

# Metal clusters and cyclopolyenes: the face-capping coordination mode

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## Contents

Abstract . . . . .	551
1. Introduction . . . . .	552
2. Synthetic aspects . . . . .	552
3. Ligand substitution reactions . . . . .	555
4. Redox chemistry . . . . .	558
5. Modification of the metal cluster framework . . . . .	561
6. A heteronuclear cluster where cot caps a $\text{Co}_2\text{Ni}$ face . . . . .	564
7. Molecular structure and stereochemical nonrigidity . . . . .	566
Acknowledgements . . . . .	568
References . . . . .	568

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## Abstract

The synthesis, structure and chemistry of tri- and tetranuclear cluster complexes with face-capping  $\text{C}_7\text{H}_7$  and  $\text{C}_8\text{H}_8$  ligands are described. Synthesis of such complexes is based on mutual steric hindrance of two of the large cyclopolyenes, which cannot both occupy apical coordination sites in a  $\text{M}_4$  ( $\text{M} = \text{Co}, \text{Rh}$ ) cluster. Reactions where the facial coordination of the cyclopolyene is retained include substitution of apical ligands and redox reactions with and without degradation of the metal cluster. A description of the characteristic features of the facial ( $\mu_3$ -) bonding mode of  $\text{C}_7\text{H}_7$  and  $\text{C}_8\text{H}_8$  is given, based on numerous crystal structures. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Cluster complexes; Cyclopolyenes; Electrochemistry; Facial ligands

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## 1. Introduction

Metal complexes of the cyclic  $\pi$ -perimeters occupy a pre-eminent position in the history and development of organo-transition metal chemistry. The three- to eight-membered carbocycles  $C_nH_n$  are capable of centrally bonding to a single metal centre (**A**), like in the sandwich complexes  $[(C_5H_5)_2Fe]$ ,  $[(C_6H_6)_2Cr]$  and  $[(C_8H_8)_2U]$ , which have become true classics of organometallic chemistry.



Much more recently, with the discovery of the facial  $\mu_3$ -coordination mode (**B**) of benzene and some of its derivatives to a  $M_3$  unit (which may be part of a larger cluster), arene chemistry has entered a new era [1]. Considerable knowledge has now already been gathered about such systems. Of the many interesting features we note here in particular the similarities of the coordination geometry and electronic structure with the adsorption states of benzene on some close-packed metal surfaces [2]. This is a classical test case for the cluster surface analogy [3]. Although this postulate suffered some erosion in the mind of the chemical community since it had been first formulated<sup>1</sup>, it is, however, still thought to be useful for the detailed understanding of certain heterogeneous catalytic processes [4].

Up to quite recently, metal cluster complexes with cycloheptatrienyl ( $C_7H_7$ ) and cyclooctatetraene ( $C_8H_8$ , cot) in the facial coordination mode had been restricted to a very few isolated cases [5]. Sparked by recent interest of the surface science community in the complex surface chemistry of cot [6] we set out to explore the facial coordination mode of  $C_7H_7$  and  $C_8H_8$  ligands in molecular transition metal cluster complexes.

## 2. Synthetic aspects

Looking through the literature we came across 20-year-old paper by a Japanese group, who had studied the reactions of  $[Co_4(CO)_{12}]$  **1** and  $[Rh_4(CO)_{12}]$  **2** with some conjugated olefins, including cycloheptatriene (cht) and cyclooctatetraene [7]. With **1** and the latter ligand the only isolated product was the dinuclear  $[Co_2(CO)_4(C_8H_8)]$ , which was formed in 2% yield. Two cluster complexes containing cht were reported,  $[Co_4(CO)_9(C_7H_8)]$  **3** and  $[Co_4(CO)_6(C_7H_8)_2]$ . An apical  $\eta^6$ -coordinated cycloheptatriene ligand was suggested for **3**. The second complex was reported to be unstable, and no detailed structure was given. We felt that in such a tetrahedral cluster two apical cycloheptatriene ligands on necessarily adjacent

<sup>1</sup> Nowadays it appears to be more popular with physicists and surface scientists.

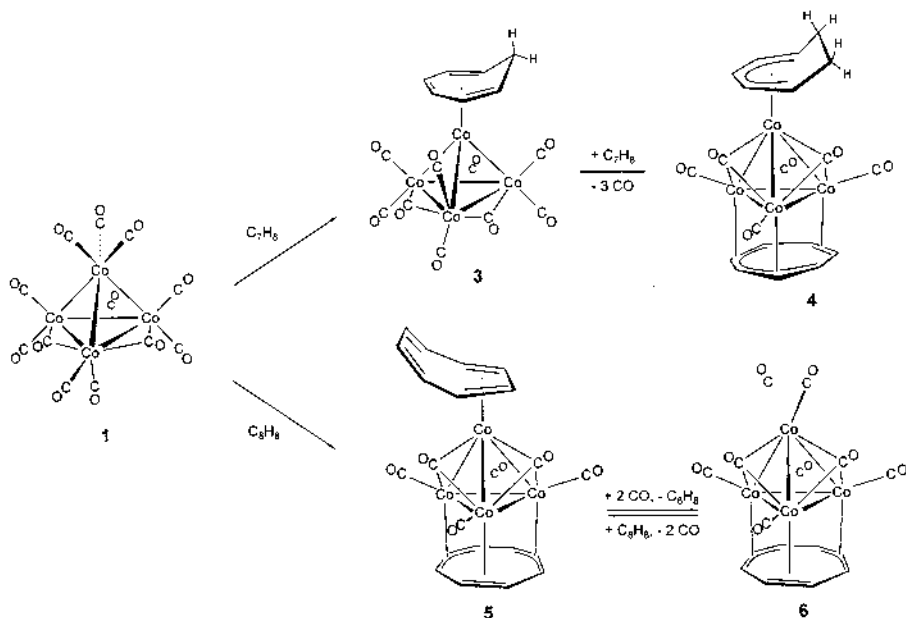
cluster vertices would result in a sterically unfavourable situation, which might be relieved by moving one ligand to a bridging coordination site.

