Reductive Degradation of Tetracobalt Cluster Complexes with a Facial C_8H_8 Ligand – Synthesis of $[Co_3(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)]^-$ and $[Ru(C_5Me_5)Co_3(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)]$

Hubert Wadepohl,*[a] Stefan Gebert,[a] Rüdiger Merkel,[a] and Hans Pritzkow[a]

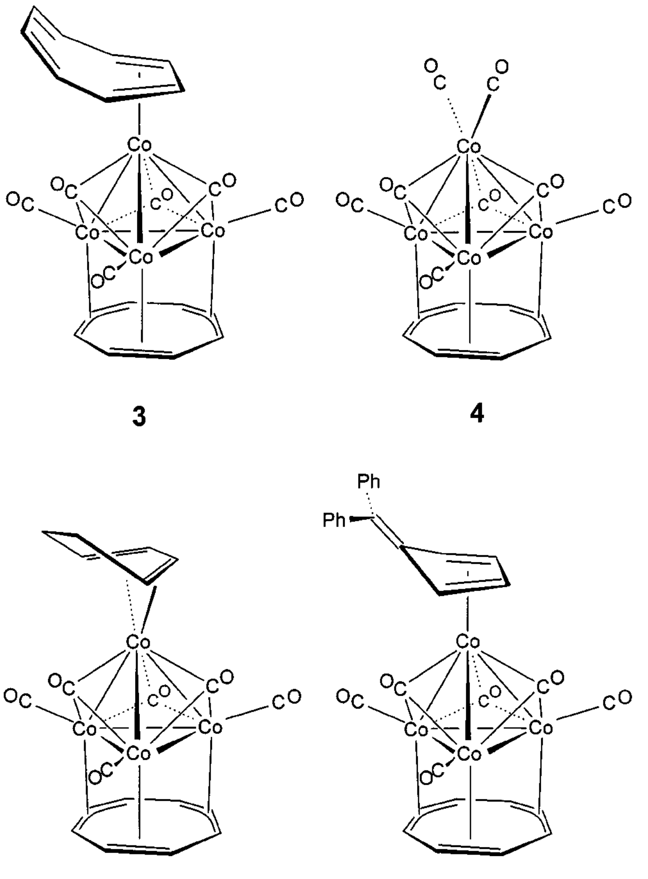
Keywords: Carbocycles / Clusters / Cobalt / Electrochemistry / Facial ligands

Chemical reduction of the cluster complexes $[Co_4(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)L_2]$ **3** ($L_2 = C_8H_8$), **4** (L = CO), **5** ($L_2 = C_6H_8$) and **6** ($L_2 = 6,6\text{-}Ph_2C_6H_4$) gives the trinuclear anion $[Co_3(CO)_3(\mu_2\text{-}CO)_3(\mu_3\text{-}C_8H_8)]^-$ (**7**) in high yield. It is proposed that formation of **7** occurs via degradation of the radical anions $[\mathbf{3}]^-$ – $[\mathbf{6}]^-$, which can be generated reversibly via cyclic voltammetry. The anion **7** is stabilised by the facial C_8H_8 ligand and does not degrade further. Reaction of **7** with $[(C_5Me_5)Ru(NCMe)_3][BF_4]$ results in the formation of $[Ru(C_5Me_5)Co_3(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)]$ (**8**). The crystal structures of $[NEt_4]^+$-**7**, $[(C_5H_5)_2Co]^+$-**7**, and **8** were determined. In **7** and **8**, the cyclooctatetraene ligand is coordinated to the Co_3 face of the cluster in the facial mode.

Introduction

Transfer of an electron is one of the most basic reactions of molecular metal cluster complexes.[1] Transition metal carbonyl clusters are usually prone to reduction, forming a more or less stable radical anion.[2] Frequently, reduction of the cluster is accompanied or followed by metal–metal bond scission, which may result in a modification of the cluster architecture, a change in nuclearity, or even complete degradation to mononuclear fragments. For example, when reduced electrochemically, $[Co_4(CO)_{12}]$ (**1**) was found to give the unstable monoanion $[Co_4(CO)_{12}]^-$ $[\mathbf{1}]^-$, which in the absence of other reactants decomposes to $[Co(CO)_4]^-$ and cobalt metal.[3] The products of the chemical reduction of **1** are very dependent on the reducing agent and the reaction conditions. With sodium in liquid ammonia, $[Co(CO)_4]^-$ is obtained.[4] The hexanuclear cluster anions $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ are formed with alkali metals or cobaltocene in THF.[5] Finally, the trinuclear $[Co_3(CO)_{10}]^-$ (**2**) can be obtained from **1** and $Li[Co(CO)_4]$.[6a]

Recently we described the preparation and structures of a series of tetracobalt cluster complexes $[Co_4(CO)_3(\mu_3\text{-}CO)_3(C_8H_8)L_2]$, e.g. **3** ($L_2 = C_8H_8$), **4** (L = CO), **5** ($L_2 = C_6H_8$), and **6** ($L_2 = 6,6\text{-}Ph_2C_6H_4$) with a cyclooctatetraene ligand in the rarely-encountered facial (μ_3-) coordination mode (Scheme 1).[7] In these derivatives of **1**, the facial C_8H_8 ligand was found to resist substitution under a variety of conditions, pointing to a particular stability of the $Co_3(\mu_3\text{-}C_8H_8)$ moiety.[7,8] As described above, degradation of the Co_4 cluster takes place upon reduction of **1**. This disintegration of the metal framework is difficult to control, and frequently leads to a complete breakdown of the cluster. The presence of the facial C_8H_8 ligand might more easily stop this catastrophe at the trinuclear stage.



