	0.8
R = C ₆ H ₄ NH ₂ (2)	0.00	–	–	–	–
	-0.58	-0.52	-0.55	60	0.8
R = C ₆ H ₄ OCH ₃ (3)	0.02	–	–	–	–
	-0.58	-0.52	-0.55	60	0.8
R = C ₆ H ₄ C ₆ H ₅ (4)	0.04	–	–	–	–
	-0.58	-0.52	-0.55	60	0.9
R = C ₆ H ₅ (5)	0.05	–	–	–	–
	-0.58	-0.52	-0.55	60	0.8
R = C ₆ H ₄ C ₆ H ₄ NO ₂ (6)	0.05	–	–	–	–
	-0.58	-0.52	-0.55	60	0.8
	-1.14	-1.02	-1.08	120	0.7
	-1.59	–	–	–	–
R = C ₆ H ₄ NO ₂ (7)	0.09	–	–	–	–
	-0.58	-0.52	-0.55	60	0.8
	-0.92	-0.84	-0.88	80	0.7
	-1.54	–	–	–	–

^a Supporting electrolyte: *n*-Bu₄NPF₆ 0.1 M; working electrode: Pt; reference electrode: calomelane; sweep rate: 200 mV/s; temperature: 20 °C; solute concentration: ca. 1 mM.

^b In the same conditions. $E_{p/2}(\text{FeCp}_2/\text{FeCp}_2^+) = 0.41$ V.

^c $\Delta E = E_a - E_c$.

Table 3
Electrochemical data for [CoCp(dppe)(*p*-NCR)][PF₆]₂ in acetonitrile^{a,b}

Compound [CoCp(dppe)(<i>p</i> -NCR)][PF ₆] ₂	E_c (V)	E_a (V)	$E_{p/2}$ (V)	ΔE^c (mV)	i_a/i_c
R = C ₆ H ₄ NMe ₂ (1)	-0.16	-0.07	-0.12	90	0.8
	-0.55	-0.49	-0.52	60	0.9
	1.12	1.20	1.16	80	0.2
R = C ₆ H ₄ NH ₂ (2)	-0.15	-0.07	-0.11	80	0.7
	-0.56	-0.49	-0.52	70	0.9
	–	1.38	–	–	–
R = C ₆ H ₄ OCH ₃ (3)	-0.15	-0.07	-0.11	80	0.8
	-0.56	-0.49	-0.52	70	1.0
R = C ₆ H ₄ C ₆ H ₅ (4)	-0.16	-0.07	-0.12	90	1.0
	-0.56	-0.50	-0.53	60	1.0
R = C ₆ H ₅ (5)	-0.16	-0.08	-0.12	80	0.8
	-0.56	-0.47	-0.52	90	0.9
R = C ₆ H ₄ C ₆ H ₄ NO ₂ (6)	-0.14	-0.08	-0.11	60	0.8
	-0.56	-0.50	-0.53	60	0.9
	-1.04	-0.98	-1.01	60	0.7
	-1.59	–	–	–	–
R = C ₆ H ₄ NO ₂ (7)	-0.14	-0.08	-0.11	60	0.7
	-0.56	-0.49	-0.52	70	0.8
	-0.87	-0.80	-0.84	70	0.8
	-1.70	–	–	–	–
R = CH ₃ (8)	-0.15	-0.08	-0.12	70	0.9
	-0.55	-0.49	-0.52	60	0.9

^a Supporting electrolyte: *n*-Bu₄NPF₆ 0.1 M; working electrode: Pt; reference electrode: calomelane; sweep rate: 200 mV/s; temperature: 20 °C; solute concentration: ca. 1 mM.

^b In the same conditions. $E_{p/2}(\text{FeCp}_2/\text{FeCp}_2^+) = 0.41$ V.

^c $\Delta E = E_a - E_c$.

