Mono-, Di-, and Trimetallic Complexes of the Nonalternating Polycondensed π-Perimeter Decacyclene, $C_{36}H_{18}$: Synthesis, Structure, and Spectroelectrochemistry of $[\{(\eta^5\text{-}Me_4EtC_5)Co\}_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_{36}H_{18})]$

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In memory of Dr. Ulrike Krautscheid

Abstract: Reaction of the half-sandwich complexes $[(\eta^5\text{-}Me_4RC_5)M(\eta^2{:}O\text{-acac})]$ (M = Co, Ni; R = Me or Et) with di- and trianions of the polycondensed π-hydrocarbon decacyclene results in formation of the first Co and Ni triple-decker complexes of this hydrocarbon. For the title compound NMR spectra as well as a crystal structure analysis reveal an antarafacial coordination of two $\{(\eta^5\text{-}Me_4EtC_5)Co\}$ fragments at the central six-membered ring and one of the neighboring five-membered rings of decacyclene. The bridging π-perimeter decacyclene displays a bowl-shaped topology. In the case of Ni, coordination of two $\{(\eta^5\text{-}Me_5C_5)Ni\}$ fragments at the central six-membered ring of decacyclene is observed, based on the results of ^1H and ^{13}C NMR studies. This coordination mode is without precedent for nickel organometallic compounds reported so far. The cobalt complex shows a rich spectroelectrochemistry. Results of cyclic voltammetry and coupled ESR experiments reveal a strong interaction of both metal centers in the mixed-valent monocation of $[\{(\eta^5\text{-}Me_4EtC_5)Co\}_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_{36}H_{18})]$. This categorizes the title compound into Robin Day class III.

Keywords: cobalt · decacyclene · hydrocarbons · nickel · sandwich complexes

Introduction

Decacyclene $C_{36}H_{18}$ (**1**) is a large nonalternating polycondensed hydrocarbon (PAH) that has recently attracted considerable attention as a precursor of gas-phase and solution-based routes to buckminsterfullerene C_{60}.[1] In addition, its high redox activity[2] and its extended large π system are ideal prerequisites for the coordination of metal–ligand fragments to this PAH. However, examples for transition metal coordination of **1** or comparable extended PAHs, in which well characterized complexes are obtained are rare.[3] For decacyclene itself, a Ag complex was reported, in which a weak η^2 coordination of the silver ion was observed in one naphthalene subunit of **1**.[4] These studies reflect the potential of decacyclene as a molecular building block for supramolecular architectures with unusual structural motifs created through weak metal–ligand interactions. However, other transition metal complexes of decacyclene have not been reported to date,[5] but can be expected to have interesting properties due to the large π-aromatic system of **1** which could facilate electronic communication between coordinated metal fragments. Moreover, the unique, helical twisted geometry of **1**[6] might lead to new structural motifs upon coordination of metal–ligand fragments. However, its low solubility presents a considerable preparative hurdle for the exploration of its chemistry. This appears to be a quite general problem connected with the coordination chemistry of large PAHs; these often tend to form highly insoluble complexes especially when no solubilizing peripheral ligands are present. Once this problem is overcome, **1** proves to be a versatile ligand in organotransition metal chemistry, both with respect to its coordination properties and its ability as mediator for electronic communication between metal centers.

Herein we report on structural and electronic properties of the first mono-, di-, and trimetallic Co and Ni complexes of **1**.

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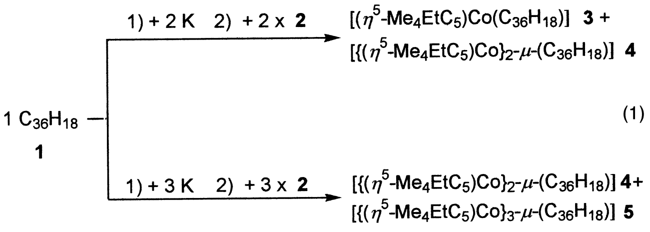
Results and Discussion

Reaction of [(η^5-Me$_4$EtC$_5$)Co(η^3:O-acac)] with [C$_{36}$H$_{18}$]$^{2-}$ and [C$_{36}$H$_{18}$]$^{3-}$ ions: Reducing polyarenes with solid alkali metals in ethers produces solvent-stabilized contact ions.[7] We found that reducing **1** with solid potassium metal in THF[8] at ambient temperature gives stable solutions of the decacyclid polyanions [C$_{36}$H$_{18}$]$^{2-}$ and [C$_{36}$H$_{18}$]$^{3-}$. These solutions are highly reactive in reductive ligand elimination reactions leading to the first mono-, di-, and trimetallic Co and Ni complexes of **1**. The preparative pathway presented herein is straightforward and well established in organometallic chemistry, but to the best of our knowledge has not been applied so far to the chemistry of large π-condensed polyaromatic compounds such as **1**.

Reaction of [(η^5-Me$_4$EtC$_5$)Co(acac)] (**2**)[9] with THF solutions containing reduced decacyclene gives brownish black solutions from which, depending on the amount of potassium metal used for the reduction of **1**, complexes **3** (Co$_1$), **4** (Co$_2$), and **5** (Co$_3$) were isolated as highly air-sensitive microcrystalline black crystals [Eq. (1); Figure 1]. In the case of **4** and **5**, compounds **3** and **4** are formed as side products, respectively, which were separated by fractional crystallization.



