

# $(\eta^4\text{-Tetraarylcyclobutadiene})(\eta^5\text{-formylcyclopentadienyl})\text{cobalt(I)}$ complexes: Facilities to finetune the electron-donating capability in dipolar organometallics

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Dedicated to Dr. Karel Mach on the occasion of his 70th birthday.

## Abstract

Five different  $(\eta^4\text{-tetraarylcyclobutadiene})(\eta^5\text{-formylcyclopentadienyl})\text{cobalt(I)}$  complexes (**1a–1e**) were synthesized in reasonable yields in a one-pot reaction of  $\text{CoCl}(\text{PPh}_3)_3$ , formylcyclopentadienyl sodium and the appropriate diarylethyne. The aryl groups of the ethyne were modified by various *para*-substituents X (X = Cl, H, Me, OMe,  $\text{NMe}_2$ ), which were intended to alter the redox potentials of the synthesized cobalt sandwich complexes. A cyclic voltammetry study revealed a linear dependence of the first oxidation potential to the Hammett parameter  $\sigma_p$ . X-ray structure analyses performed for two complexes (X = Me and  $\text{NMe}_2$ ) demonstrate only subtle changes in the solid state structure despite the large differences in electrochemical properties. A theoretical analysis by the density functional theory method has been performed on the geometries and electronic structures of the complex  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{-Co(I)}$ , its cation and dication.

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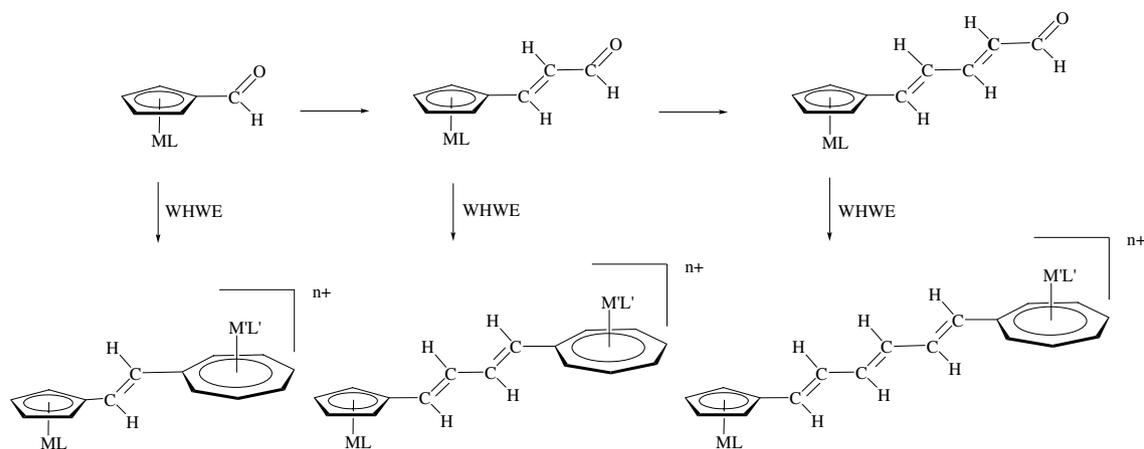
**Keywords:** Cobalt sandwich complexes; Tetraarylcyclobutadiene; Carboxaldehyde; Cyclic voltammetry; X-ray structure analysis; DFT calculations

## 1. Introduction

The concept of dipolar cationic heterobimetallic complexes for compounds with non-linear optical (NLO) properties [1], e.g. with high first order hyperpolarisability  $\beta$ , has been shown to be very useful [2]. These complexes are comprised of the combination of an organometallic electron donating and accepting group connected by a bridge, which enables electronic  $\pi$ -interaction between them. For organometallic electron accepting groups carbonyl complexes were employed [2e,2f] as well as Fischer-type carbenes [2g,2n] and cationic complexes of organic  $\pi$ -ligands [2c,d,f–o]. The most widely used donating units are sandwich type complexes based on ferrocenes and

ruthenocenes, due to their inertness and the facile synthetic availability of derivatives [2f–l,3–5]. However, to the best of our knowledge, the sandwich complex  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{cobalt(I)}$ , which is isoelectronic to ferrocene, has not been applied as an electron donating unit in dipolar heterobimetallic complexes directed towards NLO properties except for a short note in a review article [2h]. Since we are looking more closely at sesquifulvalene-type dipolar organometallic complexes with respect to their NLO properties [2i], attempts were made to coordinate the  $(\eta^4\text{-cyclobutadiene})\text{cobalt}$  moiety to the cyclopentadienyl part of a sesquifulvalene entity. In previous papers, we presented strategies to build up dipolar, mono- and dinuclear sesquifulvalene complexes and the vinylogue congeners based on ferrocene and ruthenocene derivatives. These are synthesized straightforwardly by using the appropriate cyclopentadienyl carboxaldehyde sandwich complex as starting material. Subsequent Wittig–Horner–

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Scheme 1. Overview of the routes used to synthesize vinylogue sesquifulvalene complexes by WHWE reaction starting from a sandwich carboxaldehyde [2m,6].

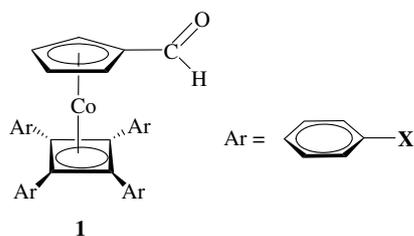
Wadsworth–Emmons (WHWE) reactions extend the olefin bridge between the donor and the acceptor of a dipolar sesquifulvalene complex (Scheme 1) [2m,6].

In this paper, we want to present syntheses, molecular structures and spectroscopic properties of carboxaldehyde building blocks as starting material for vinylogue ( $\eta^4$ -cyclobutadiene)( $\eta^5$ -cyclopentadienyl)cobalt(I) complexes as electron-donating groups. Moreover, to finetune electronic properties, the cyclobutadiene ligands are provided with four aryl substituents whose *para*-position is modified by different X-groups (Fig. 1).

