1,1′ Ferrocenylenediol as chelating ligand for cobalt in fivefold and sixfold coordination geometry: Synthesis, Electrochemistry and X-ray crystal structure of [{((1,1′ $O_2(\eta^5$-$C_5H_5)_2$Fe)$_2$}Co(OEt$_2$){(η^5-Me$_5$C$_5$)Co}$_2$] and [{((1,1′ $O_2(\eta^5$-$C_5H_5)_2$Fe)$_3$}Co((η^5-EtMe$_4$C$_5$)Co)$_2$]

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ABSTRACT

The title compounds **3** and **4** were synthesized by reaction of 1,1′ ferrocenylenediol with the Co triple decker compounds [{(η^5-Me$_5$C$_5$)Co}$_2$(η^6:η^6-toluene)] and [{(η^5-EtMe$_4$C$_5$)Co}$_2$(η^6:η^6-toluene)], respectively. The central Co atom of **3** is coordinated by five O atoms in a square-pyramidal manner. The remaining two Co atoms of **3** are coordinated to a Me$_5$C$_5$ ligand in a η^5-fashion and by the two O atoms of two 1,1′ ferrocenylenediolato ligands which serve as chelating ligands. In **4**, the central Co atom is coordinated to all six O atoms of three ferrocenylenediolato ligands in a trigonal-prismatic manner, whereas the two other Co atoms are coordinated by an EtMe$_4$C$_5$ ligand in a η^5-fashion and by three O atoms of three ferrocenylenediolato ligands resulting in an overall tripoidal structure for **4**.

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1. Introduction

Organometallic triple decker complexes with bridging arene ligands are an intriguing class of compounds in organometallic chemistry. In these complexes the arene ligands often coordinate two metal atoms in diverse coordination modes like μ-η^2:η^2, μ-η^3:η^3, or μ-η^6:η^6 [1–6]. However, in complexes of the type [{(η^5-Me$_5$C$_5$)Co}$_2$(μ-arene)] (arene = toluene, o-, m-, p-xylene, benzene) the arene ligands show a different coordination mode. They are bonded to both metal centers in an μ-η^4:η^4 manner, as observed by X-ray crystallography [7]. However, in solution the metal ligand fragment adopts an η^6:η^6 coordination, indicative of a fluxional behaviour of the arenes. The arene middle deck is weakly bonded and thus is prone to a substitution under mild conditions by various other arenes [8–11] as well as other ligands [12]. As an extension of the studies of the reaction behaviour of triple decker complexes of the type [{(η^5-Me$_5$C$_5$)Co}$_2$(μ-arene)] we now investigated reactions of [{(η^5-Me$_5$C$_5$)Co}$_2$(μ-toluene)] (1) and [{(η^5-EtMe$_4$C$_5$)Co}$_2$(μ-toluene)] (2) with 1,1′ ferrocenylenediol as chelating organometallic ligand.

2. Results and discussion

Our interest to study the reaction of the triple decker complexes [{(η^5-Me$_5$C$_5$)Co}$_2$(η^6:η^6-toluene)] and [{(η^5-EtMe$_4$C$_5$)-Co}$_2$(η^6:η^6-toluene)] with 1,1′ ferrocenylenediol was triggered by the observation that both complexes are reactive towards water as well as H2S leading to a series of unusual higher nuclearity organometallic cobalt clusters with central heterocubane units [12]. Therefore we were further interested to see whether the geometric constraint imposed by the chelating ferrocene backbone with its 1,1′ substitution pattern would steer the reaction towards other unusual coordination geometries based on the combination of [(η^5-Cp)Co] fragments and the 1,1′ substituted ferrocene moiety. Indeed both triple decker complexes **1** and **2** react with 1′1′ ferrocenylenediol in diethylether under mild conditions at room temperature generating [(η^5-Cp^R)Co] fragments, leading to formation of two cobalt clusters with unusual C–O frameworks.