3 **4** **5** **6**

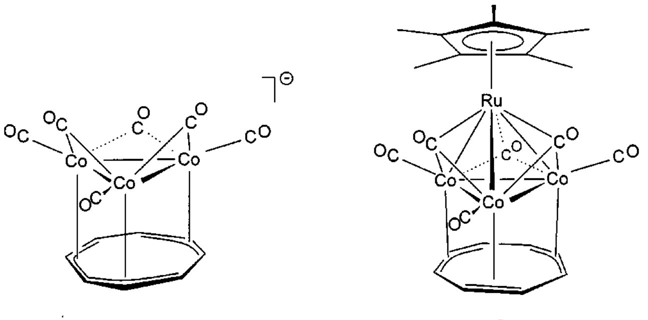
Scheme 1

Here we wish to report the exclusive and quantitative formation of the novel cluster complex anion $[Co_3(CO)_3(\mu_2\text{-}CO)_3(\mu_3\text{-}C_8H_8)]^-$ (**7**) from the reductive degradation of **3–6**, and its capping reaction with the $[(C_5Me_5)Ru]^+$ fragment

---

[a] Anorganisch-chemisches Institut der Ruprecht-Karls-Universität,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany
E-mail: bu9@ix.urz.uni-heidelberg.de

to give the heteronuclear cluster complex [Ru(C_5Me_5)$Co_3(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)$] (**8**) (Scheme 2).



7 **8**

Scheme 2

Results

Preparative and Spectroscopic Investigations

When treated with an equimolar amount of Li[$HBEt_3$], the tetranuclear cluster complexes [$Co_4(CO)_3(\mu_3\text{-}CO)_3(C_8H_8)L_2$] **3–6** are cleanly converted into the trinuclear cluster anion [$Co_3(CO)_3(\mu_2\text{-}CO)_3(\mu_3\text{-}C_8H_8)$]$^-$ (**7**). Addition of aqueous [NEt_4]Cl results in the precipitation of dark orange [NEt_4]$^+$-**7** in nearly quantitative yield. In contrast, treatment of **6** with Na_2[$Fe(CO)_4$] in THF only results in a low frequency shift of the bands in the ν(CO) region by about 45 cm^{-1}, without changing the general appearance of the infrared spectrum. Addition of aqueous [NEt_4]Cl in order to crystallise the product as the [NEt_4]$^+$ salt results in the partial reformation of the neutral starting material **6**. Treatment with [PPh_4]Cl in THF causes slow reaction to give the trinuclear anion **7**.

The [$(C_5R_5)_2Co$]$^+$ (R = H, Me) salts of anion **7** are formed as by-products (10–20% yield) in the reactions of **3** with cyclopentadiene and pentamethylcyclopentadiene, respectively, along with [$Co_4(CO)_3(\mu_3\text{-}CO)_2(\mu_3\text{-}H)(\mu_3\text{-}C_8H_8)(\eta\text{-}C_5R_5)$] **9a**, **b**[8] (60–70% yield) and [$(C_5R_5)Co(CO)_2$] (20% yield) (R = H, Me). Reaction of **3** with cobaltocene in THF gives [$(C_5H_5)_2Co$]$^+$-**7** in nearly quantitative yield. The changes in the IR spectrum after addition of 1.1 equivalents of Na[C_5H_5] to a solution of **3** in THF also indicate the quantitative formation of **7**.

When an equimolar amount of [$(C_5Me_5)Ru(NCMe)_3$][BF_4] is added to a dichloromethane solution of [NEt_4]$^+$-**7**, a colour change from dark orange to dark red is observed. The heteronuclear cluster complex [$Ru(C_5Me_5)Co_3(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)$] (**8**) can be isolated in 45% yield from this mixture after column chromatography. No reaction takes place between [NEt_4]$^+$-**7** and [$Mn(CO)_5Cl$] or [$(C_5H_5)Fe(CO)_2I$].

Four bands in the ν(CO) region of the infrared spectrum (1977, 1938, 1782, and 1743 cm^{-1}) are displayed by dichloromethane solutions of **7**. These absorptions do not depend noticeably on the counterion. Complex **8** gives only three ν(CO) bands (2000, 1978, and 1707 cm^{-1}, in CH_2Cl_2). The NMR spectra of **7** and **8**, measured at room temperature, are very simple. The facial C_8H_8 ligand gives only one proton signal [δ = 4.10 (**7**), δ = 3.97 (**8**)] and one carbon NMR resonance [δ = 75.4 (**7**), δ = 70.3 (**8**)]. The ^{13}C NMR resonances for the carbonyl ligands could not be detected, due to the rather low solubility of the complexes. Other resonances in the ^1H and ^{13}C NMR spectra are due to the C_5Me_5 ligand of **8**, and the counterions X^+ ([NEt_4]$^+$ and [$(C_5R_5)_2Co$]$^+$, respectively) in X^+-**7**.