## 2. Results and discussions

### 2.1. Synthesis

In principle two different routes can be selected for the synthesis of ( $\eta^4$ -tetraarylcyclobutadiene)( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**1**). The first one is based on the preparation developed by Rausch and Genetti [7]. Iodine is oxidatively added to  $\text{Co}_2(\text{CO})_8$  forming the thermally unstable carbonyl complex  $\text{Co}(\text{CO})_4\text{I}$  which is not separated but directly treated with formylcyclopentadienyl thallium (Scheme 2a). The isolated halfsandwich complex (dicarbonyl)( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**2**) is refluxed in *p*-xylene in the presence of the chosen diaryl-



X = Cl (**1a**), H (**1b**), Me (**1c**), OMe (**1d**),  $\text{NMe}_2$  (**1e**)

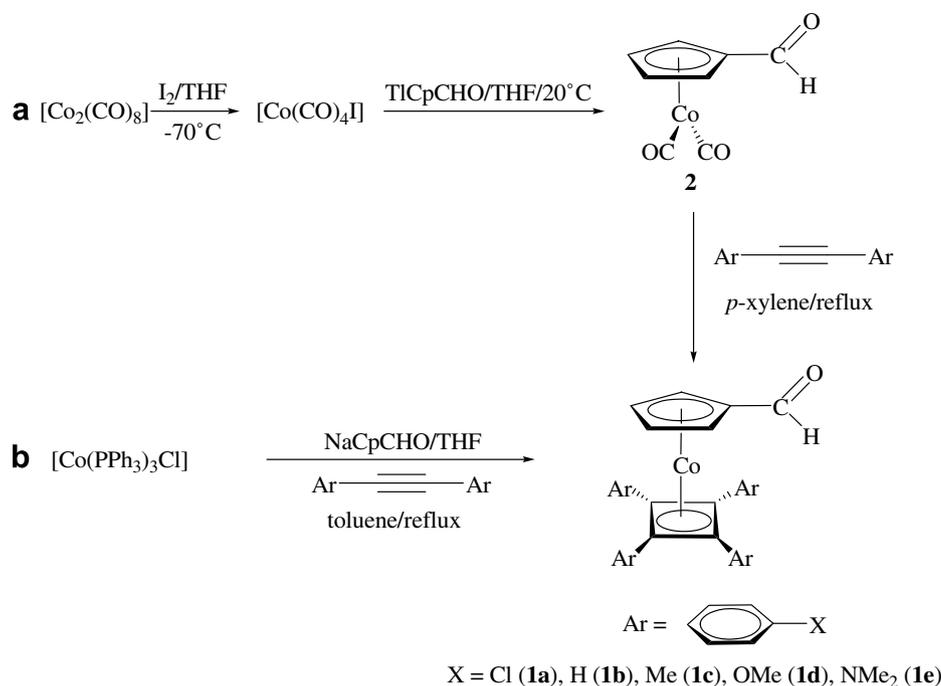
Fig. 1. ( $\eta^4$ -Tetraarylcyclobutadiene)( $\eta^5$ -formylcyclopentadienyl)cobalt(I) complexes as target compounds.

acetylene and reveals the sandwich complexes **1** in a very low overall yield [8]. The yields of the desired complexes **1a–1e** can be improved considerably, when the synthesis of **1a–1e** is performed in accord with a procedure described first by Takahashi et al. [9]. In a one-pot reaction stoichiometric amounts of  $\text{CoCl}(\text{PPh}_3)_3$ , formylcyclopentadienyl sodium and the appropriate toluene were allowed to react (Scheme 2b) [8,10]. Complexes **1a–1e** were obtained in 30–70% yield.

### 2.2. Solid state structure

Complex **1c** crystallizes in the triclinic space group  $P\bar{1}$  and for **1e** the monoclinic space group  $Pc$  is found. Both of the complexes **1c** and **1e** display very similar Co–C distances, which are slightly shorter for the cobalt–cyclobutadiene (CBD) unit (198.4(3)–199.0(3) pm for **1c** and 197.7(8)–200.4(7) pm for **1e**) than for the cobalt–cyclopentadienyl coordination (205.4(4)–207.6(4) pm for **1c** and 205.6(8)–207.9(8) pm for **1e**) (Table 1). The structural data of the sandwich core of **1c** and **1e** are quite comparable to other molecular structures of ( $\eta^4$ -cyclobutadiene)( $\eta^5$ -cyclopentadienyl)cobalt(I) complexes reported in the literature [9–15]. The difference in Co–C bond lengths suggests a stronger cobalt bonding to the CBD ligand than to the  $\text{C}_5$ -ring ligand, which is in agreement with theoretical calculations (see below) [14,15]. On the contrary, the distance between the Co atom and the centroid of the five-membered ring is slightly reduced (167.3 pm for **1c** and 168.3 pm for **1e**) compared to the distance between the Co atom and the centroid of the  $\text{C}_4$ -ring (169.3 and 169.4 pm for **1c** and **1e**, respectively). Due to the larger ring size, the five-membered ring immerses better into the coordination sphere of the Co center than the four-membered ring.

The *p*-tolyl substituents of the CBD ligand in **1c** are all tilted in the range of 23–43° with respect to the plane of the four-membered ring, and form a four-bladed propeller as found for other arylated  $\eta^4$ -cyclobutadiene ligands in Co



Scheme 2. Synthesis of ( $\eta^4$ -tetraarylcyclobutadiene)( $\eta^5$ -formylcyclopentadienyl)cobalt(I) complexes.

complexes (Fig. 2) [9–13]. However, a different situation is observed for **1e**: one *p*-dimethylamino phenyl group is almost coplanar to the *cyclo*-C<sub>4</sub>-entity, the tilt angle is only 1.5° (Fig. 3); consequently, the two adjacent aryl substituents are tilted to a larger extent (49.5° and 53.7°) and in the opposite sense. The tilt angle of the fourth aryl substituent amounts to 36.8° and is in the range of the corresponding angles of **1c**. The structural anomaly of the tilt angles of the aryl substituents in **1e** does not go along with significant distortions of the CBD ligand.

It is interesting to note that despite the different electronic properties of the aryl substituents in **1c** and **1e**, no influence can be observed on the bond lengths of the formyl group of the cyclopentadienyl ligand, which is in harmony to the spectroscopic findings (*vide infra*). The corresponding C,C and C,O bond lengths for **1c** and **1e**, respectively, are identical within the margin of error (C,C: 146.3(6) and 145.6(12) pm, and for C,O: 121.2(5) and 121.8(9) pm, respectively).

### 2.3. Spectroscopic and electrochemical properties

In order to get an indication of the influence of the aryl substituents in **1a–1e** on the electronic interaction between the two  $\pi$ -ligands, which is expected to be important in dipolar donor–acceptor complexes with SHG activities, their NMR and IR spectroscopic and electrochemical properties were studied in relation to the Hammett constants  $\sigma_p$  [16] (Table 2).

However, the shifts of the signals of the aldehyde protons vary only slightly and do not correlate with the  $\sigma_p$ -values. In contrast, a very small increasing low-field shift can

be observed for the <sup>13</sup>C resonance signals of the formyl group, when the donating ability of the aryl substituent increases. The overall shift range covers only 0.6 ppm.

Another sensitive probe for the interaction between the aryl substituents and the formyl cyclopentadienyl ligand should be the energy of the CO-stretching vibration of the aldehyde function. However, a closer look at the wavenumbers of the corresponding absorption bands in IR spectra (Table 2) illustrates that the  $\nu_{CO}$  band is hardly influenced by the electronic property of the substituent X in *para*-position of the aryl unit. Compared to **1b** (X = H) a significant but small bathochromic shift ( $\Delta\tilde{\nu} = 9 \text{ cm}^{-1}$ ) is observed for **1e** (X = NMe<sub>2</sub>).