Upon stirring the triple decker complexes with 1,1′ ferrocenylenediol in ether in a ratio 1:2 and 1:3, the mixed metal complexes [{((1,1′ O_2-η^5-$C_5H_5)_2$Fe)$_2$}Co(OEt$_2$){(η^5-Me$_5$C$_5$)Co}$_2$] (3) and [{((1,1′ O_2-η^5-$C_5H_5)_2$Fe)$_3$}Co((η^5-EtMe$_4$C$_5$)Co)$_2$}] (4) were formed in good yields (see Scheme 1).
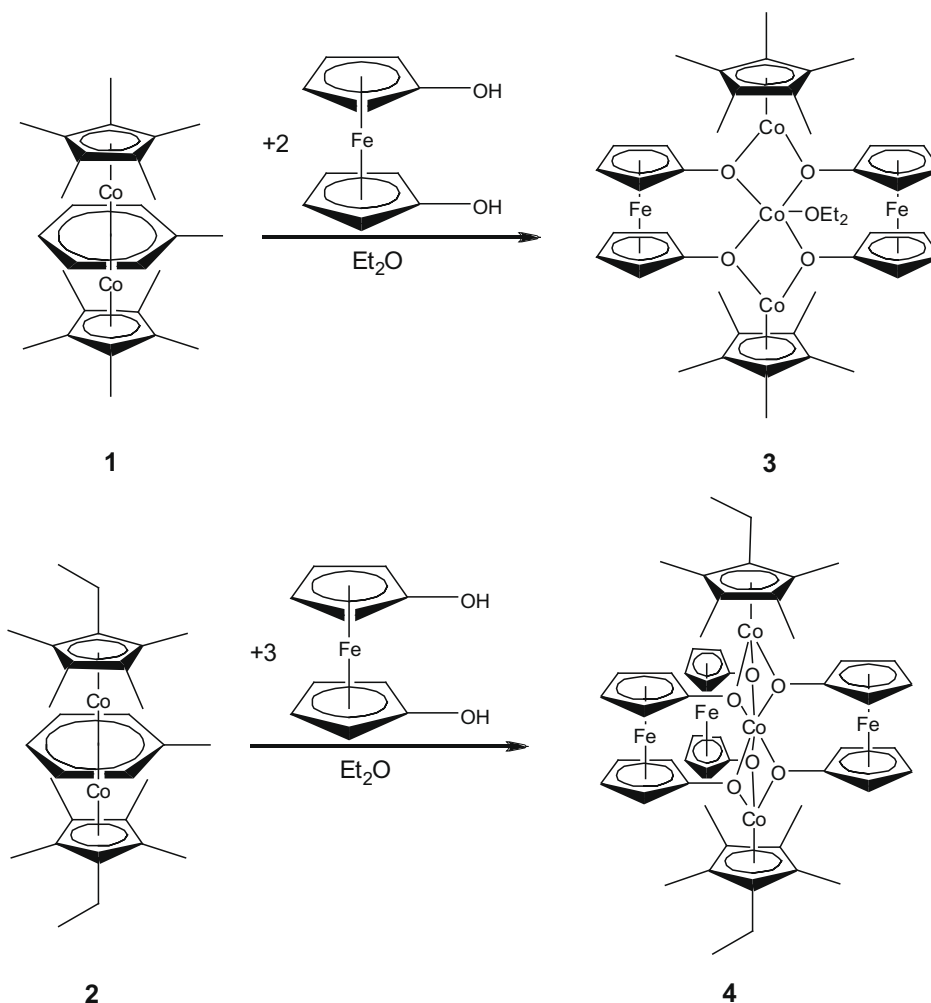
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Scheme 1. Synthesis route for **3** and **4**.

