Synthesis and structural characterization of 1,8-biscobaltocen-1′-ylium-naphthalene dication: Towards paramagnetic, cofacially stacked metallocenes

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Abstract

The double nucleophilic addition of 1,8-dilithionaphthalene to cobaltocenium cations reveals the neutral dinuclear complex 1,8-bis[(η^5-cyclopentadienyl)(η^4-1′,3′-cyclopentadien-5′-yl)cobalt(I)]-naphthalene (**2**). Abstraction of two hydrides yields the dinuclear dicationic complex 1,8-biscobaltocen-1′-ylium-naphthalene bis(tetrafluoroborate) (**3**(BF$_4$)$_2$). Both complexes are characterized by X-ray structure analysis. In addition, the redox chemistry of **3**(BF$_4$)$_2$ was investigated, demonstrating the electrochemical stability of three oxidation states +2, +1 and 0.

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Keywords: Stacked metallocenes; Cyclic voltammetry; Cobaltocenium; X-ray structure analysis; Dinuclear complexes

1. Introduction

Cofacially arranged sandwich complexes are very promising candidates with respect to novel chemical and physical properties [1]. In particular, a combination of paramagnetic metallocenes MCp$_2$ may result in very interesting magnetic properties, since some of these sandwich compounds exhibit pronounced anisotropic magnetic susceptibilities (M = V, Cr, Mn, Co, and Ni) [2], thus making it worthwhile to investigate the magnetic interaction between cofacially stacked subunits [3]. Initial preparative work on this type of compounds has been done by Rosenblum and coworkers and they successfully fixed the cofacial arrangement of metallocenes by introducing a "naphthalene clamp" (Fig. 1) [4,5].

However, this work was focused on diamagnetic metallocenes, which were symmetrically arranged. Recently, we reported on corresponding unsymmetrically dipolar bis-sandwich substituted naphthalene derivatives and their capability for second harmonic generation [6].

In this paper, we present the synthesis, electrochemical properties and crystal structure of a naphthalene compound, which is disubstituted with two cobaltocenium cations and is regarded as the precursor for the cofacially stacked paramagnetic biscobaltocene derivative.

2. Results and discussion

2.1. Synthesis

The first step towards the cofacially stacked biscobaltocenium derivative was the transformation of 1,8-diiodonaphthalene (**1**) to the dilithiated intermediate (Scheme 1) [7], which was subjected to a double nucleophilic addition with two equivalents of cobaltocenium iodide. The two hydrogen atoms bound to the sp^3-carbon atoms of the resulting 1,8-bis[(η^5-cyclopentadienyl)(η^4-1′,3′-cyclopentadien-5′-yl)cobalt(I)]-naphthalene (**2**) were eliminated as hydride ions by tritylium tetrafluoroborate [8] resulting in
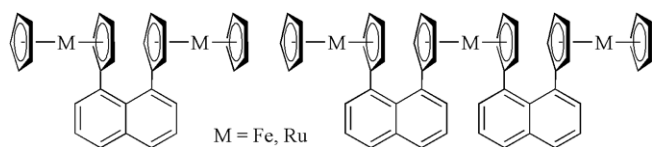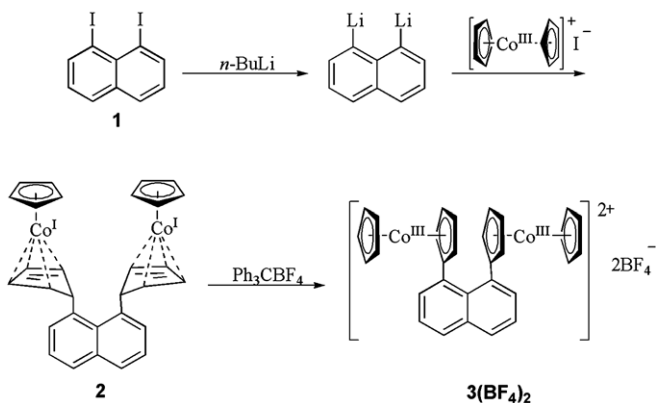
Fig. 1. Cofacially stacked metallocenes by a "naphthalene clamp" [4,5].