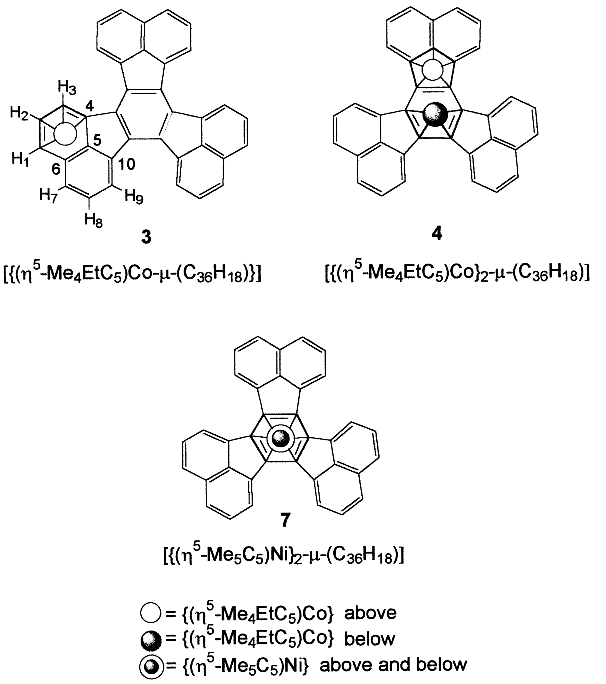


Figure 1. Coordination modes of {(η^5-Me$_4$RC$_5$)M} (M = Co, Ni; R = Me or Et) fragments in **3**, **4**, and **7**.

Close inspection of the one- and two-dimensional NMR spectra allows definitive clues towards the type of metal coordination for all new compounds (Table 1). In the case of **3**, a well established η^4-coordination of one naphthalene unit of **1** to a {(η^5-Me$_4$EtC$_5$)Co} fragment is deduced on the basis of the ^{1}H NMR data; the spectrum displays 17 of a total of 18 signals expected for this coordination mode. An AMX spin system of one naphthalene moiety shows a characteristic shift towards higher field upon coordination: (H1 ($\delta = 2.55$, d), H2 ($\delta = 6.11$, t), H3 ($\delta = 8.18$, d); Figure 1)).[10] This high-field shift is even more pronounced in the ^{13}C NMR spectrum. Compared to C2 and C3, the carbon signals of the terminal positions C1 and C4 of one naphthalene unit are substantially more shielded, in full accord with what is observed for Co complexes containing (η^4-diene) moieties.

With respect to **4**, the overall number of ^{1}H NMR signals is drastically reduced (from 18 to 9) compared to the situation for **3**. The ratio of {(η^5-Me$_4$EtC$_5$)Co} to decacyclene units is 2:1 as determined by integration of the relevant signals. In contrast to **3**, no significant upfield shift of a naphthalene unit is observed for **4**. This indicates a coordination of the inner five- and six-membered rings of **4** to the two {(η^5-Me$_4$EtC$_5$)Co} fragments. Finally for **5**, integration reveals a ratio of {(η^5-Me$_4$EtC$_5$)Co} to decacyclene of 3:1. This, as well as an additional characteristic upfield shift of one AMX naphthalene system ($\delta = 3.05$, d; $\delta = 6.20$, t; 8.50, d) compared to the NMR spectrum of dinuclear **4** is in accord with a superposition of two individual coordination modes observed for **3** and **4**.

Figure 2 shows the result of an X-ray structure determination of the molecular structure of **4** in the solid state.[11] Both {(η^5-Me$_4$EtC$_5$)Co} fragments are bound in an antarafacial coordination mode η^4 to the central six-membered ring and η^5 to an adjacent five-membered ring of **4**. This leads to an unsymmetrical bonding situation which can be categorized as a slipped triple decker and represents, to the best of our knowledge, a new type of structurally characterized Co coordination to a

Abstract in German: *Durch Umsetzung der Halbsandwichkomplexe [(η^5-Me$_4$RC$_5$)M(η^2:O-acac)] (M = Co, Ni; R = Me or Et) mit dem Di- und Trianion des Decacyclens gelingt die Darstellung der ersten Tripeldeckerkompexe dieses polykondensierten π-Perimeters. Sowohl die NMR-Spektren als auch die Kristallstruktur belegen die antarafaciale Koordination zweier {(η^5-Me$_4$EtC$_5$)Co}-Fragmente sowohl am zentralen Sechsring als auch am benachbarten Fünfring des Decacyclens. Die ungewöhnliche Art der Metallkomplexierung verursacht eine schalenförmige Topologie des π-Perimeters. Im Falle des Nickels lässt sich aus den ^{1}H- und ^{13}C-NMR-Daten zweifelsfrei die Koordination zweier [(η^5-Me$_5$C$_5$)Ni]-Fragmente am zentralen Sechsrings des Decacyclens nachweisen. Diese Koordinationsweise von Nickel an Sechsringaromaten ist präzedenzlos. Der Cobaltkomplex [{(η^5-Me$_4$EtC$_5$)Co}$_2$(μ-η^5:η^4-C$_{36}$H$_{18}$)] zeigt eine ausgeprägte Redoxchemie. Mittels CV- und gekoppelter ESR-Spektroskopie lässt sich eine starke Wechselwirkung beider Metallzentren im gemischtvalenten Monokation nachweisen. Dies entspricht einer Zuordnung zur Robin-Day Klasse III für Intervalenzverbindungen.*

Table 1. Spectroscopic data for **3**, **4**, **5**, and **7**.