2.1. Crystal structure of 3 and 4

The molecular structure of **3** consists of a molecule of [{1,1′-$O_2((\eta^5$-$C_5H_5)_2$Fe)$_2$} Co(OEt$_2$){(η^5-Me$_5$C$_5$)Co}$_2$]] (**3A**), and an additional uncoordinated ether solvent molecule in the crystal packing of **3A**. In **3A** the three Co atoms are connected via four oxygen atoms of two 1,1′ ferrocenylenediolato ligands (Fig. 1).

The Co···Co distances are 3.113(2) and 3.116(2) Å, and the Co–Co–Co angle is 163.4(2). The central Co atom is coordinated by five O atoms in a square-pyramidal manner. The four O atoms of the two chelating 1,1′ ferrocenylenediolato ligands form a rectangle with O–O–O angles in the range from 88.66° to 90.60°. Caused by the ligand bite the two edges formed by two O atoms of one ligand are much longer than the other two edges. The longer O···O distances in the O$_4$ rectangle are 3.134 and 3.165 Å, whereas the shorter ones are 2.390 and 2.440 Å. Caused by the direct σ-coordination of the ether molecule the central Co atom lies not in the rectangle plane, however it is displaced towards this coordinating ether molecule by 0.373 Å. The Co3–O bond distances of the ferrocenylenediolato ligands are in the range from 2.005(6) to 2.039(5) Å. As expected, the Co–O bond distance (2.105(5) Å) to the ether molecule is significantly elongated. The asymmetry generated by the coordination of the ether molecule to Co3 causes the non-linear arrangement of the three Co atoms resulting in an angle of 177.1(2)°.

The other two Co atoms of **3A** are coordinated by a Me$_5$C$_5$ ligand in a η^5-fashion and by two O atoms of two ferrocenylenediolato ligands each. The Co–O bond distances are in the range from 1.917(6) to 1.947(6) Å and significantly shorter than the distances to the central Co atom. The Co–C bond lengths are in the range from 2.064(8) to 2.132(8) Å and are comparable to other complexes containing a [(η^5-Me$_5$C$_5$)Co] complex fragment [7,13]. The second ether molecule shows no bonding interactions with **3A**.

In contrast to the molecular structure of **3A**, the structure of **4** contains three Co atoms which are arranged in a nearly linear fashion (Co–Co–Co angle 179.7(2)°). The Co···Co distances are 2.853(2) and 2.860(2) Å. The distances are shorter than in **3A**, but significantly longer than in metallic cobalt (fcc Co: 2.506; hcp Co: 2.507 and 2.495 Å) [14] and therefore too long for a Co–Co bond. The central Co atom of **2** is coordinated by the six O atoms of the three 1,1′ ferrocenylenediolato ligands resulting in a trigonal-prismatic coordination geometry around Co3 (Figs. 2 and 3).