Scheme 1. Synthesis of 1,8-biscobaltocen-1′-ylium-naphthalene bis(tetrafluoroborate) (**3**(BF$_4$)$_2$).

the diamagnetic complex 1,8-biscobaltocen-1′-ylium-naphthalene bis(tetrafluoroborate) (**3**(BF$_4$)$_2$).

3. Crystal structure

Solid-state structures of compounds **2** and **3** were obtained by single crystal X-ray diffraction analysis. The cobalt(I) complex **2** crystallizes in the monoclinic space group *C2/c*.

As expected, the naphthalene unit is bound in *exo*-position relative to the sandwich units. The molecule contains a

C_2 axis along the bond between C2 and C3 (Fig. 2). The bonding vector of C1–C11 and its symmetry related vector C1A–C11A are bent apart as seen by the nonbonding distances C1–C1A = 261.1(4) pm and C11–C11A = 307.7(4) pm (Table 1). The torsion angle of the *peri*-positions of the naphthalene clamp is only 1.7(1)° (compare Fig. 2: right), which allows the sandwich complex moieties to adopt a more or less parallel orientation. This weak distortion can be due to the steric demand of the two Co(I)-complexes. On the whole the naphthalene entity is only marginally affected by the sandwich substituents. The structural features of the cobalt sandwich complexes of **2** very much resemble those of the (η^5-cyclopentadienyl)(η^4-1,3-cyclopentadiene)cobalt(I) compounds reported recently [9–11]. The two five-membered rings are nearly ecliptically arranged and the two planes of the cyclic ligands enclose an angle of 4.3(2)°, demonstrating an

Table 1
Selected interatomic distances (pm) and angles (°) of **2**

Co(1)–C(12)	204.2(3)	C(15)–C(11)	152.5(4)
Co(1)–C(13)	196.8(3)	C(16)–C(17)	140.8(5)
Co(1)–C(14)	195.2(4)	C(17)–C(18)	140.7(5)
Co(1)–C(15)	201.9(3)	C(18)–C(19)	142.2(5)
Co(1)–Cent$_{[C(12)-C(15)]}$[a,b]	162.6(3)	C(19)–C(20)	141.5(5)
Co(1)–C(16)	204.8(4)	C(20)–C(16)	142.3(5)
Co(1)–C(17)	207.5(4)		
Co(1)–C(18)	208.5(3)	C(1)–C(11)[b]	154.9(4)
Co(1)–C(19)	203.6(3)	Co(1)–Co(1A)[b]	563.0(9)
Co(1)–C(20)	204.6(3)	C(1)–C(1A)[b]	261.1(4)
Co(1)–Cent$_{[C(16)-C(20)]}$[a,b]	166.9(3)	C(11)–C(11A)[b]	307.7(4)
C(11)–C(12)	153.2(4)		
C(12)–C(13)	140.6(5)	C(1)–C(11)–C(1A)–C(11A)[b]	1.7(1)
C(13)–C(14)	142.6(5)	plane$_{[C12-C15]}$–plane$_{[C16-C20]}$[b]	4.3(2)
C(14)–C(15)	142.6(5)	plane$_{[C12-C15]}$–plane$_{[C11-C12-C15]}$[b]	30.8(2)