Electrochemistry

Cyclic voltammograms were recorded in CH_2Cl_2 solution at a scan rate of 100 mV/s. The electrochemical behaviour of the cluster complexes [$Co_4(CO)_6(C_8H_8)L_2$] **3**, **5**, and **6** is characterised by pseudo-reversible reduction waves. The redox behaviour of the octacarbonyl derivative **4** (L = CO) appears to be more complex. The relevant data are given in Table 1. There are two reduction processes in every case, corresponding to the formation of the monoanions [$Co_4(CO)_6(C_8H_8)L_2$]$^-$ and dianions [$Co_4(CO)_6(C_8H_8)L_2$]$^{2-}$, respectively. For complex **4** the first reduction wave is distorted from the ideal shape, indicating a partially irreversible behaviour. The second reduction of **4** is strictly irreversible. Oxidation of the cluster complexes is irreversible, except in the case of complex **6** (L_2 = diphenylfulvene), which shows a pseudo-reversible oxidation wave (Table 1).

Table 1. Electrochemical data ($E_{1/2}$ [V] vs. SCE) for the complexes [$Co_4(CO)_6(C_8H_8)L_2$] **3–6** (in CH_2Cl_2, supporting electrolyte [nBu$_4$N][PF_6], working electrode glassy carbon, reference electrode SCE, scan rate 100 mV s^{-1})

complex	–2/–1	–1/0	0/+1
3	–1.29	–0.68	
4	–0.99[a]	–0.60[b]	
5	–1.37	–1.02	
6	–1.48	–0.81	0.41

[a] Irreversible. – [b] Partially irreversible.

Crystal and Molecular Structure of [NEt_4]$^+$-7, [$(C_5H_5)_2Co$]$^+$-7, and 8

Single-crystal X-ray structure determinations were carried out with [NEt_4]$^+$-**7** and with the tetranuclear Co_3Ru cluster complex **8**. Important bond lengths and angles are collected in Table 1 and Table 3. Views of the cluster molecules are presented in Figure 1 and Figure 2. The crystal structure of [(C_5H_5)]$_2$Co]$^+$-**7** was also determined. Unfortunately, the quality of the diffraction data obtained from this salt did not allow a complete refinement of the structure.

Table 2. Selected bond lengths [Å] and angles [°] for $[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ (**7**) in $[NEt_4]^+$-**7**.

Co1–Co1A	2.507(2)	Co1–C1	2.516(5)
Co1–Co2	2.530(2)	Co1–C2	2.105(4)
C1–C2	1.402(4)	Co1–C3	2.173(4)
C2–C3	1.409(5)	Co2–C4	2.270(4)
C3–C4	1.426(6)	Co2–C5	2.076(5)
C4–C5	1.408(4)		
Co–C(CO)$_{term.}$	1.742(4), 1.751(5)	Co–C(CO)$_{bridge}$	1.905(4), 1.918(3), 1.899(4)
C2A–C1–C2	137.6(5)	C4–C5–C4A	132.4(5)
C1–C2–C3	132.7(4)	C2–C3–C4	134.0(4)
C3–C4–C5	135.6(4)		

Table 3. Selected bond lengths [Å] and angles [°] for $[Ru(C_5Me_5)\text{-}Co_3(CO)_6(\mu_3\text{-}C_8H_8)$ (**8**)

Co1–Co2	2.526(2)	Co2–Co3	2.530(2)
Co1–Co3	2.531(2)	Ru1–Co1	2.589(2)
Ru1–Co2	2.587(2)	Ru1–Co3	2.596(2)
Co1–C44	2.125(10)	Co1–C45	2.098(10)
Co2–C46	2.383(11)	Co2–C47	2.041(10)
Co2–C48	2.226(10)	Co3–C41	2.223(9)
Co3–C42	2.067(9)	Co3–C43	2.354(10)
C41–C42	1.408(14)	C41–C48	1.425(14)
C42–C43	1.394(16)	C43–C44	1.448(16)
C44–C45	1.433(17)	C45–C46	1.425(17)
C46–C47	1.433(18)	C47–C48	1.372(17)
Co–C11, C21, C31	1.769(10)...1.781(11)	Co–C12, C22, C32	1.975(9)...2.019(9)
Ru1–C12, C22, C32	2.092(9)...2.125(9)	Ru–C(C_5Me_5)	2.207(9)...2.240(9)
C48–C41–C42	135(1)	C41–C42–C43	133(1)
C42–C43–C44	136(1)	C43–C44–C45	132(1)
C44–C45–C46	135(1)	C45–C46–C47	133(1)
C46–C47–C48	135(1)	C47–C48–C41	135(1)

