Synthesis, structure and NLO properties of a 1,3,5-substituted tricationic cobaltocenium benzene complex

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1. Introduction

The possibility of an interaction of metallocenes, precisely of the correspondent metal sites, through a conjugated π-system is of utmost interest for research on nonlinear optics (NLO), magnetic behavior or interesting electronic properties [1].

Within our group we have been working on complexes, where metallocenes were linked via a 1,8-naphthalene clamp [2], via molecular switches like the dithienylethene switch [3] or on 1,3,5-trismetallocenyl-substituted, cationic (η5-benzene)(η5-cyclopentadienyl)ruthenium(II) complexes [4].

In continuation of this work we were interested in further research on the 1,3,5-substituted C3-symmetric type of compounds, and especially in their nonlinear optical activity. Recent results had demonstrated that the first hyperpolarizability of octopolar organometallic NLOphores clearly seems to profit from a perpendicular coordinated acceptor function, like a CpRu+-fragment coordinated towards the central benzene ring. This 1D acceptor unit even seemed to be more beneficial than the 2D octopolar system made up by three donor functions in 1,3,5-positions of the ring [4c].

Facing these results, it was consistent to proceed with our investigations and strive for a solely 1,3,5-trismetallocenyl-substituted system, wherein the metallocene units this time behave as acceptor functions. Looking for an electron accepting metallocene, we were moving from diamagnetic, neutral metallocenes (e.g. ruthenocene or ferrocene) towards a cationic metallocene – the cobaltocenium entity.

Due to the disparate reaction behavior of ferrocene and cobaltocene a new synthetic strategy had to be devised in order to obtain the desired 1,3,5-substituted benzene complex with cobaltocenium substituents. In this paper, we present the synthesis, characterization, electrochemical and (non)linear optical properties of the correspondent complexes with cobalt in the oxidation states +1 and +3, respectively.

2. Results and discussion

2.1. Synthesis

1,3,5-triethynylbenzene was threefold lithiated and then reacted with cobaltocenium iodide in a nucleophilic addition, thereby leading to the exo addition product, \([1,3,5\text{-}\text{tris(\(\eta^5\)-2,4-cyclopentadienyl-1-ethynyl)-cobalt(I)}\text{benzene}]\). Upon hydride abstraction, the target compound \([1,3,5\text{-}\text{tris(\(\eta^5\)-2,4-cyclopentadienyl-1-ethynyl)-cobalt(III)}\text{benzene tris(hexafluoridophosphate})\] was obtained. Both complexes were fully characterized and, in continuation of previous investigations, investigated in terms of the influence of an octopolar arrangement of acceptor functions on the nonlinear optical activity of organometallic compounds.

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cyclopentadien-1-yl)[η3,2,4-cyclopentadieny1-1-ethyl]cobalt(1)] benzene (1) in a yield of 84% (Scheme 1). The cobalt(I) complex 1 seems to be air stable as a solid, but when dissolved in tetrahydrofuran or toluene a slow decomposition takes place, resulting in a brownish, unidentified precipitate. 1 was subjected to a threefold hydride abstraction utilizing tritylium hexafluorophosphate, which resulted in the air stable, tricationic complex [1,3,5-tris(η5-2,4-cyclopentadien-1-yl)[η5,2,4-cyclopentadieny1-1-ethyl]cobalt(III)]benzene tris(hexafluorophosphate) 2 in a yield of 75% (Scheme 1). Yields of other akin reactions, leading to a [η5-2,4-cyclopentadien-1-yl][η5,2,4-cyclopentadieny1-1-ethyl]cobalt(1) and [η5-2,4-cyclopentadien-1-yl][η5,2,4-cyclopentadieny1-1-ethyl]cobalt(III) complex, respectively, were reported with slightly higher yields [5]. This may be due to the enhanced steric hindrance in the case of complexes 1 and 2.

2.2. Molecular structure determination

Suitable crystals of compound 2 for X-ray structure analysis were obtained via gas phase diffusion of diethyl ether into a solution of 2 in acetonitrile. 2 crystallizes in the triclinic space group P̅T. The proposed structure was confirmed (Fig. 1), however, the quality of refinement suffers from disorder of the whole molecule as well as inclusion of disordered solvent molecules. Nevertheless, it can be stated that the averaged bond length of the C-C-triple bonds [1.959(9) Å] is comparable in size to the analogous, neutral or cationic ferrocenyl-substituted structures [4b,6]. A detailed discussion of the structural data, for example regarding a possible bond length alternation is unfortunately inapplicable due to the aforementioned disorders.

2.3. Spectroscopic characterization

The cobalt(III) complex 2, as well as the precursor compound 1 with cobalt in oxidation state +1 could be characterized by means of nuclear magnetic resonance spectra. The most prominent feature of the NMR spectra of 1 is the signal for the hydride attached to the sp3 hybridised carbon atom, which diminishes completely after hydride abstraction. The NMR shifts are in good agreement with other 1,3,5-substituted benzene derivatives, which are not separable under the given conditions. This result is in good agreement with other 1,3,5-substituted benzene derivatives, corroborating the intramolecular interaction between metal centers in meta position of arene derivatives to be weak [4,7].