Our reinvestigation of this work led indeed to quite different results. Under only slightly different reaction conditions (boiling heptane instead of hexane) **1** readily reacted both with cht and cot to give the tetranuclear cluster complexes  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$  **4** and  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)]$  **5**, respectively, in high yield (Scheme 1) [8].

Both products were structurally characterised in the solid state by X-ray crystal structure analyses (Fig. 1).

During the formation of **4**, the complex  $[\text{Co}_4(\text{CO})_9(\eta^6\text{-C}_7\text{H}_8)]$  **3** was observed in low concentration as a transient intermediate. It is likely, that this species takes up a second cht ligand, which would then undergo intramolecular hydrogen transfer to give the final product **4** with a facial  $\text{C}_7\text{H}_7$  and an apical  $\text{C}_7\text{H}_9$  ligand (Scheme 1). We were unable to find such an intermediate with two cycloheptatriene ligands in the reaction mixture. The alleged [7]  $[\text{Co}_4(\text{CO})_6(\text{C}_7\text{H}_8)_2]$  could also be ruled out; this material was in fact contaminated **4**, as revealed by a comparison of the published IR spectral data with those of **4**.

No intermediates could be detected during the formation of the bis-cot complex **5**. For obvious reasons, some tetracobalt mono-cot complex must be formed as one of the first steps in the reaction. Indeed, the complex  $[\text{Co}_4(\text{CO})_8(\mu_3\text{-C}_8\text{H}_8)]$  **6** with only one (face-capping) cot ligand was found along with **5**, when the reaction was quenched after a short time. We cannot, however, rule out that **6** is formed via the reaction of **5** with CO, which is of course present in the reaction mixture (Scheme



Scheme 1.

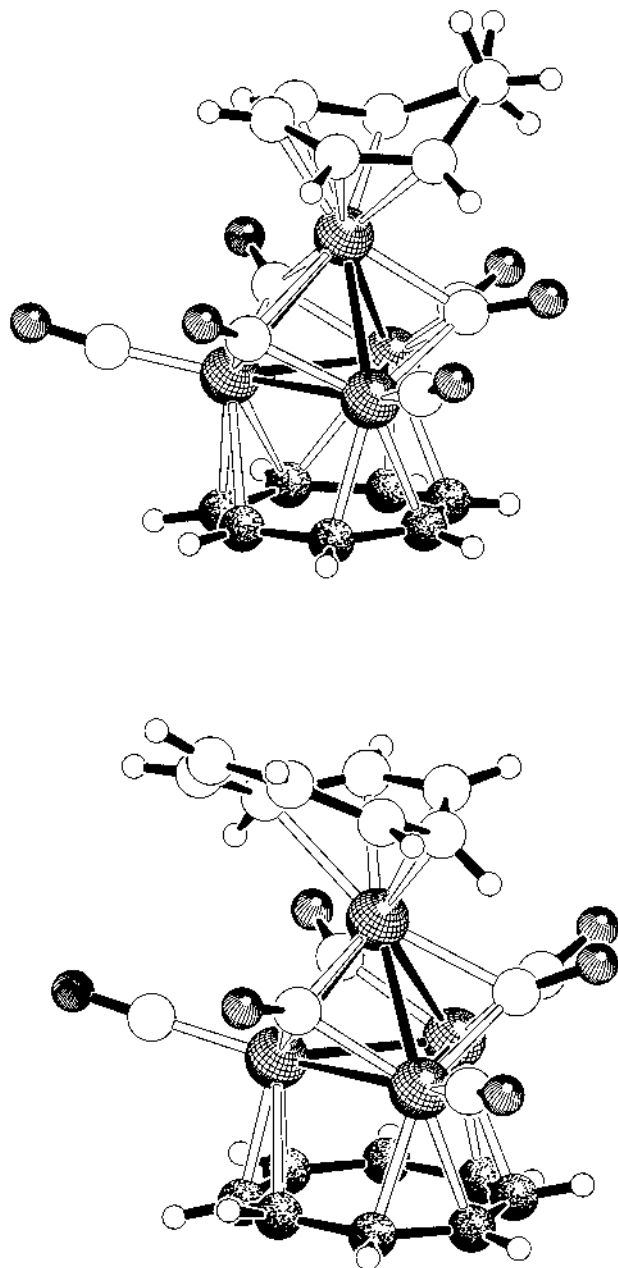


Fig. 1. Molecular structures of  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$  **4** (top) and  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)]$  **5** (bottom).