The crystal structures of the salts consist of a packing of isolated cations $[NEt_4]^+$ and $[(C_5H_5)_2Co]^+$, respectively, and anions **7**. In both cases, molecular C_s symmetry is imposed on the cluster anions **7** by the space group symmetry. The isosceles triangular array of cobalt atoms is capped by the C_8H_8 ligand in the facial μ_3-η^3:η^3:η^3 coordination mode. Within the experimental errors the anions in the two structures are essentially superimposable. The metal core of complex **8** consists of a distorted Co_3Ru tetrahedron with very nearly C_{3v} symmetry. The facial C_8H_8 ligand binds to the Co_3 face of the cluster in essentially a μ_3-η^2:η^3:η^3 fashion. In both **7** and **8**, the cyclooctatetraene ligands are somewhat puckered and approach a chair-like conformation, with endocyclic torsion angles between 2 and 24°. The pattern of carbon–carbon bond lengths within the μ_3-C_8H_8 rings is rather irregular, spanning the range of 1.402(4)...1.426(6) Å in **7** and 1.372(17)...1.448(16) Å in **8**. In both **7** and **8**, every cobalt atom bears a terminal carbonyl ligand, which is at an angle of about 20° to the Co_3 plane, bent away from the facial C_8H_8 ligand. In **7**, the three remaining carbonyls are bridging the edges of the metal cluster. In complex **8**, the three Co_2Ru faces are fairly symmetrically capped by μ_3-CO ligands.

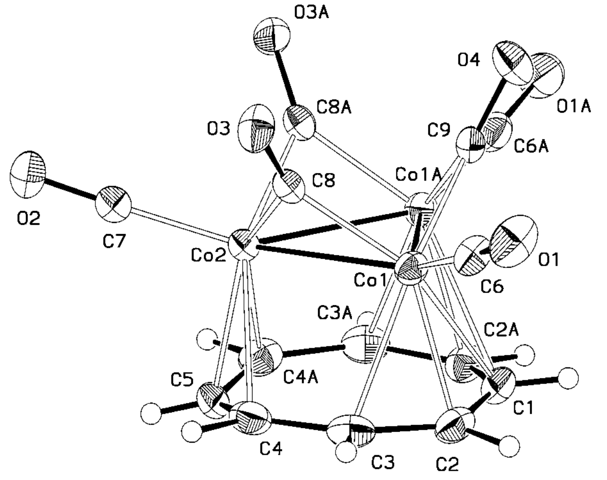


Figure 1. Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ (**7**) in the crystals of $[NEt_4]^+$-**7**

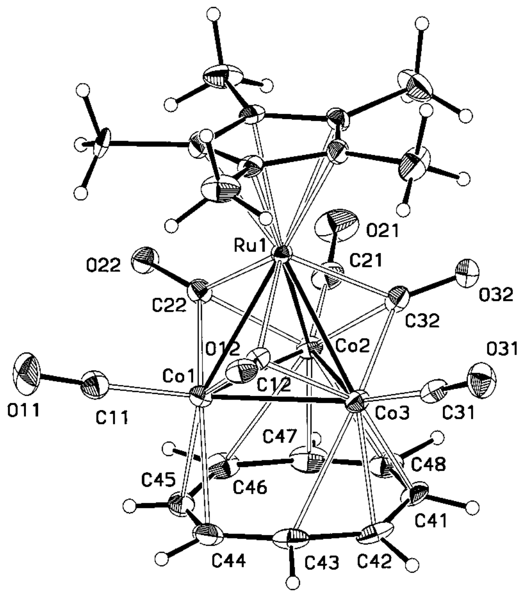


Figure 2. Molecular structure of $[Ru(C_5Me_5)Co_3(CO)_6(\mu_3\text{-}C_8H_8)]$ (**8**)

Discussion

The observed reductive degradation of the μ_3-cyclooctatetraene tetracobalt cluster complexes **3**–**6** to give the trinuclear **7** has a parallel in the reduction chemistry of the parent binary carbonyl, $[Co_4(CO)_{12}]$ (**1**). However, reduction of **1** is very difficult to stop at the trinuclear stage, $[Co_3(CO)_{10}]^-$ (**2**). This anion is quite unstable and only forms as an ion pair in the presence of a weakly solvated Li^+ counterion.[6] Removal of the stabilising Li^+ from the cluster, e.g. by means of addition of even small percentages of donor ligands such as THF, leads to complete decomposition.[6] As is expected for salts with fairly big organic cations, there is no ion pairing in the crystal structures of $[NEt_4]^+$-**7** and $[(C_5H_5)_2Co]^+$-**7**. These salts can even be heated under reflux in THF for hours without decomposition. Hence, the anion **7** must indeed be greatly stabilised by the bridging C_8H_8 ligand, compared to the isoelectronic binary carbonyl cluster complex **2**.