1: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.52$ (t, $^3J = 7.6$ Hz, 6H), 7.70 (d, $^3J = 7.6$ Hz, 6H), 8.73 (d, $^3J = 7.6$ Hz, 6H); IR (KBr): $\tilde{\nu} =$ 3052, 1595, 1485, 1455, 1433, 1421, 1367, 1226, 1084, 815, 760 cm^{-1}

3: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 0.71$ (t, 3H), 1.06 (s, 3H), 1.07 (s, 3H), 1.12 (s, 3H), 1.18 (s, 3H), 1.72 (q, 2H), 2.55 (d, $^3J = 5.5$ Hz, 1H; H1), 6.11 (t, $^3J = 5.5$ Hz, 1H; H2), 6.42 (d, $^3J = 7.5$ Hz, 1H; H7), 6.63 (t, $^3J =$ 7.5 Hz, 1H; H8), 7.39 (t, $^3J = 8.0$ Hz, 1H), 7.44 (t, $^3J = 8.0$ Hz, 1H), 7.46 (t, $^3J = 8.0$ Hz, 1H), 7.58 (d, $^3J = 8.0$ Hz, 1H; H9), 7.61 (d, $^3J = 8.0$ Hz, 1H), 7.66 (d, $^3J = 8.0$ Hz, 1H), 7.67 (d, $^3J = 8.0$ Hz, 1H), 7.73 (d, $^3J = 8.0$ Hz, 1H), 7.85 (d, $^3J = 7.5$ Hz, 1H), 8.18 (d, $^3J = 5.5$ Hz, 1H; H3), 8.68 (d, $^3J = 8.0$ Hz, 2H), 8.70 (t, $^3J = 8.0$ Hz, 1H), 8.96 (d, $^3J = 8.0$ Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6, 25 °C): $\delta = 8.8$, 8.9, 9.0, 14.3, 17.8, 57.4 (C1), 63.4 (C4), 81.3 (C3), 82.9 (C2), 90.3, 90.6, 91.8, 96.04, 115.9 (C7), 120.5 (C9), 123.1, 123.5 (C8), 123.6, 123.7, 124.1, 126.4, 126.5, 126.6, 126.7, 127.5, 127.6 (C10), 130.7, 130.8, 133.6, 133.7, 134.2, 134.3, 134.9, 136.3, 137.5 (C6), 138.1, 138.3, 138.5, 138.6, 138.8, 139.0, 148.1 (C5)

4: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.04$ (s, 6H), 0.26 (s, 6H), 0.45 (t, 3H), 0.48 (t, 3H), 0.84 (s, 6H), 0.91 (s, 6H), 1.00 (q, 2H), 1.48 (q, 2H), 6.68 (d, $^3J = 7.6$ Hz, 2H), 6.92 (d, $^3J = 7.6$ Hz, 2H), 7.32 (t, $^3J = 7.6$ Hz, 2H), 7.33 (t, $^3J = 7.8$ Hz, 2H), 7.58 (t, $^3J = 8.1$ Hz, 2H), 7.62 (d, $^3J = 7.8$ Hz, 2H), 7.74 (d, $^3J = 8.1$ Hz, 2H), 8.53 (d, $^3J = 7.8$ Hz, 2H), 8.89 (d, $^3J = 8.1$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 5.6$, 5.7, 7.1, 7.2, 13.4, 13.5, 14.8, 16.0, 83.1, 87.7, 88.8, 89.7, 89.8, 93.6, 94.4, 96.8, 98.9, 100.2, 111.6, 119.3, 122.4, 122.7, 124.7, 128.7, 128.8, 130.8, 131.9, 134.6, 141.1, 142.3, 143.0

5: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 0.54$ (t, 3H), 0.68 (t, 3H), 0.82 (t, 3H), 0.86 (s, 3H), 0.87 (s, 3H), 1.02 (s, 3H), 1.05 (s, 3H), 1.20 (s, 6H), 1.28 (s, 3H), 1.29 (s, 6H), 1.30 (s, 3H), 1.33 (s, 3H), 1.43 (s, 3H), 1.64 (q, 2H), 1.8 (q, 2H), 1.95 (q, 2H), 3.0 (d, $^3J = 5.0$ Hz, 1H), 6.2 (t, $^3J = 5.0$ Hz, 1H), 6.41 (d, $^3J = 8.0$ Hz, 1H), 6.67 (t, $^3J = 8.0$ Hz, 1H), 6.79 (d, 1H), 6.89 (m, 3H), 7.37 (m, 2H), 7.5 (m, 6H), 7.74 (d, $^3J = 8.0$ Hz, 1H), 8.5 (d, $^3J = 5.0$ Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6, 25 °C): $\delta = 6.8$, 6.9, 7.0, 7.7, 7.8, 7.9, 9.2, 9.4, 9.5, 9.6, 13.7, 13.8, 13.9, 15.9, 16.7, 17.9, 59.4, 72.7, 73.6, 74.9, 75.9, 76.2, 82.3, 82.9, 87.4, 87.7, 88.4, 88.5, 88.6, 88.7, 88.8, 88.9, 89.3, 89.4, 89.5, 90.9, 91.3, 91.9, 93.4, 94.4, 95.5, 100.5, 100.6, 101.1, 101.5, 102.6, 104.3, 106.2, 106.3, 111.6, 112.1, 112.5, 112.8, 113.5, 120.9, 123.5, 131.1, 131.4, 132.0, 132.1, 135.2, 135.5, 141.6, 141.8, 142.1