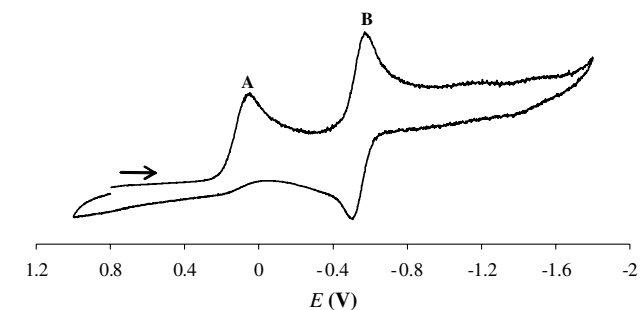


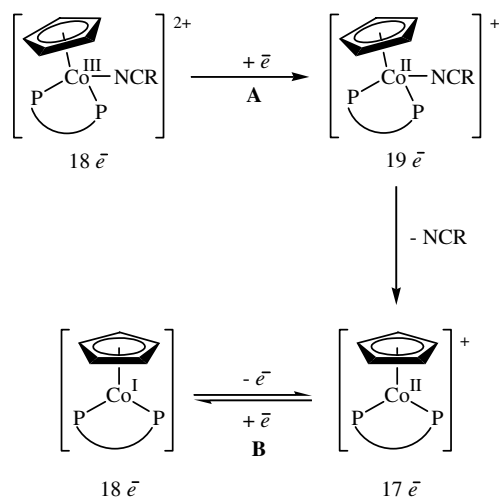
Fig. 3. Cyclic voltammogram of [CoCp(dppe)(*p*-NCC₆H₄C₆H₅)]PF₆]₂ in dichloromethane containing 0.1 M *n*-Bu₄NPF₆ ($T = 20$ °C; sweep rate = 200 mV/s).

on corresponding potentials upon coordination are not significant (10–30 mV) and agree with the expected behavior resulting from the released electron density.

The cathodic wave A, which potential depends on the coordinated nitrile, was attributed to formal Co^{III} → Co^{II} reduction of [CoCp(dppe)(*p*-NCR)]²⁺ species. This cathodic wave has no anodic counterpart even at -20 °C and the sweep direction was inverted immediately after the reduction potential. This behavior indicates that the 19-electron species [CoCp(dppe)(*p*-NCR)]⁺,

formed on the electrode surface at reduction potential, undergo fast decomposition (in an ECC process) and depleted the diffusion layer of the $[\text{CoCp}(\text{dppe})(p\text{-NCR})]^+$ species. The fact that the redox process B has an $E_{p/2}$ independent of the coordinated nitrile suggests that it is originated by decomposition of 19-electron species $[\text{CoCp}(\text{dppe})(p\text{-NCR})]^+$ formed in the process (A) due to the decoordination of nitrile ligand, leading to the formation of 17-electron species $[\text{CoCp}(\text{dppe})]^+$. These species are sufficient stable to undergo a second reduction process (B) leading to a 18-electron Co^{I} complex, $[\text{CoCp}(\text{dppe})]$. Stable 17-electron monocyclopentadienylcobalt species with large and/or π -acid ligands were already mentioned in the literature [23–25]. This hypothesis is corroborated by the $E_{p/2}$ value attributed to $[\text{CoCp}(\text{dppe})]^+ / [\text{CoCp}(\text{dppe})]$ redox couple, found in the electrochemical studies of $[\text{CoCp}(\text{dppe})]$ complex [26]. According to these results, the electrochemical behavior of the studied complexes follows the suggested reactions depicted in Scheme 2.

In acetonitrile, the anodic counterpart of the redox process A arises (Fig. 4) and the corresponding $E_{p/2}$ is independent of the coordinated nitrile. These results suggest a substitution of the nitrile ligands by the acetonitrile solvent, leading to $[\text{CoCp}(\text{dppe})(\text{NCCH}_3)]^{2+}$ species, before the reductive processes. In order to confirm this hypothesis, the complex $[\text{CoCp}(\text{dppe})(\text{NCCH}_3)]\text{PF}_6)_2$ (**8**) was synthesized and its electrochemistry studied in acetonitrile. The $E_{p/2}$ values observed for the two reductive processes are similar of those found for the complexes 1–7 (see Table 3). The lability of nitrile ligands was also confirmed chemically. The complexes were dissolved in acetonitrile and the solutions stirred during 5 min. After work-up, the samples were analyzed by ^1H NMR spectroscopy and all spectra showed the presence of resonances attributed to both the $[\text{CoCp}(\text{dppe})(\text{NCCH}_3)]^{2+}$ complex and the corresponding free nitrile ligands. These



Scheme 2. Electrochemical behavior of the complexes $[\text{CoCp}(\text{dppe})(p\text{-NCR})]\text{PF}_6)_2$ in dichloromethane.