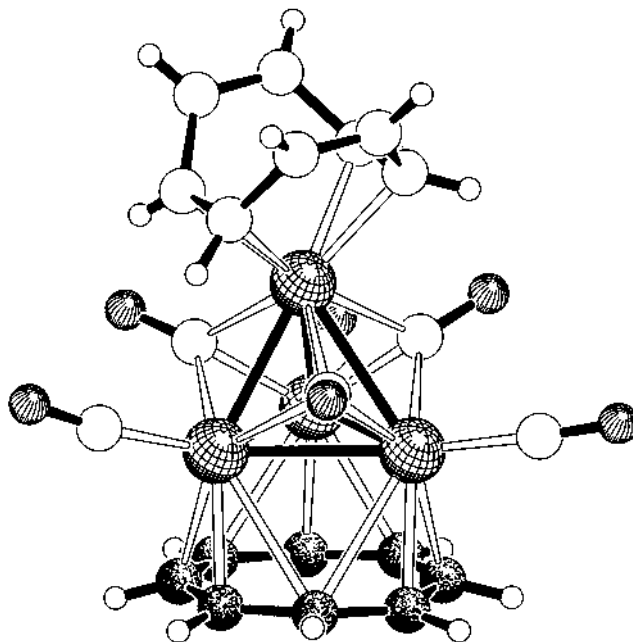


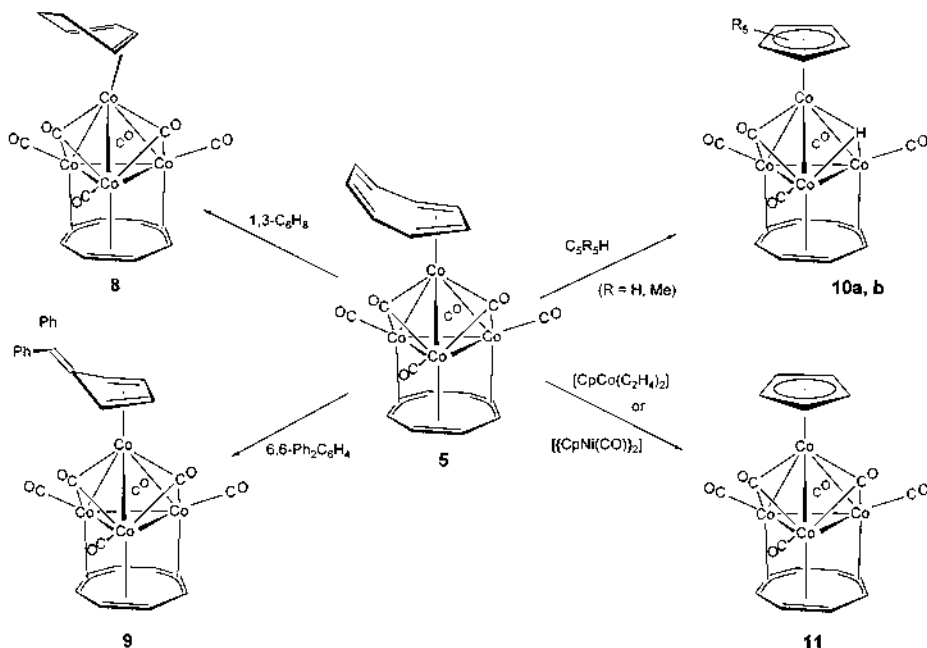
Fig. 2. Molecular structure  $[\text{Rh}_4(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)]$  **7**.

1). Complex **6** is also known to be a thermal decomposition product of **5**. It is therefore not quite clear if the first cot ligand directly enters the  $\text{Co}_4$  cluster in the facial coordination site (to give **6**), or if an as yet undetected intermediate with an apical cot ligand is involved. Such a primary species could either loose CO and take up a second cot ligand, which would then go into the facial position (to give **5**), or else rearrange to give **6**.

The reaction of  $[\text{Rh}_4(\text{CO})_{12}]$  **2** with cot has been reported by the aforementioned authors to give the complex  $[\text{Rh}_4(\text{CO})_6(\text{cot})_2]$  [**7**]. A structure with two apical  $\eta^4$ -coordinated cot ligands was suggested. This complex must now be reformulated as  $[\text{Rh}_4(\text{CO})_6(\mu_3\text{-cot})(\eta^4\text{-cot})]$  **7** (Fig. 2). Interestingly, the apical cot ligand attains the static 1,2,5,6- $\eta$  bonding mode, in contrast to the fluxional 1-4- $\eta$ -coordinated apical cot ligand in the cobalt complex **5** (Fig. 1).

### 3. Ligand substitution reactions

The reactivity of the bis-cot complexes **5** and **7** with donor ligands is quite straightforward. A typical selection of reactions is given in Scheme 2. Substitution of the apical cot ligand took place with many ligands, with retention of the facially coordinated cot. In the reactions with  $\text{C}_5\text{R}_5\text{H}$  ( $\text{R} = \text{H}, \text{Me}$ ) oxidative addition of the cyclopentadiene occurred, accompanied by extrusion of a carbonyl ligand, to give the cyclopentadienyl hydrido derivatives **10**.



Scheme 2.