These results are in agreement with observations of others. Apparently, the carbonyl function is not very sensitive to electronic changes in the *para*-position of an aromatic substituent. This is the case even if the CO function is directly coupled to the *para*-substituent of the aromatic ring via the organic  $\pi$ -bonding system as in corresponding acetophenone derivatives, e.g. the *para*-aminoacetophenone demonstrates bathochromic shift of the CO-stretching mode by only 14  $\text{cm}^{-1}$  compared to acetophenone itself [17].

It seems that the aromatic ring substituent has no significant influence on spectroscopic properties of the complexes in their ground state.

An alternative to evaluate the influence of substituents on the electronic property of the entire complex is the investigation of the redox activity. According to the cyclic voltammograms the formyl complexes **1a–1d** undergo an oxidation in dichloromethane, which is assumed to occur with an electrochemically reversible one-electron transfer

Table 1

Selected bond lengths (pm) and angles (°) obtained from X-ray structure determinations of the complexes **1c** and **1e** and from DFT-calculation of the complexes **2**, **3**, **4** and **5** (vide infra)

Compound	<b>1c</b>	<b>1e</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Co–C(1)	205.4(4)	205.6(8)	204.8	217.3	215.7	216.0
Co–C(2)	207.3(4)	205.8(9)	205.6	214.6	214.2	212.6
Co–C(3)	207.6(4)	205.8(8)	206.9	210.5	206.3	199.9
Co–C(4)	207.0(4)	207.9(8)	206.9	210.5	206.3	199.9
Co–C(5)	205.0(4)	207.5(9)	205.6	214.6	214.2	212.6
Co–C(6)	198.6(3)	198.2(8)	198.3	200.6	180.5	187.3
Co–C(7)	198.4(3)	200.4(7)	198.0	201.3	220.6	240.9
Co–C(8)	198.4(3)	197.7(8)	198.0	201.3	220.6	240.9
Co–C(9)	199.0(3)	198.5(8)	198.3	200.6	180.5	187.3
C(6)–C(10)	146.1(4)	149.2(10)				
C(7)–C(16)	146.3(4)	146.3(10)				
C(8)–C(22)	146.3(4)	148.2(9)				
C(9)–C(28)	146.2(4)	146.9(10)				
Co–Cp <sup>a</sup>	167.3	168.3	165.8	175.2	172.3	168.9
Co–CBD <sup>b</sup>	169.3	169.4	169.0	172.3	161.3	175.9
C(13)–N(1)	–	138.2(9)				
C(19)–N(2)	–	137.0(9)				
C(25)–N(3)	–	140.5(9)				
C(31)–N(4)	–	139.8(11)				
C(1)–C(2)	143.3(5)	140.5(11)	143.8	143.0	143.5	142.6
C(1)–C(5)	142.9(6)	142.1(12)	143.8	143.0	143.5	142.6
C(2)–C(3)	141.5(6)	138.0(13)	143.6	143.6	144.0	143.6
C(3)–C(4)	141.1(6)	141.6(12)	143.4	143.9	144.7	145.0
C(4)–C(5)	142.0(6)	141.5(12)	143.6	143.6	144.0	143.6
C(6)–C(7)	146.9(4)	148.1(11)	146.3	146.2	140.7	135.4
C(6)–C(9)	146.6(4)	147.3(10)	146.3	146.4	250.6	271.1
C(7)–C(8)	147.1(4)	145.8(10)	146.3	146.4	142.7	149.2
C(8)–C(9)	147.3(4)	146.6(11)	146.3	146.2	140.7	135.4
C(1)–C(41)	146.3(6)	145.6(12)				
C(41)–O(1)	121.2(5)	121.8(9)				
CBD(6–9)/Ph(10–15) <sup>c</sup>	36.8	53.7				
CBD(6–9)/Ph(16–21) <sup>c</sup>	43.3	1.5				
CBD(6–9)/Ph(22–27) <sup>c</sup>	23.1	49.5				
CBD(6–9)/Ph(28–33) <sup>c</sup>	35.4	36.8				
CBD–Co–Cp <sup>a,b</sup>	178.4	176.3	179.6	179.8	179.7	179.9
C(1)–C(41)–O(1)	124.9(4)	125.7(9)				

<sup>a</sup> Cp: centroid of the C<sub>5</sub>-ring ligand.

<sup>b</sup> CBD: centroid of the C<sub>4</sub>-ring ligand.

<sup>c</sup> Tilt angle between the best planes of the cyclobutadiene (CBD) ligand and the phenyl rings (Ph).

in agreement to other ( $\eta^4$ -cyclobutadiene)( $\eta^5$ -cyclopentadienyl)cobalt(I) complexes [15,18].

For **1d** an additional irreversible oxidation wave with almost the same peak current is found (Table 2). The appearance of a second oxidation step for **1d** at a lower potential compared to **1a–1c** is due to the stronger electron donating capability of the four *para*-methoxy substituents, which causes a general cathodic shift. The cathodic shift of the oxidation potentials is even more pronounced for **1e**, bearing the *para*-dimethylamino substituents. The cyclic voltammogram for **1e** displays three irreversible oxidation waves. The one with the highest oxidation potential ( $E_{pa} = 550 + 5$  mV vs. FcH/FcH<sup>+</sup>) is assigned to an oxidation of the *p*-dimethylamino phenyl substituents in agreement with published data of *p*-dimethylamino benzene [19]. Due to the number of aryl substituents in **1e** the corresponding peak current is almost three times as

large as the peak current of the first oxidation at  $E_{pa} = -2 + 5$  mV. In contrast to **1a–1d**, the first oxidation for **1e** is irreversible although the strong electron donating groups NMe<sub>2</sub> are expected to stabilize the positive charge. However, the small separation to the second and irreversible oxidation step (compare **1d**) makes the first one irreversible as well.

Comparing the potentials (Table 2), which enclose a range from  $E_{1/2} = 783 \pm 5$  mV (X = Cl, **1a**) to  $E_{pa} = -2 \pm 5$  mV (X = NMe<sub>2</sub>, **1e**) vs. FcH/FcH<sup>+</sup> it can be concluded that the first oxidation of **1a–1e** distinctly depends on the electronic nature of the aryl substituent: the more negative the Hammett parameter  $\sigma_p$  of the *para*-substituent X, the more the oxidation potential is shifted to lower values. Taking the peak potential of the first oxidation of **1e** approximately as half wave potential  $E_{1/2}$ , a linear correlation is found between the oxidation

