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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 $[CoCp(dppe)(p\text{-}NCR)][PF_6]_2$ (R = $C_6H_4NMe_2$, $C_6H_4NH_2$, C_6H_4OMe, $C_6H_4C_6H_5$, C_6H_5, $C_6H_4C_6H_4NO_2$, and $C_6H_4NO_2$) 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.

Keywords: Cobalt complexes; Benzonitrile derivatives; Cyclic voltammetry; Electronic coupling; Non-linear optics

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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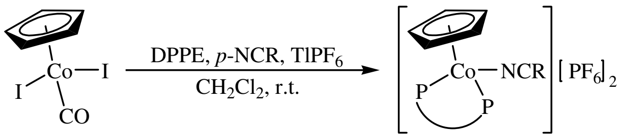
π-backdonation through d_{metal}–π^*_{ligand} interaction was found to play an important role on the second-order NLO response of this family of compounds, where the driving force is the presence of the strong acceptor NO_2 group on the end of the π-system of the chromophore [16]. In our earlier studies 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 [CoCp(dppe)(*p*-NCR)][PF_6]$_2$ (R = $C_6H_4NMe_2$, $C_6H_4NH_2$, C_6H_4OMe, $C_6H_4C_6H_5$, C_6H_5, $C_6H_4C_6H_4NO_2$, and $C_6H_4NO_2$) 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 [CoCpI_2CO] with a mixture of DPPE, $TlPF_6$ and excess of the appropriate *p*-benzonitrile derivative in dichloromethane at room temperature (Scheme 1). After work-up, orange-red crystals of [CoCp(dppe)(*p*-NCR)][PF_6]$_2$ (R = $C_6H_4NMe_2$ (**1**) [16], $C_6H_4NH_2$ (**2**), C_6H_4OMe (**3**), $C_6H_4C_6H_5$ (**4**) [16], C_6H_5 (**5**), $C_6H_4C_6H_4NO_2$ (**6**), and $C_6H_4NO_2$ (7)) were obtained with yield in the range of 62–87%. The synthesis of the complexes involves the formation of [CoCp(dppe)I]$^+$ in situ, followed by iodide abstraction by $TlPF_6$ and coordination of the different *p*-benzonitrile ligands. The compounds are quite stable 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 ^{1}H, ^{13}C and ^{31}P NMR spectra. The molar conductivities of ca. 10^{-3} M solutions of the complexes in nitromethane, in the range 165–204 Ω^{-1} cm^2 mol^{-1}, are consistent with values reported for 2:1 type electrolytes [17].



R= $C_6H_4NMe_2$ (**1**), $C_6H_4NH_2$ (**2**), C_6H_4OMe (**3**), $C_6H_4C_6H_5$ (**4**), C_6H_5 (**5**), $C_6H_4C_6H_4NO_2$ (**6**), $C_6H_4NO_2$ (**7**)

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

Typical IR bands confirm the presence of the cyclopentadienyl ligand (ca. 3050–3080 cm^{-1}), the PF_6^- anion (840 and 550 cm^{-1}) and the coordinated nitrile (2235–2275 cm^{-1}) in all complexes. A positive shift of (CN) upon coordination was observed in the range 15–55 cm^{-1}. This means a σ-coordinated nitrile in which the overall N≡C bond is strengthened upon coordination. The same behavior was found previously on [NiCp-PPh_3(*p*-NCR)[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].

^{1}H 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 0.73–0.87 ppm for *ortho* (relative to the NC group) protons and 0.08–0.31 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 N≡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