The reaction of **5** with  $[(\text{C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2]$  resulted in the formation of  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-cot})(\eta^5\text{-C}_5\text{H}_5)]$  **11**. In this case exchange of the apical cot ligand or else exchange of a complete metal vertex [substitution of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$  for  $(\eta^4\text{-C}_8\text{H}_8)\text{Co}$ ] could be involved. However, with  $\{[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\}$  and **5** the same product was formed in comparable yield, proving exchange of the ligands only. With the same reagents, complex **4** could be transformed into  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)]$  **12**. Much more drastic reaction conditions had to be employed here, consistent with the expected lower substitution lability of the odd-electron  $\text{C}_7\text{H}_9$  ligand.

No change in total cluster valence electron (VE) count is involved in going from **4** to **12** (both have 60 VE). In contrast, complex **11** has one electron too many (61 VE) [9], and therefore shows paramagnetic behaviour. An investigation of the paramagnetic NMR spectra showed a large degree of localisation of the unpaired spin on the  $(\text{C}_5\text{H}_5)\text{Co}$  apex of the cluster. This is reflected in a somewhat larger distance of the  $\text{C}_5\text{H}_5$  ring from the apical cobalt atom<sup>2</sup> in **11** (1.76) compared to **12** (1.70), although the gross molecular structures of **11** and **12** are quite similar (Fig. 3).

<sup>2</sup> In this paper, the face of the  $\text{M}_4$  cluster which binds the  $\mu_3$ -ligand will be referred to as the 'basal  $\text{Co}_3$  plane'; the forth metal is 'apical'.

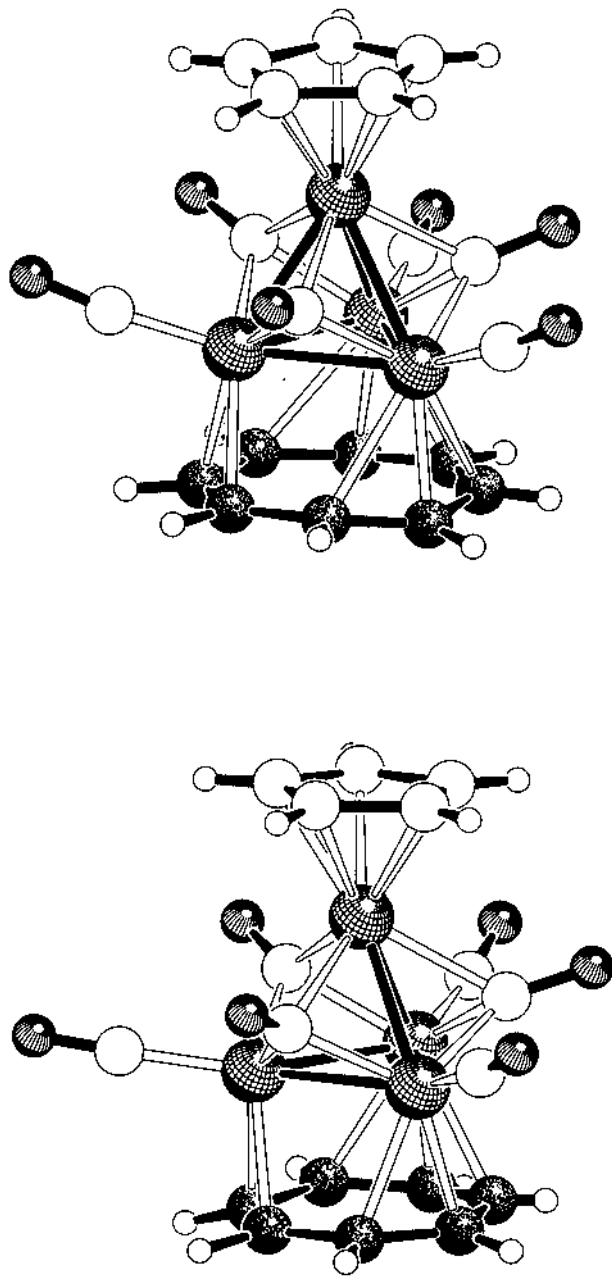
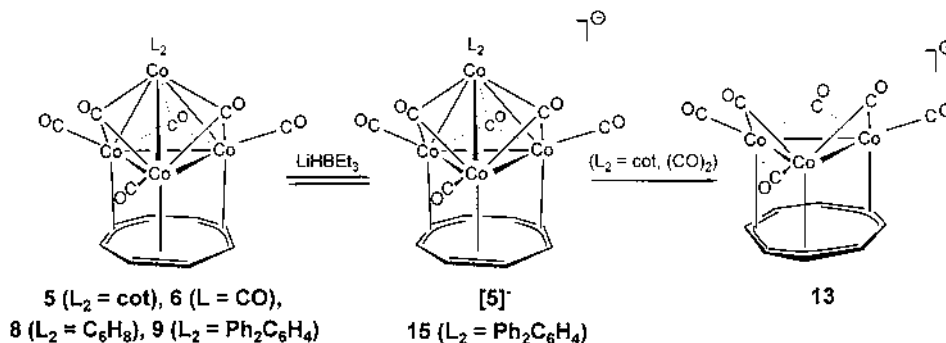


Fig. 3. Molecular structures of  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)]$  **11** (top) and  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\eta\text{-C}_5\text{H}_5)]$  **12** (bottom).