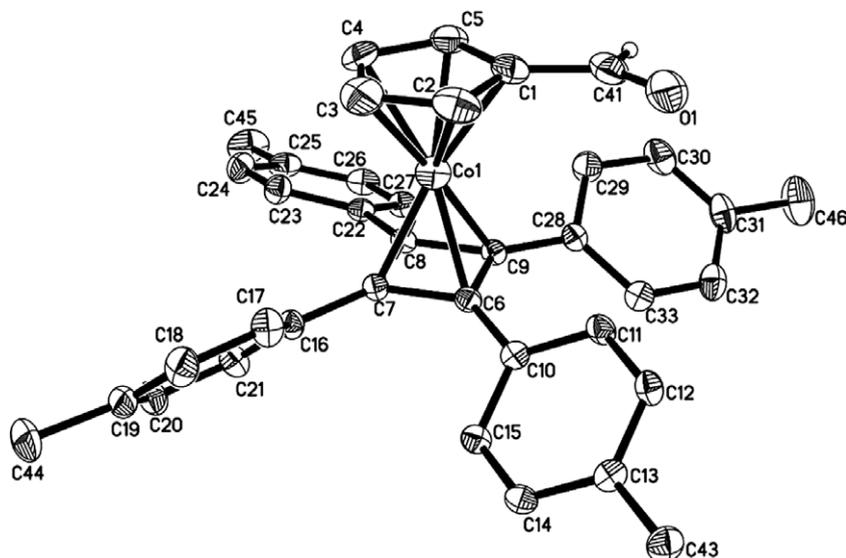


Fig. 2. Molecular structure of **1c** (with exception of the hydrogen atom of the formyl group, hydrogen atoms are omitted for clarity, the thermal ellipsoids are shown at the 50% level).

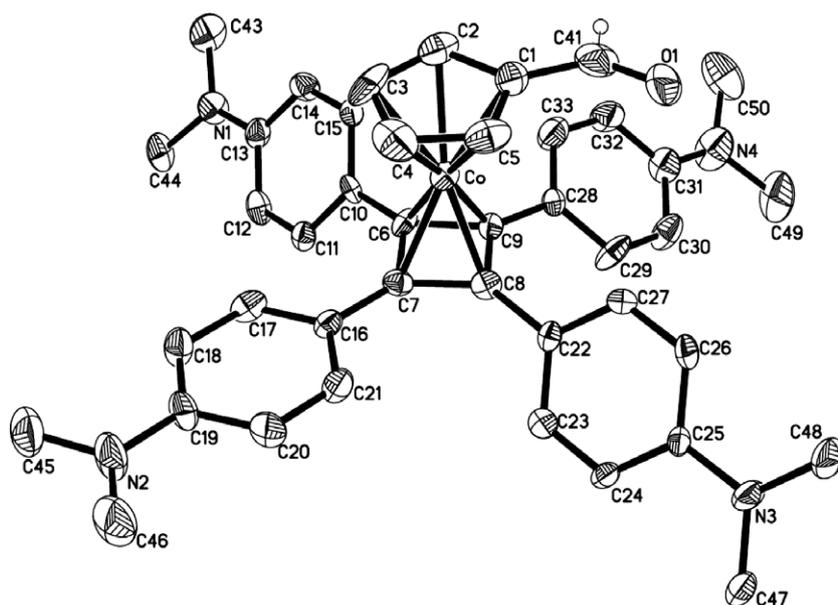


Fig. 3. Molecular structure of **1e** (with exception of the hydrogen atom of the formyl group, hydrogen atoms are omitted for clarity, the thermal ellipsoids are shown at the 50% level).

potential  $E_{1/2}$  and the electron donating power of the substituent X of the aryl group, expressed by the  $\sigma_p$ -values (Fig. 4). This correlation can be defined by the free-energy relationship in the following equation:

$$E_{1/2} = \rho_R \sigma_p + C \quad (1)$$

where  $\rho_R$  is the reaction constant,  $\sigma_p$  is electron donating capability and  $C$  is intercept.

From the linear fit in Fig. 4, a slope of 0.75 V can be calculated which is considerably larger than the  $\rho_R$ -value found for a similar study on substituted arylferrocenes with  $\rho_R = 0.070$  V [20]. The comparably large reaction constant  $\rho_R$  for the cobalt sandwich complexes indicate that they are more sensitive electron donating units than corresponding

ferrocene derivatives in dipolar complexes suitable for second harmonic generation.

#### 2.4. Electronic structure and MO-analysis

In order to gain deeper insights into the electronic structure and redox properties of  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-formylcyclopentadienyl})\text{cobalt(I)}$  complexes, we have performed a detailed analysis by the density functional theory method. In addition, the results of the DFT calculations may help to understand the irreversibility of the first oxidation step in the case of **1e**, which is reversible for the derivatives **1a–1d** with less electron donating substituents X.

Table 2  
Selected  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR and cyclic voltammetry data in relation to the Hammett constants  $\sigma_p$  of the complexes **1a–1e**

Complex	X	$\sigma_p^a$	$\delta_{\text{CHO}}^b$	$\delta_{\text{CHO}}^b$	$\bar{\nu}_{\text{CO}}$ ( $\text{cm}^{-1}$ ) <sup>c</sup>	$E_{1/2}/E_{\text{pa}}$ (mV) <sup>d,e</sup>
<b>1a</b>	Cl	0.23	9.34	190.69	1680	783 <sup>f</sup>
<b>1b</b>	H	0	9.30	190.98	1683	635 <sup>f</sup>
<b>1c</b>	$\text{CH}_3$	-0.17	9.22	191.06	1680	539 <sup>f</sup>
<b>1d</b>	$\text{OCH}_3$	-0.27	9.31	191.15	1681	432 <sup>f</sup> /868 <sup>g</sup>
<b>1e</b>	$\text{N}(\text{CH}_3)_2$	-0.83	9.30	191.29	1674	-2 <sup>g</sup> /65 <sup>g</sup> /550 <sup>g</sup>

<sup>a</sup>  $\sigma_p$  Values obtained from the literature [16].

<sup>b</sup> Measured in  $\text{CD}_2\text{Cl}_2$ .

<sup>c</sup> KBr.

<sup>d</sup> Scan rate:  $200 \text{ mV s}^{-1}$ .

<sup>e</sup> Potentials ( $\pm 5 \text{ mV}$ ) vs.  $\text{FcH}/\text{FcH}^+$  in  $\text{CH}_2\text{Cl}_2$ ,  $E_{\text{pa}}$  = peak potentials of the anodic oxidation.

<sup>f</sup> Reversible oxidation.

<sup>g</sup> Irreversible oxidation.

For calculations on the electronic structures of the neutral complexes **1a–1e**, we chose as a simple model system the complex  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})$  cobalt(I) (**2**). Geometry optimization of **2** revealed a nearly  $C_s$  symmetric structure with an almost linear arrangement of the centroids of the  $\pi$ -ligands and the metal center (CBD–Co–Cp angle of  $179.6^\circ$ ). Geometrical parameters for the optimized structure of complex **2** are listed in Table 1. For further analysis a  $C_s$  symmetric structure has been assumed (Fig. 5). Distances for Co–C(6) of 198.3 pm, Co–C(7) of 198.0 pm and Co–CBD of 169 pm are indicative for a strong Co–C interaction of the Co center to the four-membered ring. Slightly longer distances were found between the cobalt atom and the carbon atoms of the  $C_5$ -ring ligand: Co–C(1) of 204.8 pm, Co–C(2) of 205.6 pm and Co–C(3) of 206.9 pm. This would imply a weaker Co–C interaction of the Co-center to the  $C_5$ -ring, although the distance from the Co atom to the centroid of the five-membered ring (Co–Cp) of 165.8 pm is about 3 pm shorter than to the centroid of the  $C_4$ -ring. Optimized bond distances and angles are in excellent agreement with structural parameters derived through X-ray structure analyses for

structures **1c** and **1e**. Deviations are within 1 pm. An analysis of the electronic structure of complex **2** revealed that the HOMO consists mainly of a Co  $3d_{xy}$  orbital with  $\delta$ -bonding interaction with cyclopentadienyl ligand  $\pi$ -orbitals and weak antibonding overlap with a  $\sigma$ -cyclobutadiene orbital. This is in agreement with previous calculations reported in the literature [15].