[a] Cent: centroid of the corresponding Cp ligand.
[b] See ref. [12].
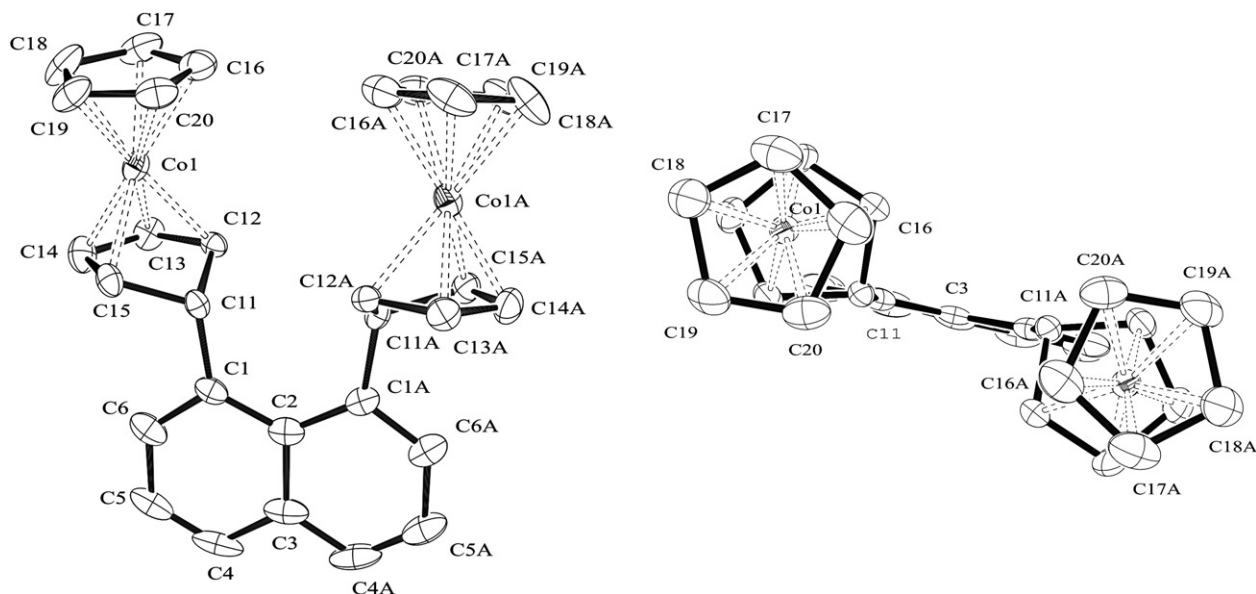
Fig. 2. ORTEP plot of **2** (50% ellipsoids, hydrogen atoms are omitted for clarity).

almost parallel alignment of the π-ligands. The sp^3 carbon atom C11 is bent out of the plane [C12–C15] by 30.8(2)°, corroborating the η^4-coordination mode of the substituted cyclopentadiene ligand.

1,8-Biscobaltocen-1′-ylium-naphthalene bis(tetrafluoroborate) (3(BF$_4$)$_2$) crystallizes in the monoclinic space group *P2(1)/n* with one molecule of water per asymmetric unit. The arrangement of the metallocene units to each other and relative to the naphthalene moiety is as known for this type of compounds and has been reported for prototype sandwich structures (Fig. 3, Table 2) [4,6,13,14]. The most distinctive feature is the torsion angle of 24.5° between the bonds of C1–C11 and C8–C21 (Fig. 4, Table 3). This strong deformation of the structure commonly occurs for naphthalene derivatives disubstituted in the 1,8-position by aromatic molecules [3,4,15,16]. The tilt angle between the best plane of the naphthalene-bound Cp ligands and the best plane of the connected six-membered naphthalene rings amounts to 48.1(2)° and 47.4(2)°, respectively, (Fig. 4,
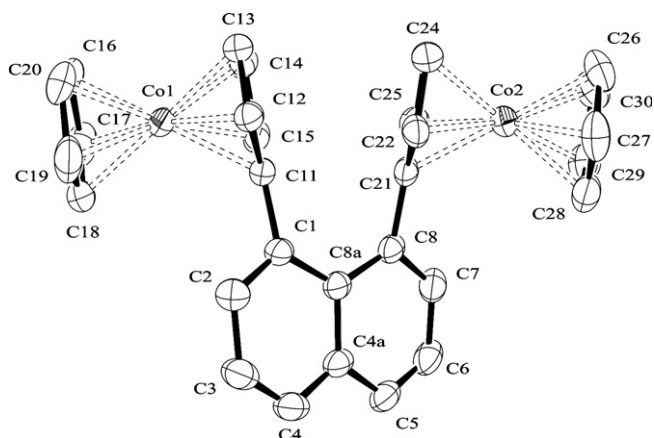
Table 3) which is due to the steric repulsion of the two cofacially arranged Cp ligands [6]. The view along the metallocene axis shown in Fig. 4 (right) demonstrates the one-dimensional stacking of the sandwich units achieved by the naphthalene clamp.

Table 3 shows a comparison of selected interplanar and torsion angles and interatomic distances for the two

Fig. 3. ORTEP plot of 3(BF$_4$)$_2$ (50% ellipsoids, hydrogen atoms, crystal water and BF$_4$-anions are omitted for clarity).