#### 4. Redox chemistry

Cathodic waves were shown in the cyclic voltammogram of the  $\mu_3$ -cot cluster complexes **5**, **6**, **8** and **9**, corresponding to one-electron reductions of these species. However, reversible potential-current response was only observed with **8** and **9**. Reduction of **5** and **6** was irreversible. When reduction of these complexes was carried out in a preparative scale using  $\text{LiHBEt}_3$  as a reducing agent, the trinuclear cluster anion  $[\text{Co}_3(\text{CO})_6(\mu_3\text{-cot})]^-$  **13** could be isolated in nearly quantitative yield.



This reaction parallels the well-known reductive degradation of  $[\text{Co}_4(\text{CO})_{12}]$  **1** to give  $[\text{Co}_3(\text{CO})_{10}]^-$ . The molecular structures of  $[\text{Co}_3(\text{CO})_{10}]^-$  and **13** (Fig. 4) are also similar, with three  $\mu_2$ -bridging carbonyl ligands. However, the homoleptic carbonyl cluster anion is quite labile and even decomposes in thf solution. In **13**, the face-capping cot ligand greatly stabilises the anionic cluster which can even be refluxed in thf for several hours without decomposition.

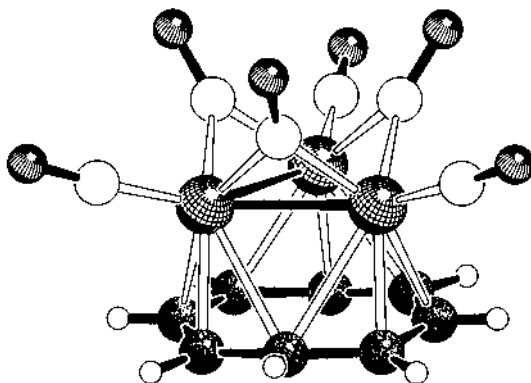


Fig. 4. Molecular structure of  $[\text{Co}_3(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)]^-$  **13** in the crystals of  $[\text{NEt}_4][\text{13}]$ .



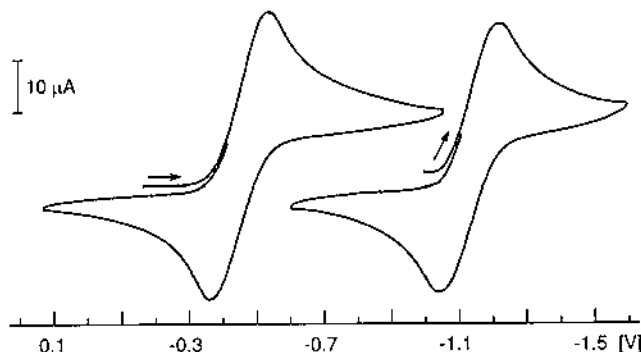
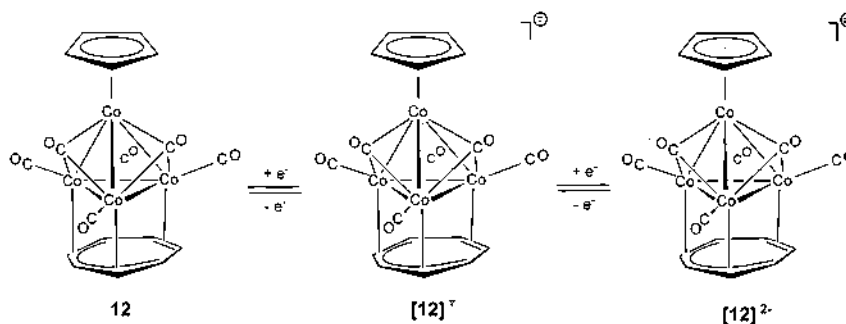


Fig. 5. Cyclic voltammograms of  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\eta\text{-C}_5\text{H}_5)]$  **12**. Scan rate:  $100 \text{ mV s}^{-1}$ ; solvent:  $\text{CH}_2\text{Cl}_2$ ; supporting electrolyte:  $\text{tBu}_4\text{NPF}_6$ ; reference: SCE. The direction of the potential scan is indicated by arrows.

The results of the electrochemical experiments suggested that the primary products of the single electron transfer reaction, the tetranuclear anions  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-cot})(\text{L})_2]^-$ , have a reasonable lifetime at least with some of the apical ligands L. Reduction of the diphenylfulvene cluster derivative **9** with an appropriate amount of Collman's reagent  $[\text{Na}_2\text{Fe}(\text{CO})_4]$  indeed generated a new ionic species. Preliminary spectroscopic evidence is consistent with the tetranuclear monoanion  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)(\eta^4\text{-Ph}_2\text{C}_6\text{H}_4)]^-$  [**9**] $^-$ .

The cyclic voltammogram of the cyclopentadienyl  $\mu_3$ -cycloheptatrienyl cluster complex **12** showed two quasi-reversible cathodic waves (Fig. 5). Hence, this complex can be reduced to give the mono- and dianions, which are stable at least on the timescale of the CV experiment (Scheme 3).



Scheme 3.