7: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.78$ (s, 30H), 7.41 (t, $^3J = 7.5$ Hz, 6H), 7.62 (d, $^3J = 7.5$ Hz, 6H), 8.34 (d, $^3J = 7.5$ Hz, 6H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 7.9$, 98.5, 118.9, 123.1, 132.2, 135.8, 142.7; IR (KBr): $\tilde{\nu} = 3052$, 2964, 2900, 2852, 1600, 1583, 1435, 1379, 1352, 1148, 1022, 819, 801, 770 cm^{-1}

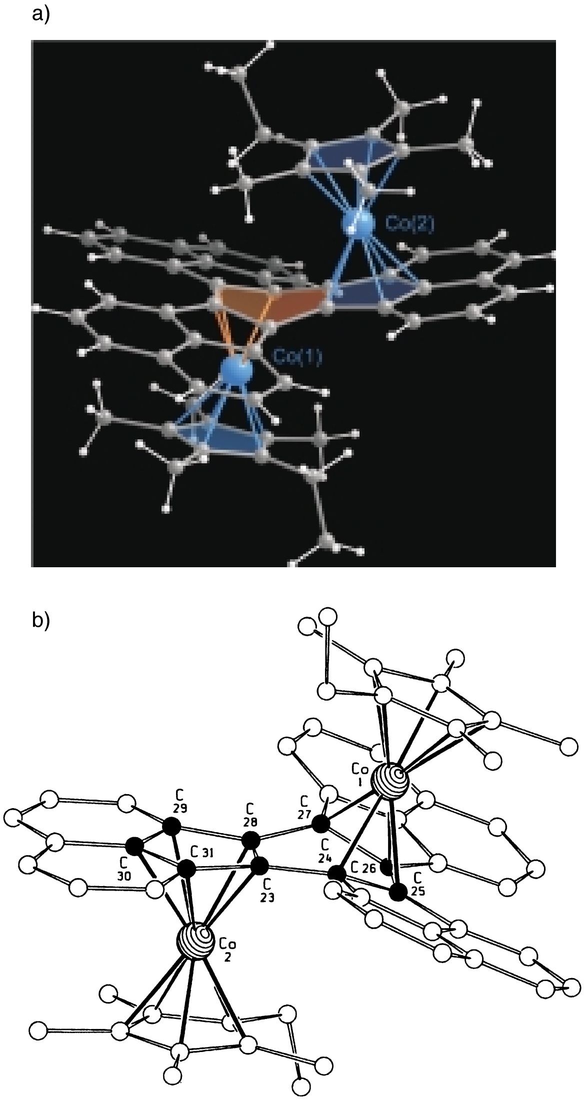


Figure 2. a) Molecular structure of **4** in the crystal. Selected bond lengths [Å] and angles [°]: Co(1)–C(24) 2.135(4), Co(1)–C(25) 1.978(4), Co(1)–C(26) 1.991(4), Co(1)–C(27) 2.140(4), Co(2)–C(23) 2.043(4), Co(2)–C(28) 2.058(4), Co(2)–C(29) 2.148(5), Co(2)–C(30) 2.098(5), Co(2)–C(31) 2.117(4), C(23)–C(24) 1.464(6), C(24)–C(25) 1.467(6), C(25)–C(26) 1.416(6), C(26)–C(27) 1.471(6), C(27)–C(28) 1.460(6), C(28)–C(23) 1.442(6); C(23)-C(24)-C(25) 121.6(4), C(28)-C(27)-C(26) 120.7(4). b) Numbering scheme for **4**.

condensed π perimeter (Figure 3).[14] The six-membered ring of **4** divides its overall η^6 coordination between two Co metal fragments (η^4 to Co1 and η^2 to Co2). The coordination of the decacyclene middle deck to the two $\{(\eta^5\text{-}Me_4EtC_5)Co\}$ fragments is therefore based on a superposition of the individually well established η^4 and η^5 Co coordination types.