The IR spectrum of 1 displays the expected stretching vibration of the C-C triple bond (ν = 2207 cm⁻¹) and confirms the abrogated aromaticity of the Cp ring via the occurrence of aliphatic CH stretching vibrations (ν = 2955 cm⁻¹ and 2855 cm⁻¹). The rearomatization of the Cp rings and the electron withdrawing nature of the cationic Co(III) centers in 2 enhances the bond strength of the C-C-triple bond (ν = 2228 cm⁻¹). This effect of the threefold acceptor unit seems to surpass the stabilizing effect of a perpendicuular coordinated acceptor function CpRu⁺ (ν = 2218 cm⁻¹) [4b,6], which might also be interesting when it comes to the nonlinear optical activity.

The redox behavior of the tris-cobaltocenium complex 2 was further investigated by cyclic voltammetry (CV) experiments (dichloromethane at r.t., 0.2 M Bu4NPF6, Pt electrodes, vs. E1/2 (FCH +/ -FCH) = 0 V, scan rate 200 mV/s, Fig. 2). In a potential range of -0.55 V to -1.55 V one reversible redox wave is observed for 2. The separation of the peak potential ΔE = 0.076 V gives, in comparison with the ferrocene standard (ΔE (Fc/Fc⁺) = 0.076 V), an indication that the reversible redox wave (E1/2 = -1.14 V) belongs to simultaneous three one-electron reduction steps (Co3+/Co2+), which are not separable under the given conditions. This result is in good agreement with other 1,3,5-substituted benzene derivatives, corroborating the intramolecular interaction between metal centers in meta position of arene derivatives to be weak [4,7].

UV/Vis spectroscopic studies were performed with solutions of compounds 1 and 2 in dichloromethane. In order to study solvatochromism, 2 was also measured in a solution of acetonitrile (Fig. 3/Table 1).

A solvatochromic effect gives an indication of the dipole change Δμ between the ground and the excited state and is thus relevant for the first hyperpolarizability β according to the two-level approximation [9]. For 2, the resolution of the high energy (HE) bands <300 nm is too low to determine a solvatochromatic effect, however, the low energy (LE) band clearly undergoes a strong hypsochromic shift with increasing solvent polarity. This negative solvatochromism of 2 can, through the two-level approximation, be assumed as an indication for a high polarizability, yielding a second-order nonlinear optical activity.¹

2.4. NLO measurements

The measurement of the second-harmonic generation (SHG) for complex 2 was performed by hyper-Rayleigh scattering [10]. Therefore, solutions of the complex 2 in acetonitrile were subjected to hyper-Rayleigh scattering (HRS) measurements with a femtosecond pulsed laser source working at 840 nm. Unfortunately, no intensity of a second-harmonic generation signal could be detected during the measurement. The hyperpolarization in the presence of irradiation provided by a femtosecond laser might be too weak to be observed.

3. Conclusion

Based on our interest in 1,3,5-substituted organometallic complexes as nonlinear optical (NLO) active chromophores, we achieved a synthetic strategy to obtain a cationic threefold cobaltocenium-substituted, ethynyl-bridged benzene compound. All compounds were sufficiently characterized by NMR, UV/Vis, and IR spectroscopy as well as mass spectrometry.

¹ The two-level approximation is primarily valid for organic 1D-NLO chromophores, but nevertheless it may give a first indication of nonlinear optical activity also for other chromophores.
In addition, the interaction of the cobalt centers was investigated utilizing cyclovoltammetry. There is no evidence for a strong communication between the cobaltocenium moieties in 2, nevertheless the observed reversible redox wave indicates that the redox process takes places within three one-electron steps and not within one three-electron step.

The HE band of 2 displayed negative solvatochromism, however, hyper-Rayleigh scattering (HRS) measurements with a femtosecond laser source (840 nm) could not indicate a NLO activity of this complex.

Summarizing our previous investigations [4b,c] on (a) 1,3,5-donor substituted benzene systems with a perpendicular coordinated acceptor function (1,3,5-D-π-A), on (b) donor-free benzene systems with perpendicular acceptor function (π-A), (c) 1,3,5-donor substituted benzene systems without a perpendicular coordinated acceptor function (1,3,5-D-π) and the present investigation (d) on 1,3,5-acceptor substituted benzene systems without perpendicular coordinated acceptor function (1,3,5-A-π), the determined nonlinear optical activities further underline the importance of the 1D attribute to the octopolar 2D arrangement of 1,3,5-attached donor or acceptor functions.

4. Experimental

4.1. General procedures

All reactions were carried out under dry nitrogen using standard Schlenk techniques. All reaction solvents were saturated with nitrogen and dried with calcium hydride (dichloromethane) and potassium (tetrahydrofuran), respectively, 1,3,5-triethynylbenzene [11], bis[η⁵-2,4-cyclopentadien-1-yl]cobalt(III)-iodide [12] and triphenylcarbenium hexafluoridophosphate [13] were synthesized according to literature procedures.