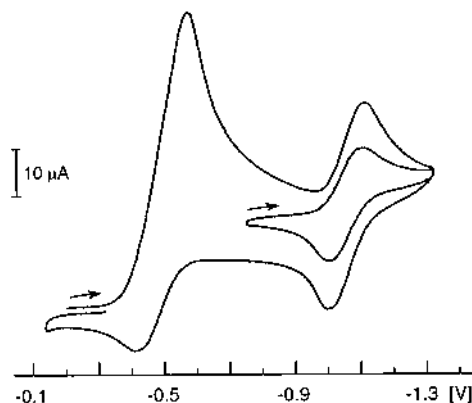


Fig. 6. Cyclic voltammograms of  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\text{C}_7\text{H}_9)]$  **4**. The inner trace was recorded at lower gain. Scan rate:  $100 \text{ mV s}^{-1}$ ; solvent:  $\text{CH}_2\text{Cl}_2$ ; supporting electrolyte:  ${}^n\text{Bu}_4\text{NPF}_6$ ; reference: SCE. The direction of the potential scan is indicated by arrows.

A different behaviour was shown by the  $\text{C}_7\text{H}_9/\mu_3\text{-C}_7\text{H}_7$  cluster complex **4**. The first reduction was only partially reversible, depending on the potential scan rate. A reversible response was observed at high scan rates (above  $2 \text{ V s}^{-1}$ ). The second reduction was always essentially reversible (Fig. 6).

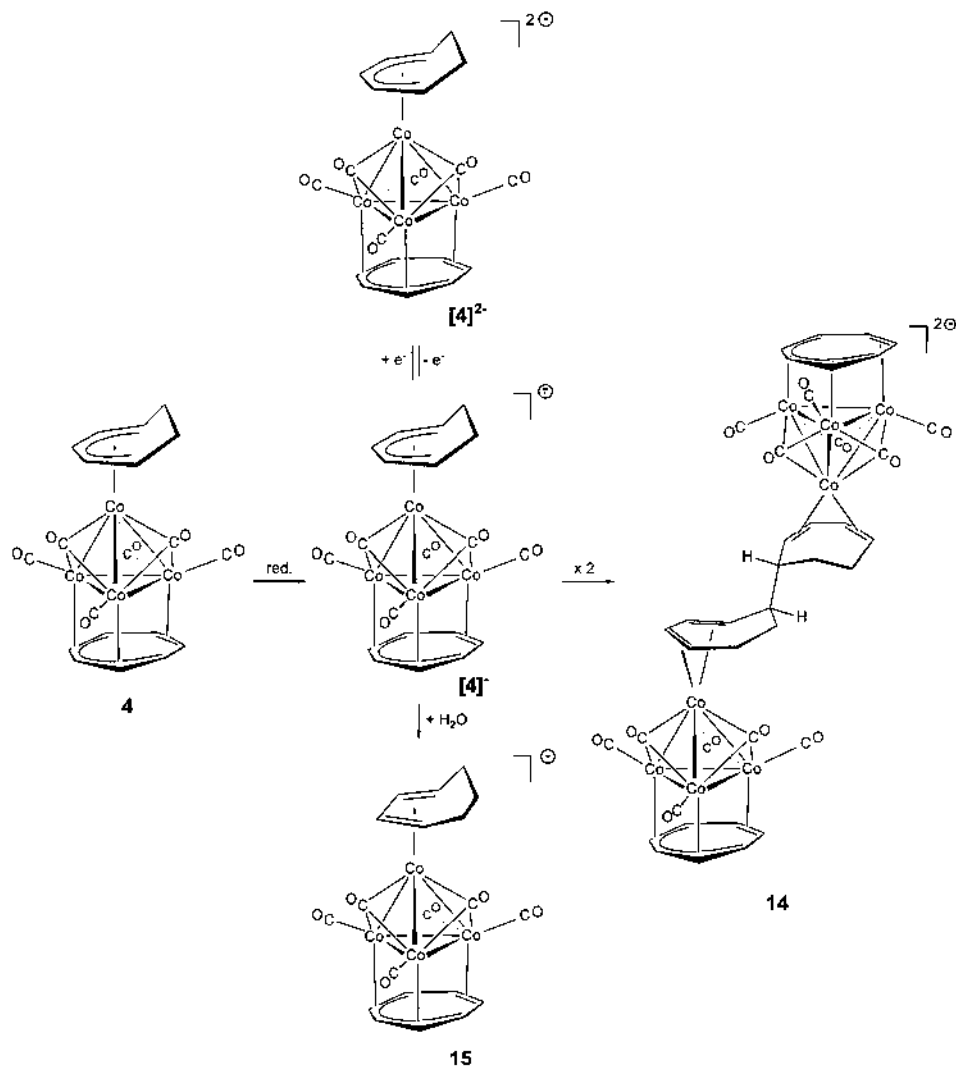
The interpretation of this behaviour is fairly straightforward (Scheme 4)<sup>3</sup>. While the dianion is a stable species, the monoanion undergoes a slow chemical reaction, which partially removes it from the electrochemical double layer. When the first reduction of **4** was carried out chemically on a preparative scale, a paramagnetic solution was obtained. After a couple of hours a new complex, **14**, could be precipitated from the solution as the  $\text{PPh}_4$  salt. This complex is the dimerisation product of the anion radical  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\text{C}_7\text{H}_9)]^-$  [**4**]<sup>−</sup>. Attempts to isolate [**4**]<sup>−</sup> in crystalline form by salt metathesis with  ${}^n\text{Bu}_4\text{NCl}$  resulted in the formation of  $[\text{Co}_4(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)(\text{C}_7\text{H}_{10})]^-$  **15**. Obviously, the unpaired electron in the 61 VE cluster complex [**4**]<sup>−</sup> is largely centered on the apical cycloheptadienyl ligand (compare the isoelectronic radical **11**).