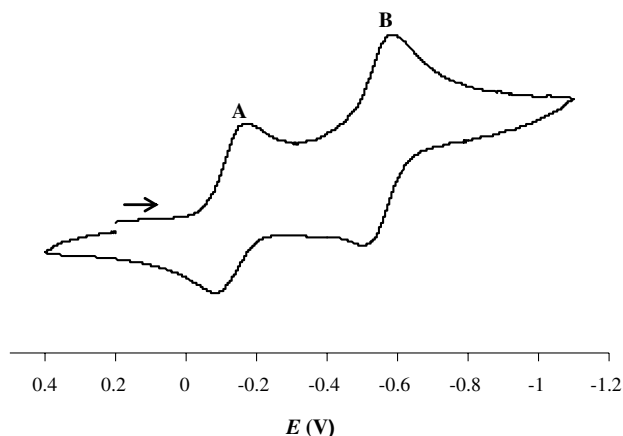


Fig. 4. Cyclic voltammogram of $[\text{CoCp}(\text{dppe})(p\text{-NCC}_6\text{H}_4\text{C}_6\text{H}_5)]\text{PF}_6)_2$ in acetonitrile containing 0.1 M $n\text{-Bu}_4\text{NPF}_6$ ($T = 20^\circ\text{C}$; sweep rate = 200 mV/s).

results confirm the suggested substitution of the nitrile ligands by the acetonitrile solvent before the electrochemical reductive processes on 1–7 complexes. As in dichloromethane, the redox waves B in acetonitrile were attributed to the $[\text{CoCp}(\text{dppe})]^+ / [\text{CoCp}(\text{dppe})]$ redox process.

As mentioned above, the cathodic potential for the $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$ reduction process in dichloromethane depends on the coordinated benzonitrile derivatives and, in spite of the narrow range observed, this potential agrees with the relative donor/acceptor character of their substituents. As the donor character of the substituents increases, the reduction potential becomes less positive, indicating an increased richness of the metal center (Fig. 5). These results are consistent with NMR spectroscopic data above, where a more shielded Cp ring results from an enhanced electron richness of the metal center, and agrees with DFT calculations performed in some of these cobalt complexes where the energy of the LUMO, mainly located on the metal fragment, follows the expected trend with the relative donor/acceptor

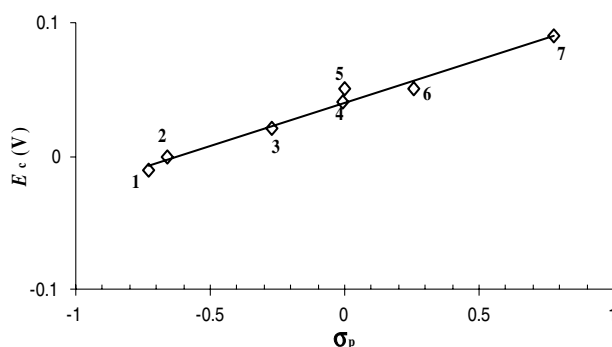


Fig. 5. Plot of cathodic potential (E_c) vs. Hammett parameters (σ_p) for the complexes $[\text{CoCp}(\text{dppe})(p\text{-NCR})]\text{PF}_6)_2$. ($R = \text{C}_6\text{H}_4\text{NMe}_2$ (1), $\text{C}_6\text{H}_4\text{NH}_2$ (2), $\text{C}_6\text{H}_4\text{OMe}$ (3), $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$ (4), C_6H_5 (5), $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$ (6), and $\text{C}_6\text{H}_4\text{NO}_2$ (7)).

character of the benzonitrile substituents [19]. The same DFT calculations showed that the LUMOs are not significantly affected by the substituents of the nitrile ligands, which explains the narrow range of cathodic potentials observed in these cobalt complexes and the low slope (0.064) of the linear relationship showed in Fig. 5. As was already recognized above by NMR spectroscopic data, this means that the electronic π -coupling between the cyclopentadienyl metal fragment and the π -system of the benzonitrile ligands is relatively weak.