Table 2
Selected bond lengths (pm) of 3(BF$_4$)$_2$ and the isoelectronic 1,8-bisferrocen-1′-yl-naphthalene (4) [4d]

	3(BF$_4$)$_2$	4
M(1)–C(11)	206.3(2)	207.6(3)
M(1)–C(12)	203.0(2)	204.3(3)
M(1)–C(13)	202.0(2)	204.2(4)
M(1)–C(14)	202.6(2)	204.3(4)
M(1)–C(15)	202.9(2)	204.4(3)
M(1)–Cent$_{[C(11)–C(15)]}$[a,b]	163.6(1)	165.7(1)
M(1)–C(16)	202.7(2)	204.3(4)
M(1)–C(17)	202.6(3)	203.5(4)
M(1)–C(18)	201.7(3)	203.7(4)
M(1)–C(19)	202.4(3)	202.7(5)
M(1)–C(20)	202.4(2)	203.8(5)
M(1)–Cent$_{[C(16)–C(20)]}$[a,b]	163.4(1)	165.5(1)
M(2)–C(21)	206.1(2)	206.7(3)
M(2)–C(22)	202.5(2)	204.3(3)
M(2)–C(23)	202.1(2)	205.0(4)
M(2)–C(24)	202.3(2)	204.4(4)
M(2)–C(25)	202.8(2)	203.4(3)
M(2)–Cent$_{[C(21)–C(25)]}$[a,b]	163.4(1)	165.8(1)
M(2)–C(26)	201.1(2)	204.4(4)
M(2)–C(27)	201.8(2)	203.8(4)
M(2)–C(28)	202.8(2)	203.1(4)
M(2)–C(29)	203.6(2)	204.0(4)
M(2)–C(30)	202.4(2)	204.7(5)
M(2)–Cent$_{[C(26)–C(30)]}$[a,b]	163.0(1)	165.8(1)
Cp-ring C–C distance[c]	139.3(4)−143.4(3)	137.5(7)−146.3(8)

[a] See ref. [12].
[b] Cent: centroid of the corresponding Cp ligand.
[c] Mean C–C bond length of the Cp ligands; standard deviations are shown in brackets.
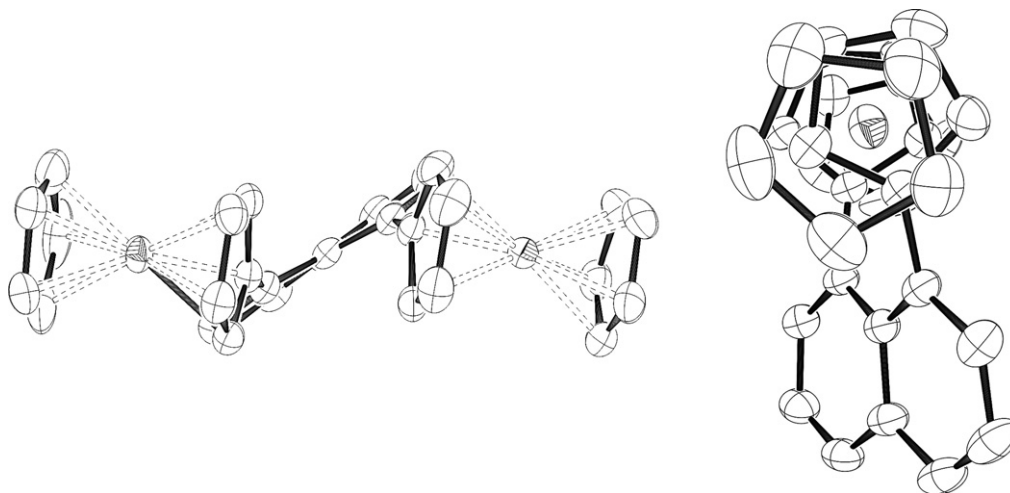

Fig. 4. ORTEP plot: Cofacial arrangement of cobaltocenium fragments in 3(BF$_4$)$_2$; left: interplanar distortion between metallocene and naphthalene; right: view along metallocene axis; (50% ellipsoids, hydrogen atoms, crystal water and BF$_4$-anions are omitted for clarity).