The Co–O bond lengths are in the range from 2.089(5) to 2.147(6) Å. The O···O distances in the trigonal plane are in the range from 2.499 to 2.547 Å and are nearly equilateral. The two other Co atoms in **4** are coordinated by three O atoms of the 1,1′ ferrocenylenediolato ligands and by a EtMe$_4$C$_5$ ligand in a η^5 manner. The Co–O distances are in the range from 1.952(5) to 1.989(5). The Co–C bond lengths to the terminally η^5-bonded EtMe$_4$C$_5$ ligands are in the range from 2.049(8) to 2.094(8) Å and are compa-
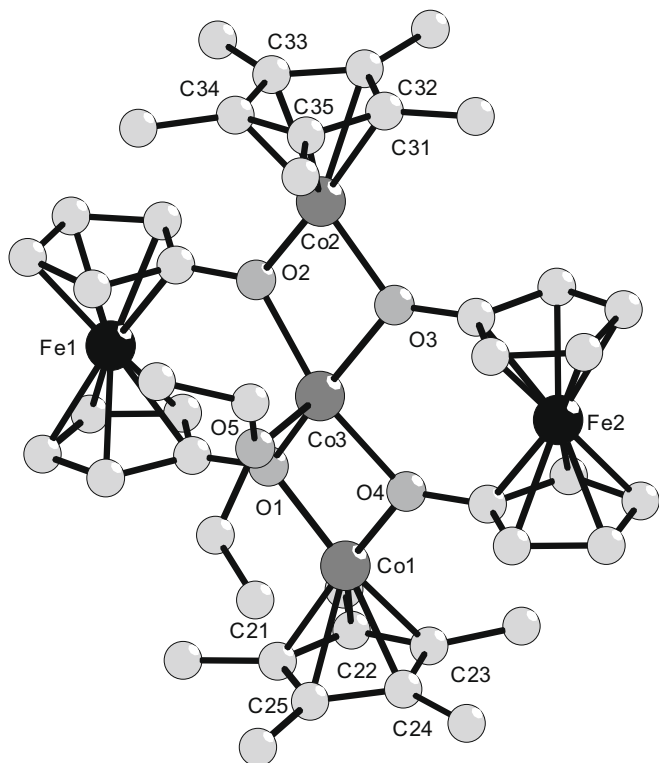
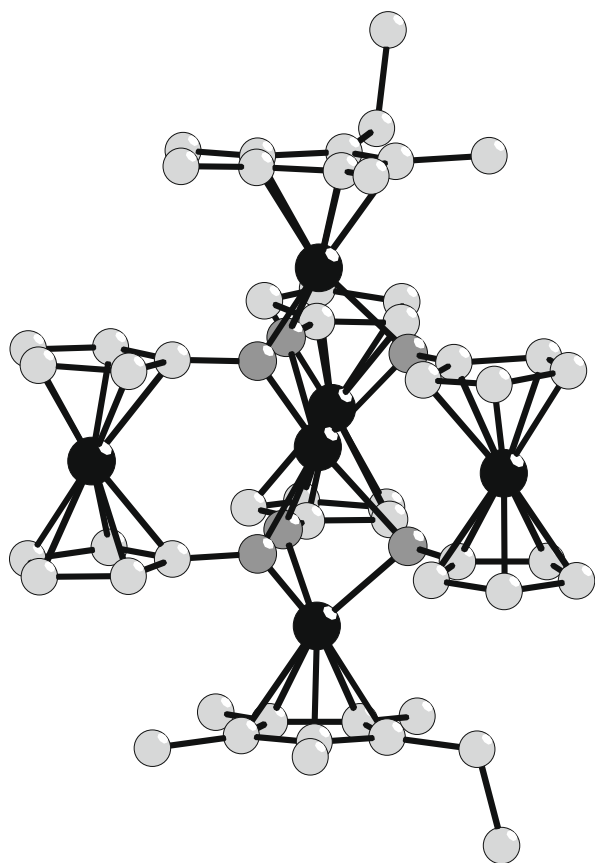**Fig. 1.** Molecular structure of **3A** (H atoms have been omitted for clarity).

Fig. 2. Molecular structure of **4** (H atoms have been omitted for clarity).

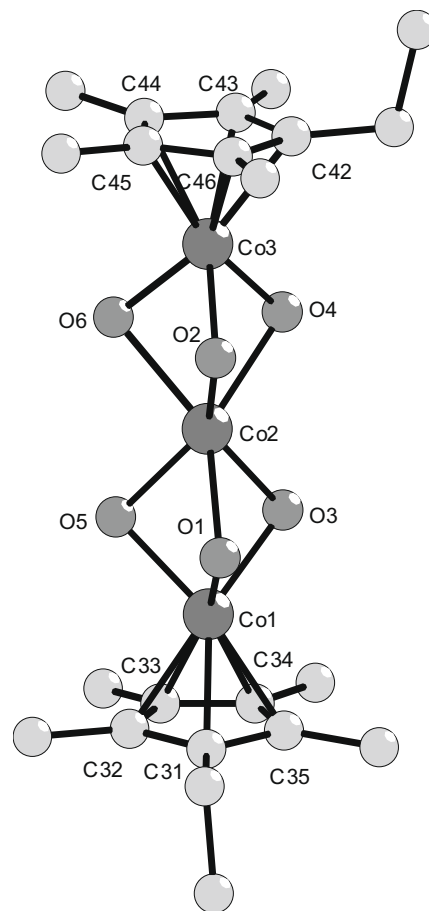**Fig. 3.** Coordination of the Co atoms in **4** (the $(\eta^5\text{-}C_5H_5)_2$Fe ligand fragments and the H atoms have been omitted for clarity).