The poor electronic communication between the organometallic fragment and the nitrile ligands, deduced from both spectroscopic and electrochemical data, lead to a slight effect of the conjugation length upon the first hyperpolarizability of these complexes. Moreover, the absence of low energy charge transfer bands between the organometallic fragment and the nitrile ligands also limits the magnitude of their second-order NLO response. These facts could explain the previously reported low first hyperpolarizabilities for two of these cobalt complexes [16]. As discussed above, the slope of the linear correlation between ΔC_p ($\Delta C_p = \delta_{C_p}(p\text{-substituted benzonitrile}) - \delta_{C_p}(\text{benzonitrile})$) and σ_p Hammett parameters of the nitrile substituents could give an insight of the electronic communicability between the nitrile ligands and the organometallic cobalt fragment. Comparison of the slope magnitude obtained from available spectroscopic data of related η^5 -monocyclopentadienyliron, ruthenium and nickel derivatives [7,8,16,18,20], show that the electronic communicability between the nitrile ligands and the organometallic fragments increases along the sequence Codppe < NiPPh₃ < Rudppe < Fediop < Fedppe. A similar trend was found for the first hyperpolarizabilities of complexes containing these organometallic fragments and *p*-NCC₆H₄NO₂ and *p*-NC(C₆H₄)₂NO₂ ligands [8,16]. An attempt to correlate the second-order NLO response of these complexes and the degree of electronic communicability between the organometallic fragments and the nitrile chromophores gave the linear relationships showed in Fig. 6. These results seem to indicate that as the electronic communication between the nitrile ligands and the organometallic fragments increases, the magnitude of first hyperpolarizability increases exponentially. These results seem to indicate that NMR spectroscopic data might be used to give an insight of the role played by the organometallic fragment on the first hyperpolarizability response of complexes containing the same chromophore. Within the same scope to relate NMR spectroscopic parameters with first hyperpolarizabilities, other authors reported a correlation between ¹H–¹H coupling constants and the first hyperpolarizability of organometallic merocyanines [27]. The linear trend found in this work can be useful to predict first hyperpolarizabilities of other monocyclopentadienylmetal complexes containing *p*-NCC₆H₄NO₂ or *p*-NC(C₆H₄)₂NO₂

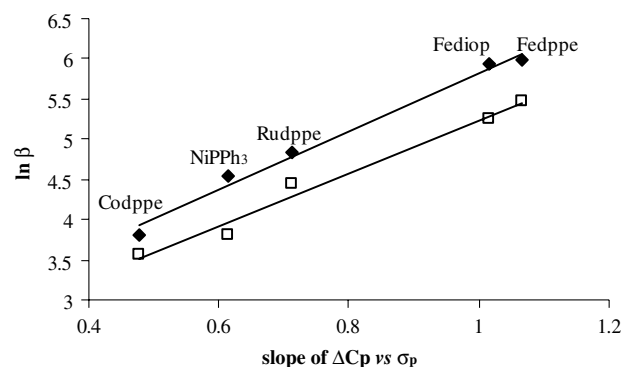


Fig. 6. Plot of $\ln \beta$ vs. ¹³C NMR data of Cp ring in the complexes [NiCp(PPh₃)L][PF₆], [CoCp(dppe)L][PF₆]₂, [RuCp(dppe)L][PF₆] and [FeCp(P-P)L][PF₆]. (L = *p*-NCC₆H₄NO₂ (◆) and *p*-NC(C₆H₄)₂NO₂ (◻); β : first hyperpolarizability; $\Delta C_p = \delta_{C_p}(Y \neq H) - C_p(Y = H)$; σ_p : Hammett parameters).

chromophores if the degree of electronic communication between the corresponding organometallic fragment and nitrile derivatives is known. Keeping this in mind, the synthesis of other monocyclopentadienylmetal complexes by varying the organometallic fragment (i.e., metal, their formal oxidation state and geometry) is currently in progress in order to confirm the quantitative relationship found in this work. Furthermore, different chromophores and metal centers are subject of similar studies in order to ensure the practicability of using NMR spectroscopic data as a probe on the second-order non-linear optical properties of different families of complexes.