Table 3
Selected interplanar and torsion angles (°) and interatomic distance [pm] between naphthalene and metallocene units[a]

3(BF$_4$)$_2$		4	
Cp$_{C(11)-C(15)}$-Cp$_{C(21)-C(25)}$	20.4(1)	Cp$_{C(11)-C(15)}$-Cp$_{C(21)-C(25)}$	29.0(1)
Cp$_{C(11)-C(15)}$-naphthalene[b]	48.1(1)	Cp$_{C(11)-C(15)}$-naphthalene[b]	40.3(1)
Cp$_{C(21)-C(25)}$-naphthalene[b]	47.4(1)	Cp$_{C(21)-C(25)}$-naphthalene[b]	42.4(1)
C(11)–C(1)–C(8)–C(21)	24.5(2)	C(11)–C(1)–C(8)–C(21)	32.7(3)
C(1)–C(11)	148.8(3)	C(1)–C(11)	148.9(5)
C(8)–C(21)	148.2(3)	C(8)–C(21)	148.6(5)
C(1)–C(8)	254.8(1)	C(1)–C(8)	255.8(5)
C(11)–C(21)	288.9(2)	C(11)–C(21)	295.9(5)
Co(1)–Co(2)	638.3(1)	Fe(1)–Fe(2)	658.9(2)
Cent$_{[C(11)-C(15)]}$-Cent[c]$_{[C(16)-C(20)]}$	326.8(2)	Cent$_{[C(11)-C(15)]}$-Cent[c]$_{[C(16)-C(20)]}$	342.1(1)
Cent$_{[C(11)-C(15)]}$-Cent[c]$_{[C(21)-C(25)]}$	321.8(2)	Cent$_{[C(11)-C(15)]}$-Cent[c]$_{[C(21)-C(25)]}$	331.1(1)
Cent$_{[C(21)-C(25)]}$-Cent[c]$_{[C(26)-C(30)]}$	326.3(2)	Cent$_{[C(21)-C(25)]}$-Cent[c]$_{[C(26)-C(30)]}$	331.6(9)

[a] See Ref. [12].
[b] Best plane of the adjacent six-membered naphthalene ring.
[c] Cent: centroid of the corresponding Cp ligand.

complexes 3(BF$_4$)$_2$ and 1,8-bisferrocen-1′-yl-naphthalene (4) [4d]. The data demonstrate that the naphthalene framework in 3(BF$_4$)$_2$ is less affected than in the ferrocenyl congener 4. The cobalt sandwich units are closer to a perpendicular arrangement with respect to the naphthalene plane and the nonbonding distances between the carbon atoms C(1)–C(8) and C(11)–C(21) are smaller in 3(BF$_4$)$_2$. In addition, the torsion angle C(11)–C(1)–C(8)–C(21) is significantly decreased: 24.5(2)° versus 32.7(3)°. This may be due to the higher positive charge of the central metal atom in 3(BF$_4$)$_2$; the Co^{III} ions cause an electrostriction, which results in a weaker repulsion of the cyclopentadiendiyl rings bound to the aromatic backbone. The effect is best recognized in the metal-metal distance, which is about 20 pm shorter in the dinuclear cobalt complex compared to ferrocene derivative 4, whereas the distance between the metal atom and the centroids of the Cp ligands only differs by 2 pm.

4. Redox properties

1,8-biscobaltocen-1′-ylium-naphthalene bis(tetrafluoroborate) (3(BF$_4$)$_2$) has been investigated by means of cyclic voltammetry. The cyclic voltammogram displays two not completely separated redox couples with potentials in the range of the cobaltocenium cation (dotted line in Fig. 5, Table 4), indicating the stability of the complex in three different oxidation states and the possibility of reducing the dicationic compound 3^{2+} to the neutral, paramagnetic 1,8-biscobaltocenyl-naphthalene. The difference between the two redox couples amounts to 230 mV, in accordance with 1,8-bisferrocen-1′-yl-naphthalene (4), which displays a corresponding difference about 200 mV [6] (see Table 4).
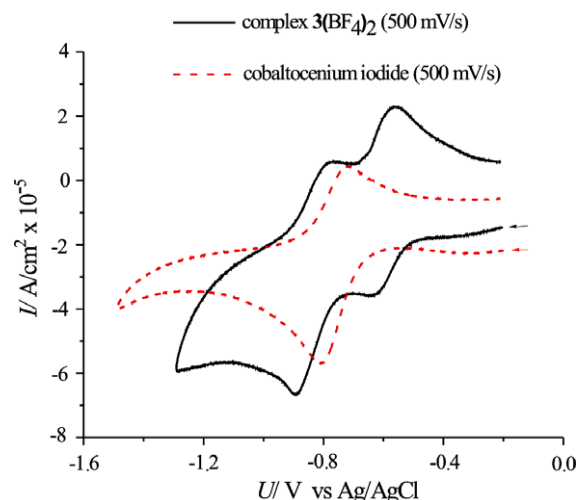