The degree of distortion of a trigonal-prismatic geometry can be characterized by the twist angle φ ($\varphi = 0°$ for an ideal trigonal-prismatic geometry, $\varphi = 60°$ for an ideal octahedral geometry) [15]. For **4** the average twist angle is only 1.81° thus indicating an almost ideal trigonal-prismatic coordination of the central Co atom. The O···O distances of the three edges of the three oxygen rectangles of the trigonal prism are in the range from 3.072 to 3.087 Å and are comparable to the longer O···O distances of the O_4 rectangle of **3A**. For an ideal trigonal-prismatic coordination the distances in the O_4 plane are all equal, therefore the trigonal-prismatic coordination of the six oxygen atoms to the central cobalt atom in **4** is somewhat elongated. This elongation must be caused by the ligand bite of the 1,1′ ferrocenylenediolato ligands, which force longer O···O distances between the two O_3 triangles. Typically metals with a coordination number of six are octahedral coordinated, trigonal-prismatic coordination geometries are rather rare [16] and only a few number of examples are known for Co [17–22].

Reasons for the preference of the octahedral over the trigonal-prismatic coordination are the larger ligand field stabilisation energy Δ_{lfse} of octahedral complexes compared with the analogous trigonal-prismatic species and the greater inter ligand repulsion present in a trigonal-prismatic compared to an octahedral coordination [23,24]. In some cases a trigonal-prismatic coordination may be also caused by packing forces. In **4** the observed trigonal-prismatic coordination geometry of the central Co atom is caused by the ligand bite of the 1,1′ ferrocenylenediolato ligands. A comparable arrangement of the 1,1′ ferrocenylene moieties has been found in the trinuclear Gallium ferrocenophane complex [{Fe(C$_5$H$_4$)$_2$}$_3$(GaNC$_5$H$_5$)$_2$] [25] in which three ferrocen-1,1-yl frag-

rable to those ones in complexes containing a [(η^5-Me$_5$C$_5$)Co] fragment [7,13].
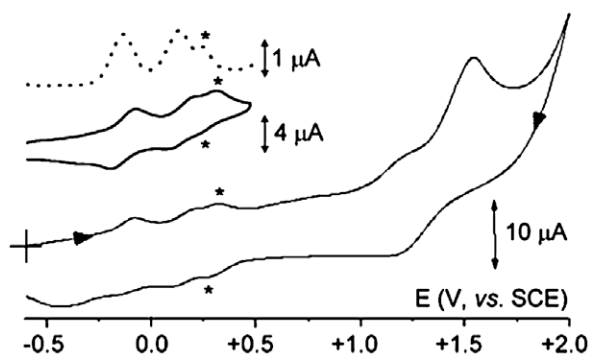
Fig. 4. Cyclic (−) and differential pulse (DPV) (••••) voltammograms recorded at a platinum electrode in o-C$_6$H$_4$Cl$_2$ solution containing **3** (1.0 × 10^3 mol dm^{-3}). [NBu$_4$][ClO$_4$] (0.1 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1}.

ments are bonded to two Ga atoms in a trigonal manner. Highly distorted octahedral geometric environments, again with similar sixfold oxygen coordination as in **3** and **4** have been reported [22]. The cobalt (II) centers therein reveal an antiferromagnetic exchange coupling with large deviations of the calculated values from the measured ones attributed to strong intermolecular hydrogen bonding. Since we do not observe such structural interactions in the solid structures of **3** and **4** it would be interesting to compare the magnetic interplay of experiment and theory with respect to this regard for **3** and **4**.