Upon oxidation, complex cation **3** was obtained (Fig. 5). Geometry optimization of cation **3** revealed bonding parameters listed in Table 1. The bond lengths Co–C(1) (217.3 pm), Co–C(2) (214.6 pm) and Co–C(3) (210.5 pm) are about 10 pm longer than those in complex **2**, with corresponding cobalt–carbon atom bond lengths of 204.8–206.9 pm. Also, the calculated distances Co–C(6) of 200.6 and Co–C(7) of 201.3 pm to the  $C_4$ -ring ligand are about 3 pm longer (Co–CBD of 172.3 pm), although the arrangements of the ligands around the metal center remained linear (CBD–Co–Cp angle of  $179.8^\circ$ ). Thus, the interaction of the Co atom with the cyclopentadienyl ligand is weakened while interaction between the Co atom and the  $C_4$ -ring nearly remains. This can also be seen by orbital analysis: the former HOMO in complex **2** becomes singly occupied and the bonding interaction between the Co-atom and the  $C_5$  ring is weakened. Due to electronic and geometrical rearrangements the HOMO in complex **2** becomes HOMO-7 ( $\alpha$ ) in cation **3**.

Further oxidation resulted in the dication **4** (Fig. 5). For geometry optimization of dication **4**, we used the geometry of monocation **3** as starting point and obtained the dicationic complex **4** depicted in Fig. 5. The distances Co–C(1) of 215.7 pm, Co–C(2) of 214.2 pm, Co–C(3) of 206.3 pm, Co–C(6) of 180.5 pm and Co–C(7) of 220.6 pm are indicative of a Co-center inserted into one of the C–C bonds of the  $C_4$ -ring revealing a metallacyclopentene moiety. This unusual reaction raises the question for the changes in electronic structure of complex **2** to cation **3** and dication **4**.

From molecular orbital analysis it can be concluded that upon insertion of the Co atom into the C–C bond of the  $C_4$ -ring, the loss of a C–C bonding interaction strongly destabilizes one of the nearly degenerate HOMOs ( $1a'$ ) (Fig. 6). The other orbital ( $1a''$ ) becomes

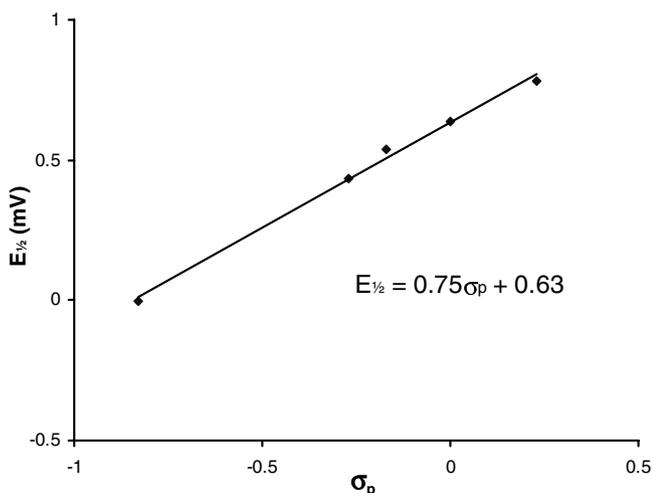


Fig. 4. Correlation between the oxidation potentials of **1a–1e** and the corresponding Hammett parameter  $\sigma_p$ .

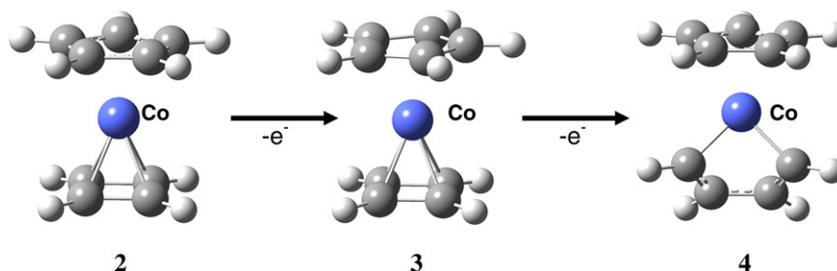


Fig. 5. Optimized structures of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-C}_4\text{H}_4)$  derivatives (left). Structure of the neutral complex **2**, structure of the monocation **3** (middle) and structure of the dication **4** (right).

stabilized because of the loss of C–C antibonding interaction and increasing Co–C overlap. The overall reaction of the insertion in complex **2** is endothermic which is in agreement with experimental observations. When two electrons are withdrawn from the system, the destabilization of **1a'** (Fig. 6) does not contribute to the reaction energy and thus the reaction from **2** to **4** becomes feasible.

Another interesting feature comes from the avoided crossing of the empty orbital  $2a''$  which becomes more stable than **1a'** along the reaction coordinate (Fig. 6). This would suggest that a metallacyclopentadiene Co(III)-complex would be thermodynamically unstable, as indicated by cyclic voltammetry studies, but could have some kinetic inertness towards cyclobutadiene formation. To test this hypothesis a putative complex **5**, which can be obtained by adding two electrons to complex **4**, was optimized. The resulting stable complex **5** exhibits a clear metallacyclopentadiene structure with geometry parameters in agreement with previously reported Lewis-base adducts of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co(III)}(-\text{CH}=\text{CH}-\text{CH}=\text{CH}-)(\text{L})$  complexes [21]. The energy of complex **2** is calculated to be 38 kcal/mol

below complex that of **5** which has been presumed to be an intermediate in the cyclodimerization of alkynes by Co complexes (Scheme 2) [22].

### 3. Conclusions

In addition to the known compound **1b**, four novel  $(\eta^4\text{-tetraaryl}(\text{cyclobutadiene})(\eta^5\text{-formylcyclopentadienyl})\text{-cobalt(I)}$  complexes were synthesized by the Takahashi route in yields suitable for further WHWE coupling reactions forming dipolar donor–acceptor compounds. The tetraaryl groups bear substituents X of different electronic properties in *para*-position (X = Cl, H, Me, OMe, NMe<sub>2</sub>).