We assume that the primary step in the formation of **7** is the transfer of an electron from the reducing agent to the starting clusters **3–6**, to give the tetranuclear radical anions [**3**]$^-$ – [**6**]$^-$. An alternative nucleophilic attack of **3–6** by hydride from $Li[HBEt_3]$, followed by degradation of the addition product is unlikely. Such a mechanism would not account for the formation of **7** during the reaction of **3** with the cyclopentadienes. We assume that cobaltocene or decamethylcobaltocene, respectively, is formed here from C_5R_5H and $[(C_5R_5)Co(C_8H_8)]$, which is one of the other reaction products. Reduction of the remaining **3** by $[(C_5R_5)_2Co]$ would then lead to the same intermediate as in the reaction with $Li[HBEt_3]$. This view is corroborated by the results of the direct reaction of **3** with cobaltocene that quantitatively generates $[(C_5H_5)_2Co]^+$-**7**.

Spectroscopic evidence for the transient formation of an anionic tetranuclear species comes from the reaction of **6** and $Na_2[Fe(CO)_4]$. The infrared absorptions of the primary product display the pattern characteristic of a $Co_4(CO)_3(\mu_3\text{-}CO)_3$ cluster core; their bathochromic shift relative to those of **6** ($\Delta\tilde{\nu}$ = 40–45 cm^{-1}) is consistent with an anionic tetranuclear cluster, which could be [**6**]$^-$ or even [**6**]$^{2-}$.

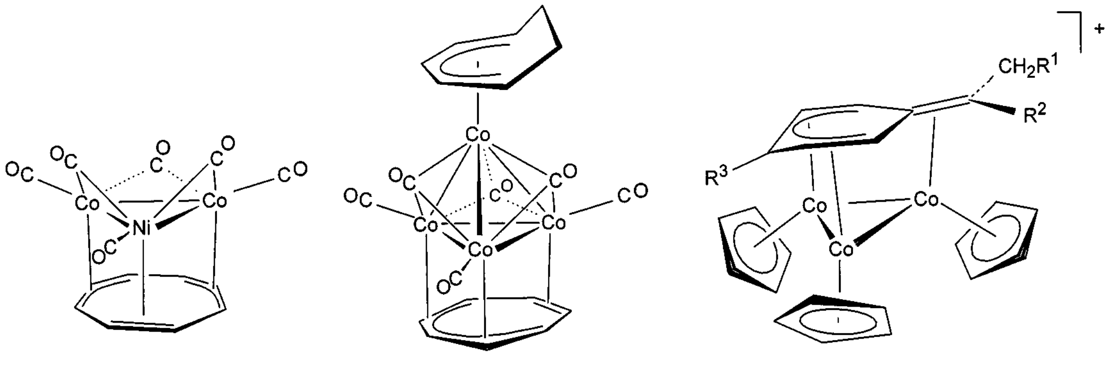
As shown by the cyclic voltammetry experiments, the anions [**3**]$^-$, [**5**]$^-$ and [**6**]$^-$ have a considerable lifetime, at least in the electrochemical double layer. The fragmentation reaction observed after chemical reduction in a preparative scale could be promoted by the different solvent (THF instead of CH_2Cl_2) or else be too slow to have a great effect on the cyclic voltammograms. Complex [**4**]$^-$ appears to be more labile in the timescale of our electrochemical experiments. It is however not clear if the observed potential current response is due to the onset of cluster degradation, or to a facile dissociation of carbon monoxide[9] from [**4**]$^-$.[10]

The low stability of anionic tetranuclear cluster complexes of cobalt was noted by Chini 30 years ago.[5,11] A stabilisation by the presence of chelating di- and triphosphane ligands was observed.[3] We note here that capping of a Co_3 face in $[Co_4(CO)_{12}]$ (**1**) with the tripodal ligand $HC(PPh_2)_3$ results in a system which does not degrade at all upon reduction,[9,12] in contrast to our C_8H_8-capped cluster **4**.

The structure of the trinuclear anion **7** does not depend on the counterion; it is quite similar to that of its neutral isoelectronic analogue, $[Co_2Ni(CO)_3(\mu_2\text{-}CO)_3(\mu_3\text{-}C_8H_8)]$ (**10**)(Scheme 3).[13] Minor differences are the shorter mean metal–metal distance in **10** (2.514 Å),[13] due to the smaller nickel atom, and the somewhat different coordination mode of the facial C_8H_8 ligand, which is μ_3-η^3:η^3:η^3 in **7** and more like μ_3-η^2:η^3:η^3 in **10**. In the Co_3Ru complex **8**, the C_8H_8 ligand also attains the μ_3-η^2:η^3:η^3 coordination mode, which is the one more commonly found for facially coordinated C_8H_8.[8] In a localised view of the bonding, the π-system of the μ_3-η^2:η^3:η^3-cyclooctatetraene may be grouped into one η^2-coordinated 'ene' and two η^3-'enyl' subunits. In the μ_3-η^3:η^3:η^3 ligand, there are three η^3-'enyl' units, two of which are sharing one carbon atom. This atom (C1 in **7**) is at a very long distance from the nearest Co atoms [Co1 and Co1a, 2.516(5) Å in **7**]. A similar situation was encountered previously involving part of the μ_3-η^2:η^3:η^3-cycloheptatrienyl ligand in the related complex $[Co_4(CO)_3(\mu_3\text{-}CO)_3(\eta^5\text{-}C_7H_9)(\mu_3\text{-}C_7H_7)]$ (**11**) (Scheme 3),[7] and the μ-η^3:η^3-coordinated cyclohexadienyl part of the benzyl ligand in the cations $[\{(C_5H_5)Co\}_3(\mu_3\text{-benzyl})]^+$ (**12**) (Scheme 3).[14]