The molecular structure of **14**, as determined by a crystal structure analysis, is shown in Fig. 7. Dimerisation of [**4**]<sup>−</sup> generates two centres of chirality, on the ‘bridgehead’ carbons C1 and C21. Two diastereomeric forms, *R,R*-**14** and *R,S*-**14** were formed [*R* and *S* refers to the absolute configuration of C1 and C21, respectively (Fig. 7)]. The *R,R* form is somewhat less soluble than the *R,S* isomer and could be separated by fractional crystallisation.

<sup>3</sup> The electrochemical behaviour of these and related systems are presently being studied in more detail by Prof. D. Osella and his coworkers at the University of Torino, Italy.

## 5. Modification of the metal cluster framework

Anionic metal cluster complexes are valuable educts for cluster expansion, by means of reaction with cationic fragments. The trinuclear cluster anion **13** could



Scheme 4.

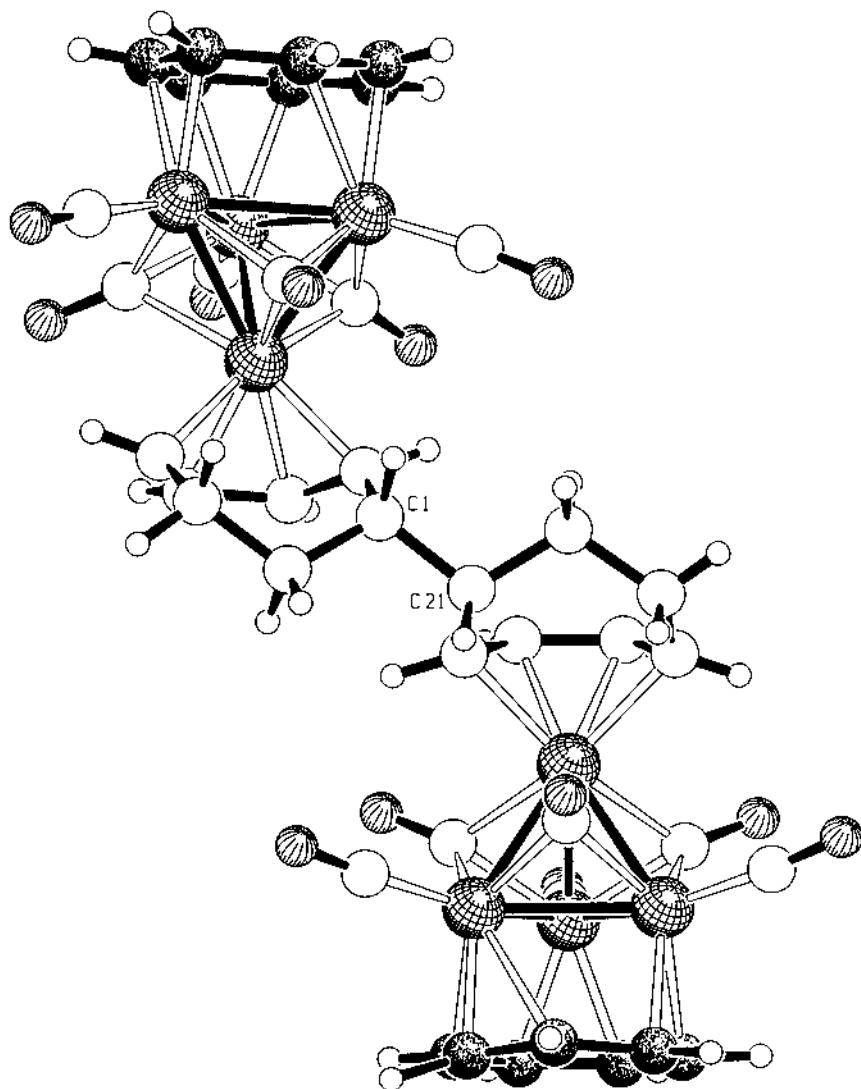


Fig. 7. Molecular structure of  $[\{Co_4(CO)_6(\mu_3-C_7H_7)\}_2\{\mu_2-(\eta^4-C_7H_9)_2\}]^{2-}$  **14** in the crystals of  $[PPh_4]_2[\mathbf{14}]$ .

be capped with cationic metal fragments to give heteronuclear cluster complexes with a  $MCo_3(\mu_3-C_8H_8)$  core. For example, treatment with  $[(C_5Me_5)Ru(NCMe)_3]^+$  gave the complex  $[(C_5Me_5)RuCo_3(CO)_6(\mu_3-C_8H_8)]$  **16** (Fig. 8) in 45% yield.

Interestingly, a similar reaction was observed when the  $\mu_3$ -cycloheptatrienyl complex **4** was first reduced with  $LiHBet_3$  and then treated with  $[(C_6H_6)Ru(NCMe)_3][BF_4]_2$ . The complex  $[(C_6H_6)RuCo_3(CO)_6(\mu_3-C_7H_7)]$  **17** was isolated from this reaction in about 20% yield.