3. Conclusion

The family of [CoCp(dppe)(*p*-NCR)][PF₆]₂ complexes with different benzonitrile derivatives has been synthesized. IR spectroscopic data for these complexes shows that the coordination of the nitrile ligands to the metal centre has mainly a σ -type character and has no evidence of metal–ligand π -backdonation contribution. NMR and cyclic voltammetry data suggest a poor electronic π -coupling between the η^5 -cyclopentadienylmetal fragment and the π -system of the nitrile ligands. This poor electronic communication and the absence of any charge transfer band between the organometallic fragment and the nitrile ligands, also recognized by their optical absorption spectra, are consistent with the previously reported low first hyperpolarizabilities of these complexes. The degree of electronic coupling between different η^5 -cyclopentadienylmetal fragments and the nitrile ligands, which were achieved by using NMR spectroscopic data, were correlated to the logarithm of the first hyperpolarizability of the complexes containing *p*-NCC₆H₄NO₂ or *p*-NC(C₆H₄)₂NO₂ chromophores. The linear relationship that was found can be helpful to

predict first hyperpolarizabilities of related complexes with different organometallic fragments and seems to demonstrate that NMR spectroscopic data can be used as a probe on the second-order non-linear optical responses of the family of η^5 -cyclopentadienylmetal complexes with substituted benzonitrile chromophores.

4. Experimental

4.1. General procedures

All preparations and manipulations of the complexes described in this work were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were purified according to the usual methods [28].

The starting materials [CoCp(CO)₂] and [CoCpI₂CO] were prepared as described in the literature [29,30]. The complexes [CoCp(dppe)(*p*-NCC₆H₄NMe₂)] [PF₆]₂ (**1**) and [CoCp(dppe)(*p*-NCC₆H₄C₆H₅)] [PF₆]₂ (**4**) were previously characterized [16]. The *p*-substituted benzonitrile ligands, except *p*-NC(C₆H₄)₂NO₂, were purchased from Sigma–Aldrich and used as received. The ligand *p*-NC(C₆H₄)₂NO₂ was prepared by nitration of *p*-NC-C₆H₄C₆H₅ by standard procedures.

Solid-state IR spectra were measured on a Perkin–Elmer 457 spectrophotometer with KBr pellets; only significant bands are cited in the text. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian Unity 300 spectrometer at probe temperature. The ¹H and ¹³C chemical shifts are reported in parts per million (ppm) downfield from internal Me₄Si and the ³¹P NMR spectra are reported in ppm downfield from external standard 85% H₃PO₄. Coupling constants are reported in Hz. Spectral assignments follow the numbering scheme shown in Fig. 7.

Electronic spectra were recorded at room temperature on a Shimadzu UV-1202 spectrometer in the range of 200–1100 nm. Melting points were obtained using a Reichert Thermovar. The molar conductivities of 1 mM solutions of the complexes in nitromethane were recorded with a Schott CGB55 Konduktometer at room temperature. Microanalyses were performed at Instituto Superior Técnico Laboratories using a Fisons Instruments EA1108 system. Data acquisition, integration and handling were performed using a PC with the software package Eager-200 (Carbo Erba Instruments).

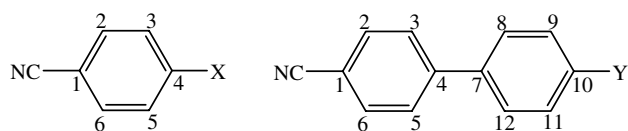


Fig. 7. Numbering scheme for NMR spectral assignments of [CoCp(dppe)(*p*-NCR)] [PF₆]₂ complexes. (X = NMe₂, NH₂, OMe, H, NO₂; Y = H, NO₂).

4.2. Preparation of [CoCp(dppe)(*p*-NCR)] [PF₆]₂

All the complexes were prepared as follows. A solution of [CoCpI₂CO] (0.98 mmol) in dichloromethane (20 ml) was added to a mixture of TlPF₆ (3.00 mmol), dppe (1.10 mmol) and the appropriate *p*-benzonitrile derivative (5.00 mmol) in the same solvent (20 ml). The resultant suspension was stirred at room temperature for 72–120 h. A change was observed from dark-violet to reddish with simultaneous precipitation of TlI. After filtration, the solvent was evaporated under vacuum and the solid residue washed several times with diethyl ether to remove the excess of *p*-benzonitrile derivative. The crude solid was recrystallized from acetone/ethyl ether or dichloromethane/ethyl ether affording the desired complexes as orange-red microcrystalline products.