X-ray structure analysis of the methyl and the dimethylamino derivatives **1c** and **1e**, respectively, reveals structural data quite similar to known structures of  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{Co(I)}$  complexes, except for the tilt angle of one phenyl unit in **1e** with respect to the cyclobutadiene plane. However, no significant additional structural anomalies could be observed, which might give a clue to the reason for this structural peculiarity.

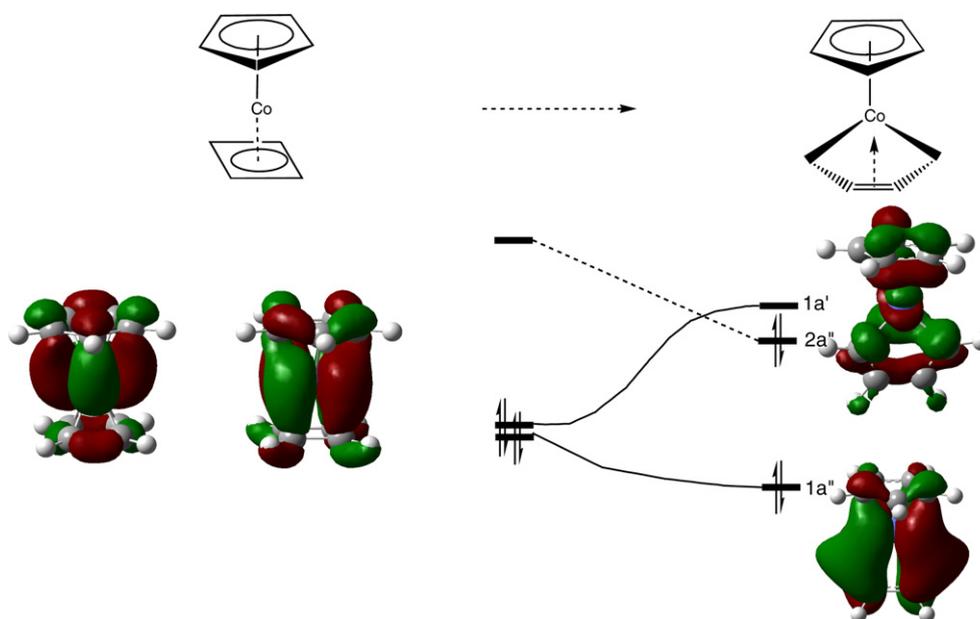


Fig. 6. Walsh diagram along the insertion path of the Co-center into the C–C bond.

IR and  $^{13}\text{C}$  NMR studies of the formyl function of the Cp ligands demonstrate only a weak influence of the electronic properties of the aryl substituents X on the energy of the CO-stretching mode and on the  $^{13}\text{C}$  shift of the formyl function, respectively.

In contrast, cyclic voltammetry measurements uncover a linear dependence of the first oxidation potential on the  $\sigma_p$  values, pointing out a distinct electron donating capability of the Co complex in the case of negative  $\sigma_p$  values like for X = OMe, NMe<sub>2</sub>. The electron donating aryl ligand lowers the oxidation potential significantly. Thus, a decomposition via insertion of the Co-center into the cyclobutadiene ring and further degradation of the ensuing Co(V) center occurs. The oxidation process reverses the dimerization of the alkyne ligands as can be concluded from DFT-calculations.

The strong electron donating properties make the ( $\eta^4$ -cyclobutadiene)( $\eta^5$ -cyclopentadienyl)Co(I) complexes most promising for compounds with SHG activities.

## 4. Experimental

### 4.1. General methods

Manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk technique. All solvents were saturated with nitrogen. Diethyl ether (Et<sub>2</sub>O), tetrahydrofuran (THF), *n*-hexane and toluene were freshly distilled from the appropriate alkali metal or metal alloy. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and nitromethane (MeNO<sub>2</sub>) were dried over calcium hydride. NMR: Varian Gemini 200 BB; Bruker AM 360; measured at 295 K rel. TMS. UV–Vis: Perkin–Elmer Model 554. IR: KBr pellets; FT-IR, Perkin–Elmer Model 325. MS: Finnigan MAT 311 A (EI-MS). Elemental analyses: CHN-O-Rapid, Fa. Heraeus, Zentrale Elementanalytik, Department Chemie, Universität Hamburg. Formylcyclopentadienyl sodium [23], formylcyclopentadienyl thallium [24], tris(triphenylphosphine)cobalt(I) chloride [25], and the *p*-substituted diarylethyne [26] were prepared according to the literature procedures.

### 4.2. General procedure for the synthesis of the ( $\eta^4$ -tetraaryl-cyclobutadiene)( $\eta^5$ -formylcyclopentadienyl)cobalt complexes **1a–1e**

To a suspension of tris(triphenylphosphine)cobalt(I) chloride in toluene a solution of THF with one equivalent of formylcyclopentadienyl sodium was added. The reaction mixture was stirred for 30 min at room temperature, during which the colour of the solution turned red. A toluene solution containing two equivalents of the appropriate diarylethyne was added. The reaction mixture was stirred for 2.5–8 h under reflux. The reaction was monitored by thin layer chromatography. Finally, the reaction mixture was evaporated to dryness and the desired product was separated by column chromatography. The products were obtained as orange-red crystalline material.

#### 4.2.1. [ $\eta^4$ -Tetrakis(4-chlorophenyl)cyclobutadiene]( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**1a**)

Tris(triphenylphosphine)cobalt(I) chloride (538 mg, 0.61 mmol) in toluene (5 mL), formylcyclopentadienyl sodium (70 mg, 0.61 mmol) in THF (5 mL), bis(4-chlorophenyl)ethyne (300 mg, 1.22 mmol) in toluene (15 mL), 2.5 h reflux, Al<sub>2</sub>O<sub>3</sub> neutral, 5% water; toluene/hexane 2:1.

Yield: 200 mg (51%). Mp: 254 °C. Anal. Calc. for C<sub>34</sub>H<sub>21</sub>Cl<sub>4</sub>CoO (*M* = 646.1): C, 63.19; H, 3.28. Found: C, 63.08; H, 3.41%. <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.89 (pseudo t, <sup>3</sup>*J* = 2.10 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 5.22 (pseudo t, <sup>3</sup>*J* = 2.10 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.24 (d, <sup>3</sup>*J* = 8.79 Hz, 8H, H<sub>m</sub>), 7.33 (d, <sup>3</sup>*J* = 9.03 Hz, 8H, H<sub>o</sub>), 9.34 (s, H, CHO). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  76.26 (C<sub>4</sub>Ar<sub>4</sub>), 83.55 (C<sub>5</sub>H<sub>4</sub>), 89.09 (C<sub>5</sub>H<sub>4</sub>), 92.95 (C<sub>q</sub>-C<sub>5</sub>H<sub>4</sub>), 129.01 (C<sub>m</sub>), 130.27 (C<sub>o</sub>), 133.25 (C<sub>i</sub>, C<sub>p</sub>), 190.69 (CHO). IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  3108 (CH)<sub>Ph</sub>, 1680 (C=O), 1601, 1495, 1458 (C=C)<sub>Ph</sub>, 1397 (CHO), 1119, 1012 (C=C)<sub>Cp</sub>, 1081 (CCl), 827 (CH). EI-MS: *m/z* (%) 647 (37), 645 (27) [M<sup>+</sup>], 124 (62) [CpCo<sup>+</sup>], 58 (100) [Co<sup>+</sup>].