NMR spectra were acquired at r.t. on a Bruker Fourier 300 spectrometer. Chemical shifts were referenced against residual solvent signal as an internal standard. For 2, the indication of positions α and β for the protons of substituted Cp rings is based on an arbitrary assignment. For IR spectra, samples were prepared as KBr pellets and recorded with a FT-IR spectrometer Bruker VERTEX 70. For MALDI-HRMS, n-cyano-4-hydroxycinnamic acid was used as a matrix (Bruker UltrafleXtreme).

4.2. Preparation of [1,3,5-Tris(η⁵-2,4-cyclopentadien-1-yl)(η⁴-2,4-cyclopentadienyl-1-ethynyl)cobalt(I)]benzene (1)

A solution of 1,3,5-triethynylbenzene (511 mg, 3.40 mmol) in tetrahydrofuran (43 mL) was cooled to –8°C. n-Butyllithium (1.6 M in n-hexane, 6.5 mL, 10 mmol) was added dropwise and the solution was allowed to warm to –2°C over 1.5 h. Bis[η⁵-2,4-cyclopentadien-1-yl]cobalt(III) iodide (4.31 g, 13.7 mmol) was added in three portions over the course of one hour. The greyish suspension thereby turned red. After 1.5 h stirring, the solution was allowed to warm to r.t. and was stirred for further 17.5 h. Degassed water (30 mL) was added and the reaction mixture was stirred for 1 min, after which the reaction vessel could be exposed to air without further precautions. The organic layer was separated and purified via column chromatography (Al₂O₃, petroleum ether/toluene 9/1 → pure toluene, v/v). After removal of the solvent under reduced pressure, the product was obtained as a red solid (2.05 g, 2.87 mmol, 84% yield).

1H NMR (C₆D₅CD₃, 300 MHz): δ = 7.20 (3H, s, Harom.), 5.02 (6H, AA'XX), 3J(H,H) = 1.9 Hz, H₅(Cp₂), 4.44 (15H, HC₃'), 3J(H,H) = 2.4 Hz, H₅(Cp₂), 2.59 (5H, AA'XX), 3J(H,H) = 1.9 Hz, 3J(H,H) = 2.4 Hz, H₃(C₄H₇) ppm.

13C NMR (C₄D₈O, 75 MHz): δ = 178.2 (Carom, tert), 159.2 (Carom, quart), 129.5 (Carom, tert), 124.6 (Carom, quart), 128.2 (Carom, tert), 125.1 (Carom, quart), 92.6 (CC₃), 80.1 (CC₄), 75.5 (CC₅), 41.5 (CC₆) ppm. MALDI-HRMS [m/z (intensity)]: calcld. 714.058 (100), 715.061 (15).

Fig. 1. Molecular structure of the cationic complex 2. Anions, solvents, less occupied disorders and hydrogen atoms are omitted for clarity reasons (displacement ellipsoids at a 30% probability level, non-labeled atoms are C atoms).

Fig. 2. Cyclic voltammogram of the trinuclear cobalt complex 2. Scan rate 200 mV s⁻¹, referenced against FeH/Fc⁺⁺, electrolyte 0.2 M [Bu₄N][PF₆], dichloromethane solution.

Fig. 3. UV/Vis spectra of the trinuclear cobalt complexes 1 and 2 (in acetonitrile or dichloromethane, respectively).
precipitated as yellow solid and could be separated via filtration. A co-crystallized molecule of fluoridophosphate anions show independent positional disorder of the parent cation. Co2 refined to an occupancy of 0.59486(5066). A second cobalt atom site Co21 was found close to Co2, indicating a whole molecule disorder of the parent cation. Co2 refines to an occupancy of 0.59486(5066). A co-crystallized molecule of diethyl ether refined to an occupancy of 0.70945(1334). Two of the hexafluoridophosphate anions show independent positional disorder. For details regarding the refinement of the disordered anions as well as disordered solvent molecules, please refer to the CIF file.

After complete refinement, residual electron densities could not be described by chemically reasonable models. Those residual electron densities were removed by using the SQUEEZE routine implemented within PLATON [17]. A total number of 47 electrons was squeezed from one void.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.07.021.

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Primary atom site locations for 2 were assigned with EDM [15] from electron densities obtained by SUPERFLIP [16]. Remaining secondary non-carbon atom sites were located from the difference Fourier map. All non-H atoms were refined with anisotropic displacement parameters. Carbon-bound hydrogen atoms were positioned geometrically and refined riding on their respective carbon atom. Bond lengths were fixed at 0.95 Å (aromatic H), 0.98 Å (methyl H), and 0.99 Å (methylene H). Uiso(H) was fixed at 1.5 Uiso(C) for methyl hydrogens or 1.2 Uiso(C) for the remaining hydrogens. Methyl hydrogen atoms were idealized in staggered geometry (HFIX 33).

A second cobalt atom site Co21 was found close to Co2, indicating a whole molecule disorder of the parent cation. Co2 refines to an occupancy of 0.59486(5066). A co-crystallized molecule of diethyl ether refined to an occupancy of 0.70945(1334). Two of the hexafluoridophosphate anions show independent positional disorder. For details regarding the refinement of the disordered anions as well as disordered solvent molecules, please refer to the CIF file.

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