¹H and ¹³C resonances due to the coordinated DPPE ligand are very similar for all of the complexes and are found at: ¹H NMR (d-acetone) δ 3.37–3.62 (m, 4H, CH₂), 7.68–7.84 (m, 16H, C₆H₅), 8.24–8.36 (m, 4H, C₆H₅); ¹³C NMR (d-acetone) δ 28.03 (t, CH₂, ¹J_{CP} = 21.0), 126.86–127.41 (t, C_{ipso}, ¹J_{CP} = 26.0), 131.05 (m, C_{meta}), 132.81 (s, C_{para}), 134.06 (m, C_{ortho}). The PF₆⁻ counterion gives rise to a resonance at δ -142.7 (sept, J_{PF} = 708.0) in the ³¹P NMR spectra of all complexes.

4.2.1. [CoCp(dppe)(*p*-NCC₆H₄NH₂)] [PF₆]₂ (**2**)

Red crystals; 70% yield, m.p. 183 °C (dec.). Molar conductivity (Ω^{-1} cm² mol⁻¹): 204.2. IR (KBr, cm⁻¹): (N≡C): 2240. ¹H NMR (d-acetone, δ): 6.12 (b, 2H, NH₂), 6.30 (s, 5H, η^5 -C₅H₅), 6.52 (d, 2H, H3, H5, ³J_{HH} = 8.7), 6.56 (d, 2H, H2, H6, ³J_{HH} = 9.0). ¹³C NMR (d-acetone, δ): 93.64 (C1), 94.45 (η^5 -C₅H₅), 113.98 (C3, C5), 135.80 (C2, C6), 140.05 (NC), 155.91 (C4). ³¹P NMR (d-acetone, δ): 81.16. Anal. Calc. for C₃₈H₃₅N₂P₄F₁₂Co: C, 49.05; H, 3.79; N, 3.01. Found: C, 48.57; H, 3.86; N, 2.97%.

4.2.2. [CoCp(dppe)(*p*-NCC₆H₄OMe)] [PF₆]₂ (**3**)

Red crystals; 70% yield, m.p. 181 °C (dec.). Melting point (°C): 181 (dec.). Molar conductivity (Ω^{-1} cm² mol⁻¹): 169.0. IR (KBr, cm⁻¹): (N≡C): 2250. ¹H NMR (d-acetone, δ): 3.86 (s, 3H, OMe), 6.32 (s, 5H, η^5 -C₅H₅), 6.89 (d, 2H, H3, H5, ³J_{HH} = 9.0), 6.95 (d, 2H, H2, H6, ³J_{HH} = 9.0). ¹³C NMR (d-acetone, δ): 56.45 (OMe), 94.72 (η^5 -C₅H₅), 100.69 (C1), 115.65 (C3, C5), 136.34 (C2, C6), 137.79 (NC), 166.70 (C4); ³¹P NMR (d-acetone, δ): 81.13. Anal. Calc. for C₃₉H₃₆NOP₄F₁₂Co: C, 49.54; H, 3.84; N, 1.48. Found: C, 49.48; H, 3.84; N, 1.50%.

4.2.3. [CoCp(dppe)(*p*-NCC₆H₅)] [PF₆]₂ (**5**)

Red crystals; 75% yield, m.p. 186 °C (dec.). Molar conductivity (Ω^{-1} cm² mol⁻¹): 186.5. IR (CH₂Cl₂, cm⁻¹): (N≡C): 2280. ¹H NMR (d-acetone, δ): 6.35 (s,

5H, η^5 -C₅H₅), 6.95 (d, 2H, H2, H6, $^3J_{\text{HH}} = 8.7$), 7.45 (t, 2H, H3, H5, $^3J_{\text{HH}} = 7.8$), 7.72 (d, H, H4). ¹³C NMR (d-acetone, δ): 94.84 (η^5 -C₅H₅), 109.75 (C1), 129.82 (C3, C5), 134.14 (C2, C6), 136.47 (C4), 140.36 (NC). ³¹P NMR (d-acetone, δ): 81.04. Anal. Calc. for C₃₈H₃₄NP₄F₁₂Co: C, 49.80; H, 3.74; N, 1.53. Found: C, 49.70; H, 3.90; N, 1.53%.