Fig. 5. Cyclic voltammogram of 3(BF$_4$)$_2$ (solid line) and cobaltocenium iodide (dotted line).

Table 4
Cyclic voltammetric data[a] of 3(BF$_4$)$_2$

	3(BF$_4$)$_2$
$E_{1/2}(1)$[b]	−1.161
$\Delta E_p(1)$[c]	0.078
$E_{1/2}(2)$[b]	−1.397
$\Delta E_p(2)$[c]	0.097
$\Delta E_p(FcH)$[d]	0.097
$\Delta E_p(CbcI)$[e]	0.079
ΔE[f]	0.236

[a] In CH$_2$Cl$_2$ at room temperature, [nBu$_4$N]PF$_6$ (0.4 M) as supporting electrolyte, Ag/AgCl as standard electrode referenced vs. $E_{1/2}$(ferrocene/ferrocenium) = 0 V, scan rate 200 mV/s.
[b] Potentials $E \pm 0.005$ V.
[c] $\Delta E_p = |E_{pc} - E_{pa}|$.
[d] ΔE_p of ferrocene (FcH).
[e] ΔE_p of cobaltocenium iodide (CbcI).
[f] $\Delta E = |E_{1/2}(2) - E_{1/2}(1)|$.

5. Conclusions

A fundamental synthetic route to cofacially stacked paramagnetic cobaltocenes has been demonstrated. As an intermediate product the dinuclear complex 1,8-bis[(η^5-cyclopentadienyl)(η^4-cyclopenta-1′, 3′-dien-5′-yl)-cobalt(I)]-naphthalene (2) was obtained after a double nucleophilic addition of 1,8-dilithionaphthalene to cobaltocenium cations. The molecular structure of 2 displays two cobalt sandwich entities in a more or less parallel alignment in 1,8-position of naphthalene. Ensuing hydride abstractions lead to the dicationic bismetallocene complex 3(BF$_4$)$_2$ illustrating two cofacially stacked cobaltocenium units held together by the "naphthalene clamp", as proven by X-ray structure analysis. Cyclic voltammetric studies reveal two redox couples in the range of the redox couple of cobaltocene, pointing out the stability of three oxidation states +2, +1 and 0 for the cofacially arranged biscobaltocene entities. The difference of the redox potentials indicates a "through-space" interaction between the cobaltocene

moieties. The preparative reduction of the dicationic biscobaltocenium complex **3**(BF$_4$)$_2$ to the neutral biradical complex **3** is a subject of current work.

6. Experimental

Unless otherwise noted, the reactions were carried out under dry nitrogen using standard Schlenk technique. Solvents were saturated with nitrogen. Diethyl ether (Et$_2$O) was dried by sodium potassium alloy, dichloromethane (DCM) by calcium hydride. NMR: Varian Gemini 2000 BB; Bruker AVANCE 400; measured at room temperature relative to TMS. Where possible, multiplicities of higher order were evaluated according to first order and are marked with the prefix "$m \sim$". MS: Finnigan MAT 311 A (EI). Diiodonaphthalene (**1**) [17] and 1,8-cobaltocenium iodide [18] were synthesized according to the literature procedures.