#### 4.2.2. ( $\eta^4$ -Tetraphenylcyclobutadiene)( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**1b**) [8,10]

Tris(triphenylphosphine)cobalt(I) chloride (1.88 g, 2 mmol) in toluene (10 mL), formylcyclopentadienyl sodium (232 mg, 0.20 mmol) in THF (5 mL), diphenylethyne (785 mg, 0.40 mmol) in toluene (20 mL), 6 h reflux, Al<sub>2</sub>O<sub>3</sub> neutral, 5% water, toluene/hexane 2:1.

Yield: 700 mg (67.5%). Mp: 186 °C. <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.91 (pseudo t, <sup>3</sup>*J* = 2.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 5.22 (pseudo t, <sup>3</sup>*J* = 2.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.23–7.30 (m, 12H, H<sub>m,p</sub>), 7.41–7.45 (m, 8H, H<sub>o</sub>), 9.30 (s, H, CHO). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  77.55 (C<sub>4</sub>Ar<sub>4</sub>), 83.43 (C<sub>5</sub>H<sub>4</sub>), 89.02 (C<sub>5</sub>H<sub>4</sub>), 92.97 (C<sub>q</sub>-C<sub>5</sub>H<sub>4</sub>), 127.34 (C<sub>p</sub>), 128.52 (C<sub>m</sub>), 129.17 (C<sub>o</sub>), 135.25 (C<sub>i</sub>), 190.98 (CHO). IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  3079, 3057, 3026 (CH)<sub>Ph</sub>, 1683 (C=O), 1596, 1499, 1444 (C=C)<sub>Ph</sub>, 1391 (CHO), 1155, 1026, 744, 707.

#### 4.2.3. [ $\eta^4$ -Tetrakis(4-methylphenyl)cyclobutadiene]( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**1c**)

Tris(triphenylphosphine)cobalt(I) chloride (442 mg, 0.50 mmol) in toluene (6 mL), formylcyclopentadienyl sodium (69 mg, 0.60 mmol) in THF (2 mL), bis(4-methylphenyl)ethyne (200 mg, 1.00 mmol) in toluene (3 mL), 4.5 h reflux, Al<sub>2</sub>O<sub>3</sub> neutral, 5% water, hexane/diethylether 10:1.

Yield: 165 mg (60.2%). Mp: 258 °C. Anal. Calc. for C<sub>38</sub>H<sub>33</sub>CoO(CH<sub>2</sub>Cl<sub>2</sub>) (*M* = 649.52): C, 72.12; H, 5.43. Found: C, 71.53; H, 5.54%. <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.22 (s, 12H, CH<sub>3</sub>), 4.76 (pseudo t, <sup>3</sup>*J* = 2.20 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 5.08 (pseudo t, <sup>3</sup>*J* = 2.20 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.97 (d, <sup>3</sup>*J* = 8.10 Hz, 8H, H<sub>m</sub>), 7.22 (d, <sup>3</sup>*J* = 8.10 Hz, 8H, H<sub>o</sub>), 9.22 (s, H, CHO). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  21.52 (CH<sub>3</sub>), 77.40 (C<sub>4</sub>Ar<sub>4</sub>), 83.19 (C<sub>5</sub>H<sub>4</sub>), 88.97 (C<sub>5</sub>H<sub>4</sub>), 92.90 (C<sub>q</sub>-C<sub>5</sub>H<sub>4</sub>), 128.98 (C<sub>m</sub>), 129.17 (C<sub>o</sub>), 132.28 (C<sub>p</sub>), 137.15 (C<sub>i</sub>), 191.06 (CHO). IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  3025 (CH)<sub>Ph</sub>,

2918, 2856 (CH<sub>3</sub>), 1680 (C=O), 1517, 1456 (C=C)<sub>Ph</sub>, 1380 (CH<sub>3</sub>), 1113, 1018, 817. EI-MS: *m/z* (%) 564 (100) [M<sup>+</sup>], 471 (49) [(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>CBD]Co<sup>+</sup>, 358 (15) [M<sup>+</sup>-(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>C)<sub>2</sub>].

#### 4.2.4. [ $\eta^4$ -Tetrakis(4-methoxyphenyl)cyclobutadiene] ( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**1d**)

Tris(triphenylphosphine)cobalt(I) chloride (370 mg, 0.42 mmol) in toluene (6 mL), formylcyclopentadienyl sodium (48 mg, 0.42 mmol) in THF (1.5 mL), bis(4-methoxyphenyl)ethyne (200 mg, 0.84 mmol) in toluene (2 mL), 8 h reflux, Al<sub>2</sub>O<sub>3</sub> neutral, 5% water, hexane/diethylether 1:1.

Yield: 74 mg (28%). Mp: 208 °C. Anal. Calc. for C<sub>38</sub>H<sub>33</sub>CoO<sub>5</sub> (*M* = 628.4): C, 72.60; H, 5.29. Found: C, 71.69; H, 5.42%. <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  3.81 (s, 12H, OCH<sub>3</sub>), 4.85 (pseudo t, <sup>3</sup>*J* = 2.10 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 5.19 (pseudo t, <sup>3</sup>*J* = 2.10 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.78 (d, <sup>3</sup>*J* = 8.80 Hz, 8H, H<sub>m</sub>), 7.36 (d, <sup>3</sup>*J* = 8.80 Hz, 8H, H<sub>o</sub>), 9.31 (s, H, CHO). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  55.59 (OCH<sub>3</sub>), 76.99 (C<sub>4</sub>Ar<sub>4</sub>), 82.99 (C<sub>5</sub>H<sub>4</sub>), 88.80 (C<sub>5</sub>H<sub>4</sub>), 92.65 (C<sub>q</sub>-C<sub>5</sub>H<sub>4</sub>), 113.99 (C<sub>m</sub>), 127.37 (C<sub>i</sub>), 130.20 (C<sub>o</sub>), 158.91 (C<sub>p</sub>), 191.15 (CHO). IR (KBr):  $\tilde{\nu}$ /cm<sup>-1</sup> 3034, 3000 (CH)<sub>Ph</sub>, 2952, 2931 (CH<sub>3</sub>), 2833 (COCH<sub>3</sub>), 1681 (C=O), 1606, 1515, 1459 (C=C)<sub>Ph</sub>, 1389 (CH<sub>3</sub>), 1109, 1031, 1246, 809. EI-MS: *m/z* (%) 629 (100) [M<sup>+</sup>], 476 (6) [(4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>CBD]<sup>+</sup>,

391 (8) [M<sup>+</sup>-(4-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>C)<sub>2</sub>], 124 (10) [CpCo<sup>+</sup>], 95 (20) [CpCHO<sup>+</sup>], 58 (33) [Co<sup>+</sup>].