In **3** and **4**, Co is in the oxidation state +2 which precludes high resolution NMR data due to its open shell situation. Nevertheless we have recorded NMR spectra in the paramagnetic range from +100 ppm to −50 ppm, typical for paramagnetic cobalt complexes bearing η^5-Me$_5$Cp ring ligands [26,27]. Indeed we observed characteristic signals for the substituted Cp rings of **3** and **4** in that paramagnetic shift region. Due to the different distance to the paramagnetic Co centers, the ferrocenyl proton signals in **3** are only slightly shifted compared to protons in a diamagnetic 1,1′ ferrocenylene unit (see Section 4). In contrast to that, the methyl protons of the pentamethyl- and tetramethylethyl-cyclopentadienyl rings are stronger shifted compared to the shifts of the protons of these ligands in diamagnetic complexes. This is due to the direct coordination of the paramagnetic cobalt (II) center to the substituted Cp rings in **3** and **4** and the dipolar coupling.

We studied the electrochemical response of **3** by cyclic voltammetry (Fig. 4 and Table 4). Its behaviour is mainly governed by a rather complicated pattern giving three anodic steps with signs of chemical reversibility followed by two multielectron steps again with only minor indication of reversibility. Differential pulse voltammetry confirmed that the third step is due to a minor impurity or an electrochemical oxidation product arising from either one of the first electrochemical processes (no distinction was possible here even under very high scan rates). We assign the first two electrochemical processes to ferrocene centered processes and the most anodic processes to Co(II) centered oxidations.

3. Conclusion

The reaction of the triple decker complexes of type [{(η^5-RMe$_4$C$_5$)Co}$_2$(η^6:η^6-toluene)] (R = Me, Et) with the chelating ligand 1,1′ ferrocenylenediol leads to the mixed metal complexes **3** and **4** in which the central Co atoms are coordinated in a rather rare square-pyramidal and trigonal-prismatic coordination geometries, respectively. In **3** and **4** the Co atoms are in the oxidation state +2 which calls for magnetic and electron spin studies on these spin centers. Our future studies are thus aimed towards EPR and magnetic investigations of these unique complexes.

4. Experimental

All manipulations were carried out under anhydrous and oxygen free conditions using a glove box or a Schlenk line. Ether was dried over sodium and distilled prior to use. [{(η^5-Me$_5$C$_5$)Co}$_2$μ-(η^6:η^6-toluene)] (1) [7], [{(η^5-EtMe$_4$C$_5$)Co}$_2$μ-(η^6:η^6-toluene)] (2) [7], and 1,1′ ferrocenylenediol [28] were prepared according to literature procedures. C, H, combustion analysis was performed by Kolbe Analytical Laboratory, Mülheim an der Ruhr.

4.1. Synthesis of [{((1, 1′ O2-(η^5-C$_5$H$_5$)$_2$Fe)$_2$} Co(OEt$_2$){(η^5-Me$_5$C$_5$)Co}$_2$] (3)

To a solution of [{(η^5-Me$_5$C$_5$)Co}$_2$(η^6:η^6-toluene)] (1) (0.44 g, 0.9 mmol) in 20 ml ether a solution of 1,1′ ferrocenylenediol (0.20 g, 0.9 mmol) in 20 ml ether was added at −78 °C. The resulting reaction mixture was slowly warmed to room temperature and stirred for further three days. After concentration and filtration the solution was stored at −30 °C. After two days the product was obtained as brown crystals (0.23 g, 54%). Decomp. 223 °C. ^{1}H NMR (d^8-THF), 297 K, 300 MHz, δ: 65.9 (br, 30H, η^5-Me$_5$C$_5$), 7.6 (br, 16H, C$_5$H$_4$). Anal. Calc. for C$_{48}$H$_{66}$O$_6$Co$_3$Fe$_2$ × (C$_2$H$_5$)$_2$O (1026.5); C, 56.11; H, 6.43. Found: C, 57.83; H, 5.26%.