A zwitterionic formulation of **4** accounts for the electronic situation in the η^5-Co coordinated part of **4** (Figure 4). This explains the diamagnetic character of **1** as observed by ^{1}H NMR spectroscopy. The $\{(\eta^5\text{-}Me_4EtC_5)Co\}$ fragment is η^5-coordinated to decacyclene giving rise to a cobaltocenium-like moiety (18e count). This leaves the corresponding annelated naphthalene moiety as a heptatrienyl anion. Such a zwitterionic formulation has already been proposed by Jonas for mononuclear cobalt acenaphthene complexes based on the results of detailed NMR spectroscopic investigations.[14b] However, aside from **4**, no satisfactory structural characterization of such a cobalt zwitterionic structure has been reported so far.[14b, 15]

In contrast to **1** which displays a propellerlike distortion of the three naphthalene units around its central six-membered ring,[6] no such distortion is observed for **4**. The coordination of both $\{(\eta^5\text{-}Me_4EtC_5)Co\}$ fragments in **4** gives a distinct bond alternation within the six-membered ring with strong Kekulé bond localization.[16] The C−C bond alternation in the central arene ring of **4** (C23 – C28) is $\Delta = 0.014$ Å. This is significantly smaller than that in **1** ($\Delta = 0.06$ Å). It is, however, in the same range as that found for tricyclopentabenzene ($\Delta = 0.017$ Å).[17] Owing to the η^4 coordination of Co1, the central six-membered ring (C24 – C27) is folded by 28°. This induces a bowl-shaped topology of two naphthalene units of **4** around the central arene ring (C23 – C28).

Reaction of $[(\eta^5\text{-}Me_5C_5)Ni(\eta^2\text{:O-acac})]$ with $[C_{36}H_{18}]^{2-}$: Reductive ligand elimination of $[(\eta^5\text{-}Me_5C_5)Ni(\eta^2\text{:O-acac})]$ (**6**)[9]

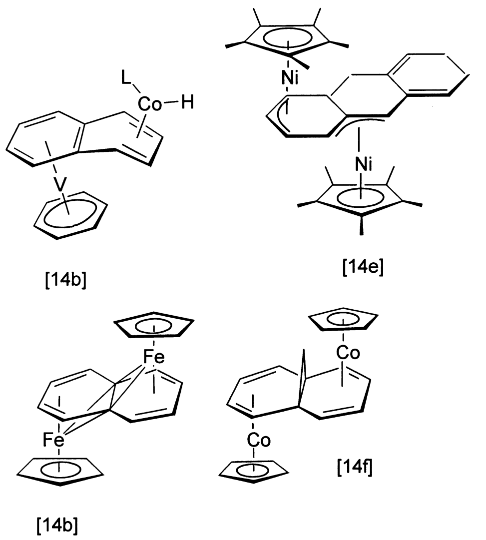


Figure 3. Examples for polycondensed π-bridging ligands displaying Kekulé bond localization.

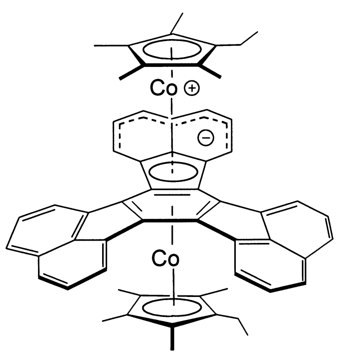


Figure 4. Zwitterionic structure of **4**.

with $[C_{36}H_{18}]^{2-}$ gives the dinuclear Ni complex **7** with a highly symmetric metal coordination [Eq. (2)]. ^{1}H and ^{13}C NMR spectroscopic analysis reveals a characteristic signal pattern which matches that for **1**; however, there is a distinct and characteristic high-field shift of the 'triplet–doublet–triplet'

$$\underset{\mathbf{1}}{1\ C_{36}H_{18}} \xrightarrow{1)\ +2\,K\quad 2)\ +2\times 6} [\mu\text{-}(C_{36}H_{18})\{(\eta^5\text{-}Me_5C_5)Ni\}_2]\ \mathbf{7} \qquad (2)$$

signal pattern upon coordination ($\Delta\delta = -0.11$, -0.08, and -0.39). Based on steric reasons, an antarafacial coordination of both $\{(\eta^5\text{-}Me_5C_5)Ni\}$ fragments to the central arene subunit of **7** is in full accord with this observation. Ni atoms π-bound to arene ligands are rare and no examples with a π coordinaton similar to **7** are known to date.[18] The high symmetry of the NMR spectra is retained even at low temperatures, indicating fluxional coordination behavior. This has already been observed for Ni, and the former for Co-arene bridged slipped triple-decker complexes.[10d, 14e]

In contrast to the Co complexes **3**–**5**, the Ni complex **7** is not stable with respect to loss of the bridging ligand **1**, which is already displaced slowly under ambient conditions in benzene, diethyl ether, or THF. This indicates the π-arene ligand lability of **7** and we aim to carry out further studies of this unusual behavior on which we will report in due course.

Formation of all decacyclene complexes depends crucially on the use of monometallic starting complexes like **2** and **6**. Reactions of dinuclear $[\{(\eta^5\text{-}Me_4RC_5)M\text{-}\mu\text{-}(X)\}_2]$ (M = Co, Ni; X = Cl, Br; R = Me, Et) complexes with decacylid di- and trianions did not lead to **3**, **4**, **5**, and **7**, but instead resulted only in the formation of metallocene derivatives.[19]