#### 4.2.5. [ $\eta^4$ -Tetrakis(4-dimethylaminophenyl)cyclobutadiene] ( $\eta^5$ -formylcyclopentadienyl)cobalt(I) (**1e**)

Tris(triphenylphosphine)cobalt(I) chloride (210 mg, 0.23 mmol) in toluene (2 mL), formylcyclopentadienyl sodium (28 mg, 0.23 mmol) in THF (1 mL), bis(4-dimethylaminophenyl)ethyne (120 mg, 0.46 mmol) in toluene (7 mL), 5 h reflux, Al<sub>2</sub>O<sub>3</sub> neutral, 5% water, dichloromethane/hexane 5:1.

Yield: 72 mg (46.5%). Mp: 260 °C. Anal. Calc. for C<sub>42</sub>H<sub>45</sub>CoN<sub>4</sub>O (*M* = 680.78): C, 74.10; H, 6.66; N, 8.23. Found: C, 74.56; H, 6.92; N, 7.83%. <sup>1</sup>H NMR: (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.95 (s, 24H, N(CH<sub>3</sub>)<sub>2</sub>), 4.81 (pseudo t, <sup>3</sup>*J* = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 5.32 (pseudo t, <sup>3</sup>*J* = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.59 (d, <sup>3</sup>*J* = 8.90 Hz, 8H, H<sub>m</sub>), 7.31 (d, <sup>3</sup>*J* = 8.90 Hz, 8H, H<sub>o</sub>), 9.30 (s, H, CHO). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  40.57 (N(CH<sub>3</sub>)<sub>2</sub>), 77.50 (C<sub>4</sub>Ar<sub>4</sub>), 82.81 (C<sub>5</sub>H<sub>4</sub>), 88.71 (C<sub>5</sub>H<sub>4</sub>), 93.03 (C<sub>q</sub>-C<sub>5</sub>H<sub>4</sub>), 112.10 (C<sub>m</sub>), 123.18 (C<sub>i</sub>), 129.86 (C<sub>o</sub>), 149.53 (C<sub>p</sub>), 191.29 (CHO). IR (KBr):  $\tilde{\nu}$ /cm<sup>-1</sup> 2852 (CH<sub>3</sub>), 1674 (C=O), 1608, 1481, 1444 (C=C)<sub>Ph</sub>, 1389 (CH<sub>3</sub>), 1126, 1035<sub>Cp</sub>, 1352, 817. EI-MS: *m/z* (%) 680 (100) [M<sup>+</sup>], 528 (9) [(4-CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>CBD]<sup>+</sup>, 57 (22) [Co<sup>+</sup>].

Table 3  
Crystallographic data of **1c** and **1e**

Compound	<b>1c</b>	<b>1e</b>
Empirical formula	C <sub>39</sub> H <sub>39</sub> HCl <sub>12</sub> CoO	C <sub>48</sub> H <sub>59</sub> CoN <sub>4</sub> O
Formula mass	649.50	766.92
<i>T</i> (K)	173(2)	293(2)
$\lambda$ (pm)	71.073	71.073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>Pc</i>
Crystal dimensions		
<i>a</i> (pm)	10.9446(10)	11.773(5)
<i>b</i> (pm)	12.125(2)	13.535(7)
<i>c</i> (pm)	12.554(2)	13.093(8)
$\alpha$ (°)	92.129	90
$\beta$ (°)	105.613(11)	97.26(4)
$\gamma$ (°)	96.989	90
<i>V</i> (10 <sup>6</sup> pm <sup>3</sup> )	1588.3(4)	2069.6(19)
<i>Z</i>	2	2
$\rho_{\text{ber}}$ (μm/g)	1.358	1.231
Absorption coefficient (mm <sup>-1</sup> )	0.739	0.455
<i>F</i> (000)	676	820
Crystal size (mm)	0.50 × 0.35 × 0.25	0.50 × 0.50 × 0.44
$\theta_{\text{min}}$ , $\theta_{\text{max}}$ (°)	1.69, 26.0	2.30, 22.56
Index range	-13 ≤ <i>h</i> ≤ 13, -15 ≤ <i>k</i> ≤ 15, -15 ≤ <i>l</i> ≤ 0	-1 ≤ <i>h</i> ≤ 12, -7 ≤ <i>k</i> ≤ 14, -14 ≤ <i>l</i> ≤ 14
Reflections collected	6608	3631
Independent reflections	6342	3200
<i>R</i> <sub>int</sub>	0.0250	0.0458
Parameter	387	556
Goodness-of-fit	1.106	1.018
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0632/0.1538	0.0472/0.0983
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0745/0.1596	0.0662/0.1061
Extinction coefficient	0.0003(9)	0.0005(6)
Largest difference in peak and hole (e Å <sup>-1</sup> )	0.684 and -1.105	-0.261 and 0.303

### 4.3. X-ray structure determination

Crystals of compound **1c** and **1e** suitable for an X-ray structure determination were obtained for **1c** by gas phase diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex at room temperature, and for **1e** by careful evaporation of the solvent from an Et<sub>2</sub>O/hexane solution. The data were collected on four-circle diffractometer Hilger and Watts, Mo K $\alpha$ ,  $\lambda = 71.073$  ppm and Syntex at 170 K and 293 K, respectively (Table 3). The structures were solved by direct methods (SHELXS-86) [27a], and the refinement on  $F^2$  were carried out by full-matrix least-square techniques (SHELXL-97) [27b]. 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 atom. Weights were optimized in the final refinement cycles. Residual electron density was observed for crystals of **1c** pointing out diffuse incorporation of solvent molecules [28]. Complex **1e** was refined as a racemic twin. In addition one molecule of hexane was found in the asymmetric unit.

### 4.4. Cyclic voltammetry

Measurements were performed in CH<sub>2</sub>Cl<sub>2</sub> with 0.4 M [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub> as supporting electrolyte. An Amel 5000 system was used with a Pt wire as working electrode and a Pt plate (0.6 cm<sup>2</sup>) as auxiliary electrode. The potentials were measured against Ag/AgPF<sub>6</sub> and were referenced against  $E_{1/2}(\text{FcH}/\text{FcH}^+) = 0$  V (=0.58–0.59 V vs. Ag/AgPF<sub>6</sub>).

### 4.5. Computational details

For all calculations on the density functional theory level, the Program GAUSSIAN-03 was used [29]. Energies and geometries were developed on the non-local level of theory. For geometry optimization the energies were corrected for non-local exchange according to Becke [30] and for non-local correlation according to Perdew (BP86) [31] in the self-consistent procedure. The 6-311G(3d,3p)-split valence basis set was used for all atoms which is supplied by the program [29]. In addition, a MO-analysis was performed using the program system CACAO [32].

## 5. Supplementary material

CCDC 630612 and 630611 contain the supplementary crystallographic data for **1c** and **1e**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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