4.2. Synthesis of [{((1,1′ O$_2$-(η^5-C$_5$H$_5$)$_2$Fe)$_3$}Co((η^5-EtMe$_4$C$_5$)Co)$_2$] (4)

To a solution of [{(η^5-EtMe$_4$C$_5$)Co}$_2$(η^6:η^6-toluene)] (0.26 g, 0.5 mmol) in 20 ml ether a solution of 1,1′ ferrocenylenediol (0.22 g, 1.0 mmol) in 20 ml ether was added at −78 °C. The result-

Table 1
Selected bond lengths (Å) and angles (°) of 3.

Co1–O1	1.917(6)	Co1–O4	1.935(6)
Co1–C21	2.101(9)	Co1–C22	2.132(8)
Co1–C23	2.102(8)	Co1–C24	2.064(8)
Co1–C25	2.122(8)	Co2–O2	1.947(6)
Co2–O3	1.932(6)	Co2–C31	2.060(8)
Co2–C32	2.121(8)	Co2–C33	2.074(8)
Co2–C34	2.087(8)	Co2–C35	2.095(8)
Co3–O1	2.012(5)	Co3–O2	2.021(5)
Co3–O3	2.039(5)	Co3–O4	2.005(6)
Co3–O5	2.105(5)		
O1–Co3–O2	102.0(2)	O1–Co3–O3	159.5(3)
O1–Co3–O4	73.1(2)	O1–Co3–O5	102.9(2)
O2–Co3–O3	73.9(2)	O2–Co3–O4	157.8(3)
O2–Co3–O5	100.6(2)	O3–Co3–O4	103.0(2)
O3–Co3–O5	97.5(2)	O4–Co3–O5	101.6(2)

Table 2
Selected bond lengths (Å) and angles (°) of **4**.

Co1–O1	1.970(5)	Co1–O3	1.952(5)
Co1–O5	1.978(6)	Co1–C31	2.075(8)
Co1–C32	2.051(8)	Co1–C33	2.094(8)
Co1 C34	2.076(8)	Co1 C35	2.049(8)
Co2 O1	2.117(5)	Co2–O2	2.129(5)
Co2–O3	2.125(6)	Co2–O4	2.089(5)
Co2–O5	2.118(5)	Co2–O6	2.147(6)
Co3–O2	1.952(6)	Co3–O4	1.953(5)
Co3–O6	1.989(5)	Co3–C42	2.071(8)
Co3–C43	2.066(8)	Co3–C44	2.079(9)
Co3–C45	2.074(8)	Co3–C46	2.085(8)
O1–Co2–O2	93.3(2)	O1–Co2–O3	73.8(2)
O1–Co2–O4	140.5(2)	O1–Co2–O5	73.2(2)
O1–Co2–O6	139.6(2)	O2–Co2–O3	142.7(2)
O2–Co2–O4	74.2(2)	O2–Co2–O5	138.3(2)
O2–Co2–O6	72.4(2)	O3–Co2–O4	93.6(2)
O3–Co2–O5	72.2(2)	O3–Co2–O6	138.3(2)
O4–Co2–O5	139.1(2)	O4–Co2–O6	72.8(2)
O5–Co2–O6	92.4(2)		

Table 3
Crystallographic data of **3** and **4** (see Supplementary material).