Spectroelectrochemistry of 4: Owing to the coordination of two Co centers in adjacent rings of **4**, the question of intramolecular communication mediated by the bridging π-perimeter arose for **4**. Indeed, as **1** and its hexa-*tert*-butyl derivative, **4** shows remarkable redox activity.[2, 20] Under ambient conditions two reversible, one-electron oxidations are observed by cyclic voltammetry and are confirmed by independent coulometric experiments (−0.46 V and 0.24 V vs. SCE; Figure 5a). A quasireversible reduction is observed at −1.6 V ($i_{pa}/i_{pc} = 0.7$ at 0.05 V s^{-1}), thus occuring at nearly the same potential as for **1**. However, compared to each of the two reversible oxidations, the peak current of this electron transfer process is doubled (Figure 5b), corresponding to a ligand-centered two-electron reduction of **4**. Coupled in situ EPR experiments (X-band, 100 K) of electrochemically generated $4^{+\bullet}$ gives a strong anisotropic EPR signal with a magnetic hyperfine splitting typical for Co^{II} ($S = 1/2$, $g_l = 2.196(8)$, $g_m = 2.170(8)$, $g_h = 2.158(8)$, $> g < = 1/3(g_l + g_m + g_h) = 2.175(8)$; Figure 5c). In situ generation ($E_w = +0.5$ V) of the second electroactive species as well as solutions of neutral **4** are EPR silent.

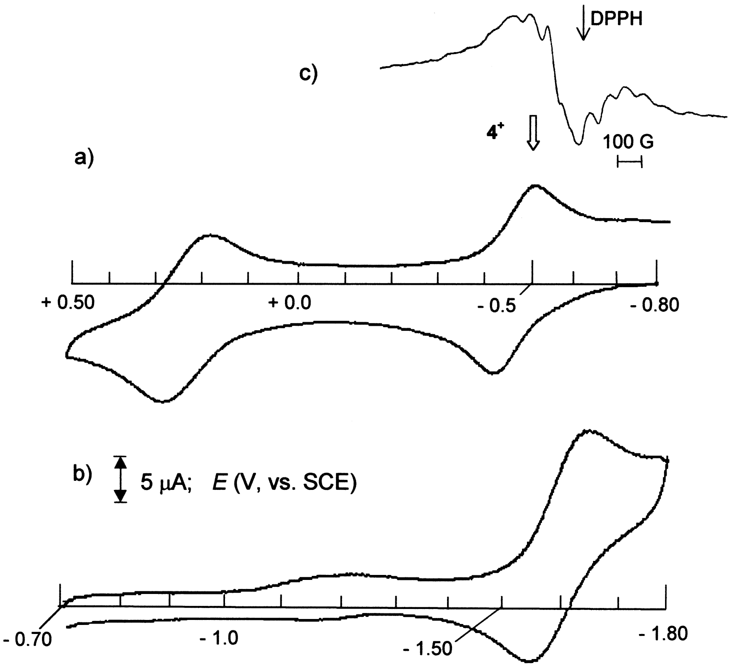


Figure 5. Cyclic voltammogram of **4** (0.5×10^{-3} mol dm^{-3}, recorded at a Pt electrode, supporting electrolyte 0.1 mol dm^{-3} $[NBu_4][PF_6]$). a) Region between +0.5 and −0.8 V; b) region between −0.7 and −1.8 V. c) EPR spectrum of the radical cation $4^{+\bullet}$ at 100 K in CH_2Cl_2 obtained by in situ generation at 253 K, $E_w = -0.2$ V. DPPH = diphenylpycrylhydrazyl.

The time scale of EPR spectroscopy (10^9 s^{-1}) is between those of NMR and IR, and the EPR linewidth is strongly influenced by electron transfer processes with rates of the order of 10^7 to 10^{11} s^{-1}. A comproportionation constant of $K_{\text{com}} = 7 \times 10^{-11}$ was estimated from the separation of the two reversible oxidation processes in the cyclic voltammetry experiment. This result points towards a strong electronic coupling of both Co centers in the mixed-valence slipped triple-decker monocation **4**$^{+\bullet}$ for which Robin Day class III behavior can be assumed.[21] Since the Co1–Co2 distance is too large (4.509 Å), an electronic communication solely mediated through the π perimeter seems obvious for **4**$^{+\bullet}$. The strong magnetic interaction of both metal centers in the mixed-valence cation **4**$^{+\bullet}$ is reflected by the large hyperfine field splitting in the EPR spectrum (I-Co = 7/2, 100%, a(Co) = 55.0(8) G). So far, it has not been possible to make an assignment of the two anodic one-electron oxidation processes of **4** to one of the two possible redox sequences $Co^{I}Co^{I}/Co^{II}Co^{I}/Co^{II}Co^{II}$ or $Co^{II}Co^{II}/Co^{III}Co^{II}/Co^{III}Co^{III}$.

Conclusion

Mono-, di-, and trinuclear Co and Ni triple-decker complexes of decacyclene displaying η^4, μ-η^4:η^5, and fluxional behavior in the case of nickel coordination are accessible by means of reductive ligand elimination from [(η^5-Me$_4$RC$_5$)M(η^2:O-acac)] (M = Co, Ni; R = Me or Et) with potassium metal in THF. Although this preparative route is well established in organometallic chemistry, it has been only rarely studied in connection with metal complexation of PAHs. Our results indicate that this technique might have general potential, mainly due to its simplicity and potentially wide applicability for the introduction of PAHs as ligands in organotransition metal chemistry. A huge number of di- and polyanions of PAHs have already been well explored.[1a, 3f] Thus it seems realistic to assume that combining the described reduction/complexation technique might open up new avenues into the complexation chemistry of these molecules.