6.1. 1,8-bis[(η^5-cyclopentadienyl)(η^4-1′,3′-cyclopentadien-5′-yl)-cobalt(I)] naphthalene (2)

To a solution of 1,8-diiodonaphthalene (**1**) (4.72 g, 12.4 mmol) in Et$_2$O (150 ml) at 0 °C *n*-butyllithium (19.5 mL, 15% in *n*-hexane) was added. The mixture was stirred for 15 min and cooled to −78 °C. Cobaltocenium iodide (10.12 g, 32.02 mmol) was added to the solution. The reaction mixture was warmed to room temperature and stirred for additional 22 h. Water (8 mL) was added to the reaction mixture and stirred for 1 h. The orange suspension was filtered, the precipitate dissolved in boiling toluene and filtered again. Crystallization at 6 °C yielded **2** as a red powder. The mother liquor was concentrated and additional product was obtained. In total, 4.83 g (77%) product could be isolated. Larger crystals were obtained from a solution in CH$_2$Cl$_2$ by slow evaporation of the solvent.

M.p. 180–185 °C (decomp.). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, TMS, for numbering see Fig. 6 (left)): $\delta = 7.43$, 6.96 (m $\sim$ d, $J = 7.5$ Hz, $J = 6.8$ Hz, 4H, H-2, H-2′, H-4, H-4′), 7.16 (m $\sim$ t, $J = 7.3$ Hz, $J = 7.5$ Hz; 2H; H-3, H-3′), 5.26 (m $\sim$ s, 4H, H-10, H-10′, H-10″, H-10‴), 5.05 (s, 10H, Cp-H), 4.90 (m $\sim$ s, 2H, sp^3-H), 3.17 (m $\sim$ s, 4H, H-11, H-11′, H-11″, H-11‴) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, TMS, 25 °C) $\delta = 127.26$, 125.64, 124.38 (C-2, C-2′, C-3, C-3′, C-4, C-4′), 79.37 (Cp-C), 74.96 (C-10, C-10′, C-10″, C-10‴), 54.55 (sp^3-C), 46.42 (C-11, C-11′, C-11″, C-11‴) ppm [19]. MS (EI) [*m/z* (%)]: 504 (6) [M$^+$], 252 (17) [M^{2+}], 189 (100) [Cp$_2$Co$^+$], 124 (21) [CpCo$^+$]. Anal. Calc. for C$_{30}$H$_{26}$Co$_2$ (504.37): C, 71.44; H, 5.20. Found: C, 71.62; H, 5.23%.

6.2. 1,8-Biscobaltocen-1′-ylium-naphthalene bis(tetrafluoroborate) (3(BF$_4$)$_2$)

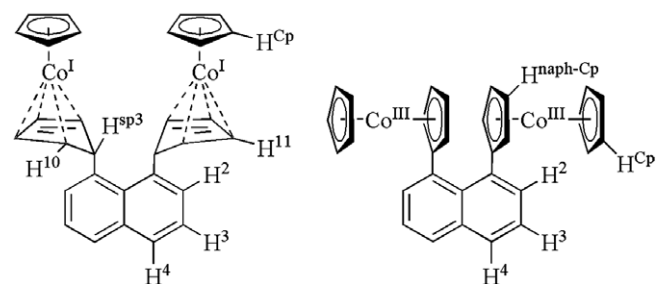To a solution of **2** (210 mg, 0.55 mmol) in CH$_2$Cl$_2$ (40 mL) was added a solution of tritylium-tetrafluorobo-

Fig. 6. Numbering scheme for **2** (left) and **3**(BF$_4$)$_2$ (right).

rate (340 mg, 1.03 mmol) in CH$_2$Cl$_2$ (40 mL). After stirring at room temperature for 20 h the resulting yellow precipitate was purified by filtration over silica with nitromethane. After evaporation of the solvent, the product (160 mg, 23.7 mmol, 54%) was obtained as a yellow-orange powder. Crystals suitable for X-ray structure determination were obtained from a solution in 1,2-dichloroethane saturated with water, and diethyl ether added via gas phase diffusion.