It should be stressed, however, that we do not wish to attach much significance to the variations in the actual orientation of the facial C_8H_8 ring relative to the bonding M_3 plane, as observed in the crystals. Topologically, there is little difference between these coordination modes; they can be converted into one another by a rather small (less than 8°) rotation of one ring. As indicated by the NMR spectra, rotation of the facial μ_3-cyclooctatetraene 'on top' of the metal triangle is very easily accomplished in solution. Although the anisotropic displacement parameters of the C_8H_8 ring carbons do not show a large distortion, this dynamic process might be operative in the crystals as well.

The chair-like conformation and the irregular pattern of the carbon–carbon bond lengths of the μ_3-C_8H_8 rings in **7** and **8** are quite similar to those established earlier for other tri- and tetranuclear cluster complexes with such li-



10 **11** **12**

Scheme 3

gands.[7,8,13] The somewhat greater spread of carbon–carbon bond lengths in the Co_3Ru complex **8** is not significant, due to the larger errors in this structure. The cobalt–cobalt distances in **8** [2.526(2)...2.531(2) Å] are also similar to the corresponding parameters in the Co_4 complexes **3–5** [2.507(2)...2.538(2) Å][7] and in the trinuclear **7** [2.507(2), 2.530(2) Å]. To our knowledge, complex **8** is the first structurally-characterised cobalt containing tetrahedral cluster with a $(C_5R_5)Ru$ vertex. A comparison with data from Co_3Ru clusters with a $Ru(CO)_{3-n}(PR_3)_n$ ($n = 0, 1$) vertex[15] indicates that Co–Ru bonds are generally slightly longer in these species. This is not unexpected in view of the higher formal oxidation state for Ru in **8**.

In general, the geometry of the $M_3(\mu_3\text{-}C_8H_8)$ subunit does not seem to be influenced much by the nuclearity (three in **7**, four in **3–6** and **8**) and overall charge of the cluster.

Conclusion

In contrast to $[Co_4(CO)_{12}]$ (**1**), reduction of some of its derivatives with a facial C_8H_8 ligand follows a single pathway, and leads to extrusion of a cobalt vertex from the cluster. The product $[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ (**7**) is appreciably more stable than the corresponding binary carbonyl $[Co_3(CO)_{10}]^-$ (**2**). It is obvious that this is due to an effective stabilisation of the triangular array of cobalt atoms by the bridging cyclopolyene ligand.

Experimental Section

General Procedures: All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3–11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Silica used as a stationary phase for column chromatography was heated to 180–200 °C under vacuum for several days and then stored under nitrogen. The cluster complexes **3–6** were prepared by published methods.[7] – NMR spectra were obtained on Bruker AC 200 and AVANCE DRX200 instruments (200.1 MHz for ^1H, 50.3 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are reported vs. $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. – Infrared spectra were recorded in CaF_2 cells with a Bruker IFS-28 Fourier transform spectrometer (optical resolution 0.5 cm^{-1}). – Electrochemical experiments were carried out using a EG & G PARC Model 173 potentiostat and a Model 175 Universal Programmer. Redox potentials are referenced to the standard calomel electrode (SCE). – Elemental analyses were performed locally by the microanalytical laboratory of the Organisch-Chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen.

$[NEt_4]^+[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ ($[NEt_4]^+$-7): An equimolar amount of $Li[HBEt_3]$ (1 M solution in THF) is slowly added to 1.63 g (2.7 mmol) of $[Co_4(CO)_6(C_8H_8)_2]$ (**3**) in THF (20 mL). The mixture is stirred for 30 min at room temperature. The solvent is removed under reduced pressure and the residue is redissolved in 5 mL of THF. A solution of 1.0 g (6.0 mmol) of $[NEt_4]Cl$ in 30 mL of water is added dropwise within 30 min. After stirring for 1 h the precipitation of the product is completed by addition of 20 mL of *n*-heptane. The precipitate is collected on a fine glass frit (D4) and

Table 4. Details of the crystal structure determinations of $[NEt_4]^+[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ ($[NEt_4]^+$-**7**) and $[Ru(C_5Me_5)Co_3(CO)_6(\mu_3\text{-}C_8H_8)]$ (**8**)