Experimental Section

General information: Decacyclene (96%) was purchased from Aldrich and sublimed prior to use. Due to extreme moisture and air sensitivity of the decacylene complexes, all solvents were dried and handled under appropriate conditions. [(η^5-Me$_4$RC$_5$)M(η^2:O-acac)] (M = Co, Ni; R = Me or Et) were prepared according to the literature methods.[9] NMR samples were sealed under vacuum. The NMR solvent was dried and then vacuum transferred onto the samples in order to provide optimum anaerobic conditions.

General procedure for the synthesis of 3, 4, 5 and 7: Freshly sublimed **1** (0.5 g, 1.1 mmol; 300 °C/10^{-1} Pa) was suspended in dry THF (80 mL) and was stirred for 72 h above a potassium mirror made from freshly cut potassium metal (100 mg, 2.5 mmol). At −78 °C **2** (675 mg, 2.2 mmol) was added and the reaction mixture was gradually warmed to room temperature over 12 h. Removal of all volatiles in vacuum and recrystallization of the crude black residue from diethyl ether gave extremly sensitive **3** (0.29 g; 40%). Within a few days of subsequent further cooling, **4** (0.31 g; 32%) was obtained as second crop of the crystallization. From **1** (1.1 mmol), potassium (3.8 mmol), and a mixture of **4** and **5** (3.3 mmol, 0.81 g; 68%, ratio 1:10 from NMR analysis) was obtained as brown crystals as described above.

7: Compound **7** was obtained as brown microcrystals (0.66 g, 71%) and prepared as described above from **1** (1.1 mmol) and potassium (2.8 mmol).

Owing to their extreme sensitivity, even recrystallized samples of **3**–**5** and **7** gave CH combustion analysis with systematically up to 2% lower C,H values than expected. All complexes showed extensive decomposition in EI-MS experiments above 150 °C. No molecular ions, except that of the free ligand **1** (formed upon decomposition) were observed for all decacylene complexes.

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[1] a) M. Zander, *Polycyclische Aromaten*, Teubner, Stuttgart, **1995**; b) L. T. Scott, M. S. Bratcher, S. Hagen, *J. Am. Chem. Soc.* **1996**, *118*, 8743; c) R. B. M. Ansems, L. T. Scott, *J. Am. Chem. Soc.* in press; as well as L. T. Scott, 118. ACS National Meeting, 11.–15. July **1999**, contribution: ORGN 0211 New Orleans, USA; d) J. Osterrodt, A. Zett, F. Vögtle, *Tetrahedron* **1996**, *52*, 4949.

[2] a) J. Heinze, *Angew. Chem.* **1984**, *23*, 831; *Angew. Chem. Int. Ed. Engl.* **1984**, *96*, 823. Compound **1** shows five independent reduction steps. The first at −1.59 eV ($i_{pa}/i_{pc} = 1$) is in agreement with with the one observed for **4** reported herein; b) J. B. Torrance, P. S. Bagus, I. Johannsen, A. I. Nazzal, S. S. P. Parkin, J. *Appl. Phys.* **1988**, *63(8)*, 2962.

[3] a) T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. R. Robben, M. Wuensch, M. D. Ward, *J. Am. Chem. Soc.* **1993**, 115, 3182.

[4] M. Munakata, L. P. Wu, G. L.Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, N. Maeno, *J. Am. Chem. Soc.* **1999**, *121*, 4968.

[5] Cr(CO)$_3$ half-sandwich complexes of the hexa-*tert*-butyl derivative of **1** are mentioned, but no further details have been given see: a) K. Zimmermann, R. Goddard, C. Krüger, M. W. Haenel, *Tetrahedron Lett.* **1996**, *37*, 8371; b) K. Zimmermann, M. W. Haenel, *Synlett.* **1997**, 609.

[6] D. M. Ho, R. A. Pascal, Jr., *Chem. Mater.* **1993**, *5*, 1358.

[7] a) H.Bock, W.Herrmann, D. Fenske, H. Goesmann, *Angew.Chem.* **1988**, *100*, 1125; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1067; b) H. Bock, C. Arad, C. Näther, *J. Organomet. Chem.* **1996**, 520, 1; c) H. Bock, K. Gharagozloo-Hubmann, C. Näther, N. Nagel, Z. Havlas, *Angew. Chem.* **1996**, *108*, 720; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 631; d) H. Bock, H.-F. Hermann, *J. Am. Chem. Soc.* **1989**, *111*, 7622; e) C. Schnieders, K. Müllen, W. Huber, *Tetrahedron* **1984**, *40*, 1701; f) M. Rabinovitz, *Top. Curr.Chem.* **1988**, *146*, 99; g) M. Baumgarten, K. Müllen, *Top. Curr. Chem.* **1994**, *169*, 1; h) A. Ayalon, A. Sygula, P-C. Cheng, M. Rabinovitz, P. W. Rabideau, L. T. Scott, *Science*, **1994**, 265; i) M. Baumgarten, L. Ghergehl, M. Wagner, A. Weitz, M. Rabinovitz, P. C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1995**, *117*, 6254.

[8] L. B. Ebert in *Adv. Chem. Ser.* **1988**, *217*.