4.2.4. [CoCp(dppe)(p-NCC₆H₄C₆H₄NO₂)]/[PF₆]₂ (6)

Red crystals; 81% yield, m.p. 154 °C (dec.). Molar conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 177.8. IR (KBr, cm^{-1}): (N≡C): 2265. ¹H NMR (d-acetone, δ): 6.38 (s, 5H, η^5 -C₅H₅), 7.11 (d, 2H, H2, H6, $^3J_{\text{HH}} = 8.7$), 7.88 (d, 2H, H3, H5, $^3J_{\text{HH}} = 9.0$), 7.98 (d, 2H, H8, H12, $^3J_{\text{HH}} = 8.7$), 8.35 (d, 2H, H9, H11). ¹³C NMR (d-acetone, δ): 94.95 (η^5 -C₅H₅), 109.77 (C1), 124.94 (C9, C11), 128.66 (C3, C5), 129.44 (C8, C12), 134.83 (C2, C6), 141.08 (NC), 145.16 (C4), 145.95 (C7), 148.99 (C10). ³¹P NMR (d-acetone, δ): 80.85. Anal. Calc. for C₄₄H₃₇N₂O₂P₄F₁₂Co: C, 50.93; H, 3.59; N, 2.70. Found: C, 51.46; H, 3.56; N, 2.82%.

4.2.5. [CoCp(dppe)(p-NCC₆H₄NO₂)]/[PF₆]₂ (7)

Red crystals; 65% yield, m.p. 174 °C (dec.). Molar conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 173.2. IR (KBr, cm^{-1}): (N≡C) 2275. ¹H NMR (d-acetone, δ): 6.40 (s, 5H, η^5 -C₅H₅), 7.28 (d, 2H, H2, H6, $^3J_{\text{HH}} = 8.7$), 8.26 (d, 2H, H3, H5, $^3J_{\text{HH}} = 8.7$). ¹³C NMR (d-acetone, δ): 95.15 (η^5 -C₅H₅), 115.50 (C1), 124.58 (C3, C5), 135.78 (C2, C6), 140.81 (NC), 152.10 (C4). ³¹P NMR (d-acetone, δ): 80.75. Anal. Calc. for C₃₈H₃₃N₂O₂P₄F₁₂Co: C, 47.53; H, 3.46; N, 2.92. Found: C, 46.91; H, 3.37; N, 2.90%.

4.2.6. [CoCp(dppe)(NCCH₃)]/[PF₆]₂ (8)

Red crystals; 59% yield, m.p. 147 °C (dec.). Molar conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 192.6. IR (KBr, cm^{-1}): (N≡C) 2260. ¹H NMR (d-acetone, δ): 1.93 (s, 3H, CH₃), 6.19 (s, 5H, η^5 -C₅H₅). Anal. Calc. for C₃₃H₃₂NP₄F₁₂Co: C, 46.44; H, 3.78; N, 1.64. Found: C, 46.16; H, 3.63; N, 1.62%.

4.3. Electrochemical experiments

The electrochemistry instrumentation consisted of a EG&A Princeton Applied Research Model 273A Potentiometer and experiments were monitored in a PC computer loaded with Model 270 Electrochemical Analysis Software 3.00 of EG&A from Princeton Applied Research. Potentials were referred to a calomel electrode containing a saturated solution of potassium chloride. The working electrode was a 2-mm piece of platinum wire for voltammetry. The secondary electrode was a platinum wire coil. Cyclic voltammetry experiments were performed at room temperature and -20 °C in a PAR polarographic cell. Solutions studied were 1 mM

in solute and 0.1 M in tetrabutylammonium hexafluorophosphate as supporting electrolyte. The electrochemical system was checked with a 1 mM solution of ferrocene in acetonitrile and dichloromethane for which the ferrocenium/ferrocene electrochemical parameters ($E_{\text{p}/2} = 0.38 \text{ V}$ in acetonitrile and $E_{\text{p}/2} = 0.41 \text{ V}$ in dichloromethane; $\Delta E = 60\text{--}70 \text{ mV}$; $i_{\text{a}}/i_{\text{c}} = 1$) were in good agreement with the literature [31,32].

The electrolyte was purchased from Sigma–Aldrich, recrystallized from ethanol, washed with diethyl ether, and dried under vacuum at 110 °C for 24 h. Reagent grade acetonitrile and dichloromethane were dried over P₂O₅ and CaH₂, respectively, and distilled before use under argon atmosphere. An argon atmosphere was maintained over the solution during the experiments.

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