	$[NEt_4]^+$-**7**	**8**
empirical formula	$C_{22}H_{28}Co_3NO_6$	$C_{24}H_{23}Co_3O_6Ru$
crystal system	monoclinic	triclinic
space group	$P2_1/m$	P-1
a [Å]	7.922(4)	9.037(4)
b [Å]	16.663(9)	9.692(5)
c [Å]	8.854(5)	13.663(7)
α [°]	90	90.76(4)
β [°]	95.37(5)	93.69(4)
γ [°]	90	106.33(3)
V [Å^3]	1164(1)	1145.4(10)
Z	2	2
M_r	579.25	685.28
d_c [g cm^{-3}]	1.653	1.987
F_{000}	592	680
μ(Mo-K_α) [mm^{-1}]	2.15	2.82
X-radiation, λ [Å]	Mo-K_α, graphite monochromated, 0.71069	
data collect. temperat. [°C]	–70	–70
2 θ range [°]	3–50	3-56
hkl range	±9, 0/19, 0/10	–11/+9, –11/+12, 0/16
reflections measured		
unique reflections	2141	4250
observed [$I \geq 2\sigma(I)$]	1828	2997
parameters refined	217	345
R (obs. reflections only)	0.034	0.055
w$R2$ (all reflections)	0.088	0.133
($w = 1/[\sigma^2(F) + (A\ P)^2 + B\ P]$,		
A, B	0.0502, 0.59	0.0313, 8.18
P	$[\max(F_o^2, 0)+2\ F_c^2]/3$	
GOF	1.058	1.098
Largest diff. peak and hole [eÅ^{-3}]	0.49/–0.44	0.73/–0.85

washed with water, toluene and pentane to give pure dark orange polycrystalline $[NEt_4]^+$-**7** (1.57 g, 100%). – ^1H NMR (in CD_2Cl_2): δ = 1.35 (m, 12 H, NCH_2CH_3), 3.24 (m, 8 H, NCH_2CH_3), 4.10 (s, 8 H, C_8H_8). – $^{13}C\{^1H\}$NMR (in C_6D_6): δ = 7.7 (NCH_2CH_3), 53.0 (t, J_{CN} = 3.0 Hz, NCH_2CH_3), 69.1 (C_8H_8). – IR (ν(CO), in CH_2Cl_2): $\tilde{\nu}$ = 1977 (s), 1938 (vs), 1782 (s), 1743 (s) cm^{-1}. – $C_{22}H_{28}Co_3NO_6$ (579.3): C 45.62, H 4.87, N 2.42; found C 45.47, H 4.93, N 2.35.

$[(C_5H_5)_2Co]^+[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ ($[(C_5H_5)_2Co]^+$7): A 285 mg (0.46 mmol) sample of **3** and 330 mg (1.7 mmol) of $[(C_5H_5)_2Co]$ are dissolved in 100 mL of toluene at room temperature. A black precipitate is formed immediately, which is collected on a glass frit and washed two times with 10 mL of toluene. The product was recrystallised from THF to give 290 mg (100%) of red $[(C_5H_5)_2Co]^+$-**7**.

$[Ru(C_5Me_5)Co_3(CO)_6(\mu_3\text{-}C_8H_8)]$ (8): A mixture of 720 mg (1.2 mmol) of $[NEt_4]^+$-**7** and 550 mg (1.2 mmol) of $[(C_5Me_5)Ru(NCMe)_3][BF_4]$ in 50 mL of CH_2Cl_2 is stirred at room temperature for 1 h. After filtration of the solution the solvent is removed under reduced pressure and the residue washed with *n*-hexane. The black residue is chromatographed on silica (20·2.5 cm). A broad yellow-brown band is removed first with *n*-hexane/toluene (1:1). The dark red band obtained with CH_2Cl_2 is collected to give black polycrystalline **8** (360 mg, 44%) after removal of solvent in vacuo. ^1H NMR (in CD_2Cl_2): δ = 1.84 (s, 15 H, CH_3), 3.97 (s, 8 H, C_8H_8). – $^{13}C\{^1H\}$NMR (in C_6D_6): δ = 9.2 (C_5Me_5), 70.3 (C_8H_8), 105.8 (C_5Me_5). – IR (ν(CO), in THF): $\tilde{\nu}$ = 2000 (sh), 1978 (vs), 1707 (s) cm^{-1}. – $C_{24}H_{23}Co_3O_6Ru$ (685.3): C 42.06, H 3.38; found C 42.24, H 3.41.

Crystal Structure Determinations: Single crystals were grown from a dichloromethane solution at –20 °C ($[NEt_4]^+$-**7**) or by slowly cooling a hot (80 °C) solution in toluene (**8**). Intensity data were collected on a Siemens-Stoe AED2 four circle diffractometer at low temperature and corrected for Lorentz, polarisation and absorption effects (Table 4). A semi-empirical absorption correction was applied (Psi-scans). Crystals of **8** were found to be twinned; the structure was solved and refined using only the nonoverlapping reflections of the individuum which gave the higher intensities. The structures were solved by direct methods, and refined by full matrix least squares based on F^2. All nonhydrogen atoms were given anisotropic displacement parameters. The hydrogen atoms of the cyclooctatetraene rings were located from difference Fourier syntheses and refined with isotropic displacement parameters. All other hydrogens were placed in calculated positions.[16] A limited set of reflection data was also collected from a poorly crystalline specimen of $[(C_5H_5)]_2Co]^+$-**7**. The low quality of this data set allowed the structure to be solved, but was not sufficient for a complete refinement. The calculations were performed using the programs SHELXS-86 and SHELXL-93.[17] Graphical representations were drawn with ORTEP-II[18]

Acknowledgments

This work was supported by the Sonderforschungsbereich 247 der Universität Heidelberg and the Fonds der Chemischen Industrie. H. W. gratefully acknowledges the award of a Heisenberg Fellowship.