[9] J. M. Manriquez, L. Valle, E. E. Bunel, *Organometallics*, **1985**, *4*, 1680.

[10] a) K. Jonas, E. Deffense, D.Habermann, *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem. Int. Ed.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005; b) earliest crystal structure investigation of a [(η^5-Cp)Co(η^4-diene)] complex see: M. R. Churchill, R. Mason, *Proc. R. Soc. London Ser. A*, **1964**, *279*, 191; recent examples: c) R. Diercks, B. E. Eaton, S. Gürtzgen, S. Jalisatgi, A. J. Matzger, R. H. Radde, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1998**, *120*, 8247; d) J. J. Schneider, U. Denninger, O. Heinemann, C. Krüger, Angew. Chem. **1995**, *107*, 631; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 592.

[11] Crystal structure analysis of **4**: $C_{58}H_{52}Co_2$, monoclinic, space group $P2_1/c$, $a = 13.0421(13)$, $b = 22.1508(2)$, $c = 15.0218(14)$ Å, $\beta = 103.09(1)^\circ$, $V = 41.044(7) \times 10^6$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.403$ g cm^{-3}, $T =$

133(2) K, $\mu(\mathrm{Mo}_{K\alpha}) = 0.85\ \mathrm{mm}^{-1}$, 36162 measured reflections, 5093 independent reflections; 551 parameters refined. $R_1 = 0.43$, $wR_2 = 0.088$. Bruker-Huber-Stoe diffractometer (home-built CCD system), monochromator: graphite; semiempirical absorption correction; structure solution with direct methods; refinement for F^2; H positions calculated with: C–H 0.69 Å. Computer programms used: SHELXTL-PLUS,[12] SCHAKAL[13]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135961. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] G. M. Sheldrick, SHELXTL-PLUS, Göttingen, **1997**.

[13] E. Keller, SCHAKAL. Universität Freiburg, **1997**.

[14] a) K. Jonas, *Pure Appl. Chem.* **1990**, *62*, 1169; b) K. Jonas, *J. Organomet. Chem.* **1990**, *200*, 165; c) W. J. Evans, S. L. Gonzales, J. W. Ziller, *J. Am. Chem. Soc.* **1994**, *116*, 2600; d) K. H. Thiele, S. Bambirra, J. Sieler, S. Yelonek, *Angew. Chem.* **1998**, *110*, 3016; *Angew. Chem. Int. Ed.* **1998**, *37*, 2886; e) J. J. Schneider, D.Wolf, U. Denninger, R. Goddard, C. Krüger, *J. Organomet. Chem.* **1999**, *579*, 139; f) P. Mues, R. Benn, C. Krüger, Y.-H. Tsay, E. Vogel, G. Wilke, Angew. Chem. **1982**, *94*, 879; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 868; *Angew. Chem. Suppl.* **1982**, 1891.

[15] A preliminary structure report of a mononuclear Co zwitterionic structure is reported in M. G. J. Tadic, Dissertation, Ruhr Universität Bochum, **1990**.

[16] Selected examples for Kekulé π-bond localization: a) K. Jonas, *Angew. Chem.* **1985**, *97*, 292; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 295; b) K. Jonas, G. Koepe, L. Schieferstein, R. Mynott, C. Krüger, Y.-H. Tsay, *Angew. Chem.* **1983**, *95*, 637; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 620; *Angew. Chem. Suppl.* **1983**, 920; c) K. Jonas, *Pure Appl. Chem.* **1984**, *63*, 56; d) H. Lehmkuhl, H. Nehl, R. Benn, R. Mynott, *Angew. Chem.* **1986**, *98*, 628; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 646.

[17] a) E. R. Boyko, P. A. Vaughan, *Acta Crystallogr.* **1964**, *17*, 152; b) For an in depth discussion of alternating bond orders in tris-annelated benzene derivatives see: K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 9583.

[18] For Ni coordination to π-arene ligands see: a) K. Jonas, *J. Organomet. Chem.* **1974**, *78*, 273; b) L. J. Radonovich, K. J. Klabunde, C. B. Behrens, D. P. M. Mc Collor, B. B. Anderson, *Inorg. Chem.* **1980**, *19*, 1221 c) F. Scott, C. Krüger, P. Betz, *J. Organomet. Chem.* **1990**, *387*, 113; d) A. Stanger, R. Boese, *J. Organomet. Chem.* **1992**, *430*, 235; e) R. Boese, A. Stanger, P. Stellberg, A. Shazar, *Angew. Chem.* **1993**, *105*, 1500; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1475; f) T. Nickel, R. Goddard, C. Krüger, K.-R. Pörschke, *Angew. Chem.* **1994**, *106*, 908; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 879.

[19] J. J. Schneider, N. Czap, D. Spickermann, M. Fontani, F. Laschi, P. Zanello, *J. Organomet. Chem.* **1999**, *590*, 7.

[20] T. Kubo, K. Yamamoto, K. Nakasuji, T. Takui, I. Murata, *Angew. Chem.* **1996**, *108*, 456; *Angew. Chem. Int. Ed.* **1996**, *35*, 439.

[21] M. B. Robin, P. Day, *Inorg. Chem. Radiochem.* **1967**, *10*, 247.

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