	3	**4**
Empirical formula	$C_{48}H_{66}O_6Co_3Fe_2$	$C_{54}H_{60}O_6Co_3Fe_3$
Formula weight (g mol^{-1})	1027.50	1149.36
Measurement temperature (K)	150	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	CC	$P\bar{1}$
Unit cell		
a (Å)	23.002(5)	11.873(2)
b (Å)	12.002(2)	13.917(3)
c (Å)	19.998(4)	16.063(3)
α (°)		113.52(3)
β (°)	123.54(3)	99.58(3)
γ (°)		97.19(3)
Volume (Å^3)	4601.3(16)	2345.3(8)
Z	4	2
D_{calc} (mg/m^3)	1.483	1.628
Absorption coefficient (mm^{-1})	1.721	1.992
$F(000)$	2140	1182
Crystal size (mm^3)	$0.23 \times 0.22 \times 0.16$	$0.32 \times 0.20 \times 0.18$
Crystal colour	Brown	Brown
Θ range (°)	2.00–27.04	1.42–25.05
Index range	$-29 \leqslant h \leqslant 28$	$-14 \leqslant h \leqslant 14$
	$-15 \leqslant k \leqslant 15$	$-16 \leqslant k \leqslant 16$
	$-25 \leqslant l \leqslant 25$	$-19 \leqslant l \leqslant 19$
Collected reflections	34,054	29,833
Independent reflections [$R_{(int)}$]	9855 (0.1062)	8312 (0.1539)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters	532	577
Goodness-of-fit (GOF) on F^2	0.954	1.082
Data [$I > 2\sigma(I)$]	9855	8312
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0572$	$R_1 = 0.0738$
	$wR = 0.0724$	$wR = 0.1816$
R Indices for all data	$R_1 = 0.0970$	$R_1 = 0.1060$
	$wR = 0.0807$	$wR = 0.1983$

Table 4
Formal electrode potentials (*V* versus SCE) and peak-to-peak separation (mV) for the redox changes exhibited by **3** in $o\text{-}C_6H_4Cl_2$ solution.

Complex	Co(II) centered oxidations				Ferrocene-centered oxidations			
	$E^{\circ\prime}$	ΔE_p [a]	$E^{\circ\prime}$	ΔE_p [a]	$E^{\circ\prime}$	ΔE_p [a]	$E^{\circ\prime}$	ΔE_p [a]
3	+1.25	[c]	+1.58[d]	–	0.12	123	+0.15[b]	–

[a] Measured at 0.2 V s^{-1}.
[b] From DPV measurement.
[c] Difficult to determine.
[d] Peak-potential value for irreversible processes.

ing reaction mixture was slowly warmed to room temperature and stirred for further three days. After concentration and filtration the solution was stored at $-30\,^{\circ}$C. After two days the product was obtained as brown crystals (0.24 g, 61%). Probably due to the high sensivity and/or the incomplete combustion during the analysis of **4** (even with V2O5 additive) it was not possible to obtain a reliable C, H combustion analysis, although repeated attempts were undertaken. Decomp. 165 °C. ^{1}H NMR (d^8-THF), 296 K, 300 MHz, δ: 43.3 (br, 24H, Me), CH$_2$ of EtMe$_4$ not detected, 7.55 (br, 16H, C$_5$H$_4$) (see Tables 1 and 2).

4.3. X-ray data collection and structure solution and refinement of **3** and **4**

Crystals of **3** and **4** were selected under a microscope in a dry box, mounted in glass capillaries and checked on a STOE IPDS

diffractometer. The data collection was carried out at 150 K. Details of the data collections are given in Table 3.

Several heavy atoms were readily located by direct methods (SHELXS-97 [29]). Difference Fourier analysis and least square cycles (SHELXL-97 [30]) allowed the location of the other atoms. The positions of hydrogen atoms were geometrically determined for all carbon and nitrogen atoms using the riding model with fixed bond lengths and fixed temperature factors for the refinement. The molecules and fragment shown in Figs. 1–3 are plotted by using DIAMOND [31].

Appendix A. Supplementary material

CCDC-713310 (**3**) and 713311 (**4**) contain 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.2008.11.042.

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