---

[1] H. Vahrenkamp, *Adv. Organomet. Chem.* **1983**, *22*, 169.

[2] W. E. Geiger, *Progr. Inorg. Chem.* **1985**, *33*, 275.

[3] J. Rimmelin, P. Lemoine, M. Gross, D. de Montauzon, *Nouv. J. Chem.* **1983**, *7*, 453.

[4] H. Behrens, R. Weber, *Z. Allg. Anorg. Chem.* **1955**, *281*, 190.

[5] P. Chini, V. Albano, S. Martinengo, *J. Organomet. Chem.* **1969**, *16*, 471.

[6] [6a] G. Fachinetti, *J. Chem. Soc., Chem. Commun.* **1979**, 396. – [6b] H.-N. Adams, G. Fachinetti, J. Strähle, *Angew. Chem.* **1980**, *92*, 411.

[7] H. Wadepohl, S. Gebert, H. Pritzkow, D. Braga, F. Grepioni, *Chem. Eur. J.* **1998,** *4,* 279.

[8] H. Wadepohl, Coord. Chem. Rev. **1999**, *185-186*, 551.

[9] J. Rimmelin, P. Lemoine, M.Gross, A. A. Bahsoun, J. A. Osborn, *Nouv. J. Chem.* **1985**, *9*, 181.

[10] A more detailed study of the electrochemistry of **3**–**6** currently in progress.

[11] P. Chini, B. T. Heaton, *Top. Curr. Chem.* **1977**, *71*, 1.

[12] A. A. Bahsoun, J. A. Osborn, C. Voelker, J. J. Bonnet, G. Lavigne, *Organometallics* **1982**, *1*, 1114.

[13] H. Wadepohl, S. Gebert, R. Merkel, H. Pritzkow, *Chem. Commun.* **1999**, 389.

[14] H. Wadepohl, M. J. Calhorda, M. Herrmann, C. Jost, P. E. M. Lopes, H. Pritzkow, *Organometallics* **1996**, *15*, 5622.

[15] [15a] M. Hidai, M. Orisaku, M. Ue, Y. Koyasu, T. Kodama, Y. Uchida, *Organometallics* **1983**, *2*, 292. – [15b] P. Braunstein, J. Rosé, A. Dedieu, Y. Dusausoy, J.-P. Mangeot, A. Tiripicchio, M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.* **1986**, 225. – [15c] J. Pursiainen, T. A. Pakkanen, *J. Organomet. Chem.* **1986**, *309*, 187. – [15d] S. Rossi, J. Pursiainen, M. Ahlgren, T. A. Pakkanen, *Organometallics* **1990**, *9*, 475. – [15e] J. Pursiainen, P. Hirva, T. A. Pakkanen, *J. Organomet. Chem.* **1991**, *419*, 193. – [15f] P. Braunstein, Feng Ying Jiao, J. Rosé, P. Granger, F. Balegroune, O. Bars, D. Grandjean, *J. Chem. Soc., Dalton Trans.* **1992**, 2543. – [15g] P. Braunstein, L. Mourey, J. Rosé, P. Granger, T. Richert, F. Balegroune, D. Grandjean, *Organometallics* **1992**, *11*, 2628. – [15h] H. J. Kakkonen, M. Ahlgren, T. A. Pakkanen, J. Pursiainen, *Acta Crystallogr., Sect. C (Cryst. Struct. Comm.)* **1994**, *50*, 528. – [15i] P. Braunstein, J. Rosé, D. Toussaint, S. Jaaskelainen, M. Ahlgren, T. A. Pakkanen, J. Pursiainen, L. Toupet, D. Grandjean, *Organometallics* **1994**, *13*, 2472. – [15j] T. Teppana, S. Jaaskelainen, M. Ahlgren, J. Pursiainen, T. A. Pakkanen, *J. Organomet. Chem.* **1995**, *486*, 217. – [15k] H. J. Kakkonen, M. Ahlgren, J. Pursiainen, T. A. Pakkanen, *J. Organomet. Chem.* **1996**, *507*, 147. – [15l] H. J. Kakkonen, M. Ahlgren, T. A. Pakkanen, J. Pursiainen, *J. Organomet. Chem.* **1996**, *518*, 203.

[16] 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-135215 ($[NEt_4]^+$-**7**) and 135216 (**8**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (Internat.) + 44 1223/336 033; E-mail: deposit-@ccdc.cam.ac.uk).

[17] *SHELXS-86*: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; *SHELXL-93*: G. M. Sheldrick, Universität Göttingen **1993**.

[18] *ORTEP-II*: C. K. Johnson, Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Received October 4, 1999
[I99345]