^{1}H NMR (200 MHz, CD$_3$NO$_2$, 25 °C, TMS, for numbering see Fig. 6 (right)) $\delta = 8.26$, 8.18 (m $\sim$ dd, $J = 7.2$ Hz, $J = 8.4$ Hz, $J = 1.2$ Hz, 4H, H-2, H-2′, H-4, H-4′), 7.76 (m $\sim$ dd, $J = 7.2$ Hz, $J = 7.2$ Hz, $J = 1.0$ Hz, 2 H, H-3, H-3′), 5.83, 5.63 (m $\sim$ t, $J = 2.1$ Hz, $J = 2.0$ Hz,

Table 5
Crystallographic data of **2** and **3**(BF$_4$)$_2$

	2	**3**(BF$_4$)$_2$
Empirical formula	C$_{30}$H$_{26}$Co$_2$	C$_{30}$H$_{26}$Co$_2$B$_2$F$_8$O
M_r (g/mol)	504.37	693.99
T (K)	153(2)	152(2)
λ (pm)	71.073	71.073
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	*P2$_1$/n*
a (pm)	959.58(16)	1394.44(10)
b (pm)	1194.37(19)	923.69(7)
c (pm)	1894.9(3)	2171.79(16)
β (°)	97.975(3)	98.1010(10)
V (10^6 pm^3)	2150.8(6)	2769.4(4)
Z	4	4
$\rho_{calcd.}$ (Mg/m^3)	1.558	1.664
μ (mm^{-1})	1.56	1.28
$F(000)$	1040	1400
Crystal size (mm)	0.41 × 0.10 × 0.07	0.38 × 0.36 × 0.22
$\theta_{min,max}$	2.17–27.48	1.89–27.50
Index range	−12 ⩽ h ⩽ 12,	−18 ⩽ h ⩽ 18,
	−10 ⩽ k ⩽ 15,	−11 ⩽ k ⩽ 12,
	−24 ⩽ l ⩽ 20	−28 ⩽ l ⩽ 27
Reflections total	7000	32420
Reflections independent	2428	6327
R_{int}	0.0644	0.0311
Reflections [$I > 4\sigma(I)$]	1547	5287
Parameters	146	426
Goodness-of-fit [a]	0.866	1.012
R_1/wR_2 [$I > 2\sigma(I)$] [b]	0.0464/0.0965	0.0379/0.1068
R_1/wR_2(all data)	0.0755/0.1038	0.0446/0.1105
Min./max. residue (e Å^3)	−0.618/1.090	−0.426/0.617

[a] GOF = "Goodness-of-fit" = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = number of reflections, p = number of parameters).
[b] $R_1 = \Sigma||F_o| - |F_c||$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)_2]/\Sigma[w(F_o^2)]\}^{1/2}$.

8H, naph-Cp-H), 5.58 (s, 10H, Cp-H) ppm. ^{13}C NMR (100 MHz, CD_3NO_2, 25 °C): $\delta = 132.72$, 129.66 (C-2, C-2′, C-4, C-4′), 124.51 (C-3, C-3′), 84.75 (C-Cp), 82.82, 81.44 (C-11, C-11′, C-12, C-12′) ppm [19]. MS (EI) [m/z (%)]: 377 (10) [M^+–(CpCo)], 313 (100) [M^+–(Cp_2Co)], 189 (45) [Cp_2Co^+], 124 (22) [$CpCo^+$]. Anal. Calc. for $C_{30}H_{24}Co_2B_2F_8(H_2O)$ (694.01): C, 51.92; H, 3.78. Found: C, 51.33; H, 3.75% [20].

7. Cyclic voltammetry

Measurements were performed in CH_2Cl_2 with 0.4 M [n-Bu_4N]PF_6 as supporting electrolyte. An Amel 5000 system was used with a Pt wire as working electrode and a Pt plate (0.6 cm^2) as auxiliary electrode. The potentials were measured against Ag/AgPF$_6$ and were referenced to $E_{1/2}$(ferrocene/ferrocenium) $= 0$ V.

8. X-ray structure determination

The data were collected with a Bruker AXS Smart APEX CCD, Mo Kα, $\lambda = 0.71073$ Å. For crystallographic data of **2** and **3**(BF_4)$_2$ see Table 5. The structures were solved by direct methods (SHELXS-97) [21] and the refinements on F^2 were carried out by full-matrix least-squares techniques (SHELXL-97) [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic parameter of their carrier atoms. Weights were optimized in the final refinement cycles.

Acknowledgement

Appendix A. Supplementary material

CCDC 643890 and 643891 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.041.

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