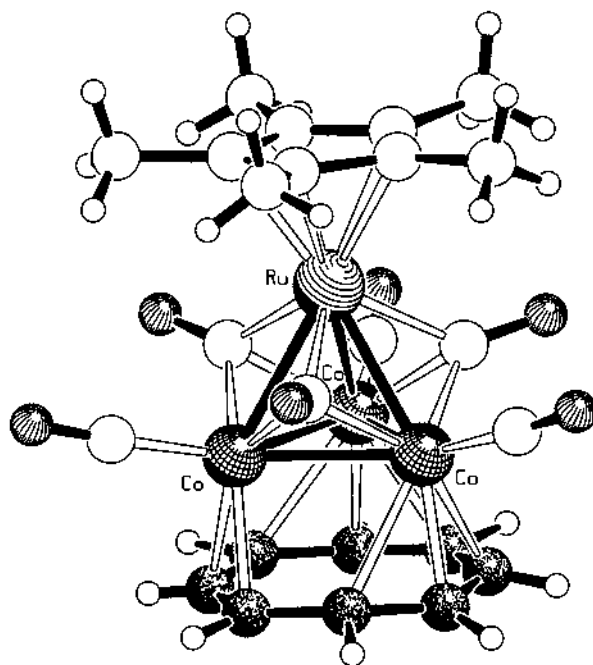
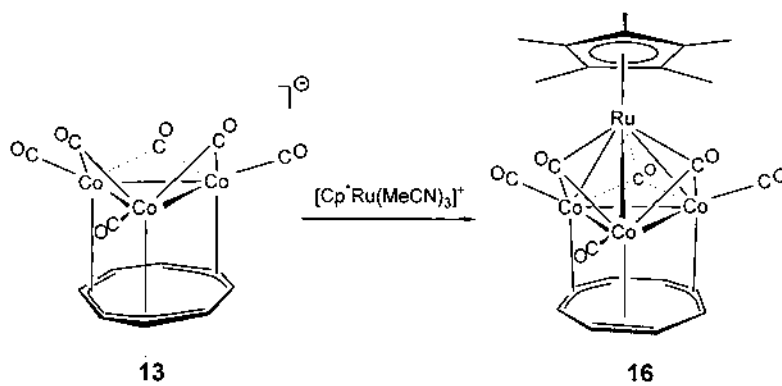


Fig. 8. Molecular structure of  $[(\text{C}_5\text{Me}_5)\text{RuCo}_3(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)]$  **16**.

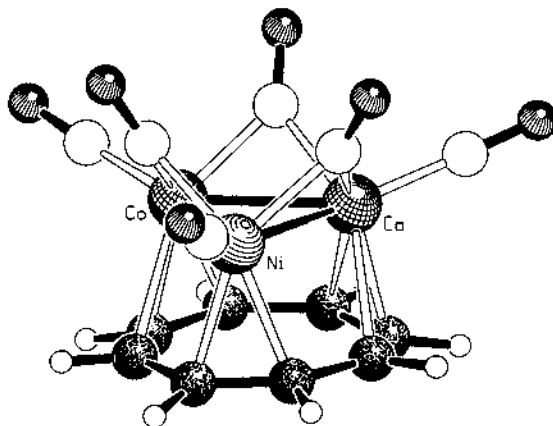
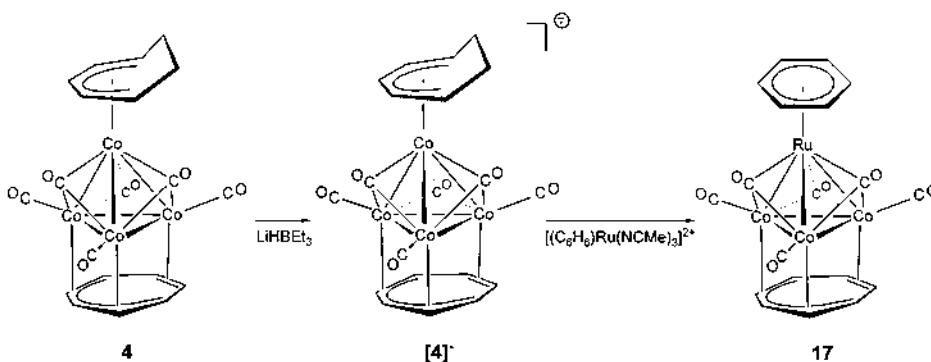


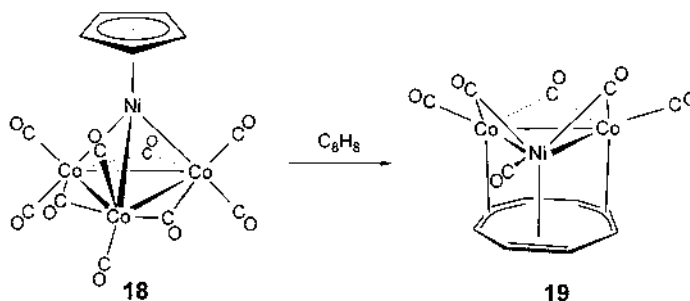
Fig. 9. Molecular structure of  $[\text{NiCo}_2(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)]$  **19**. The assignment of cobalt and nickel atoms is only tentative.



In chemically reduced solutions of **4** there was no evidence of the dianion  $[\mathbf{4}]^{2-}$ ; this species could only be generated in the CV experiment. Formation of **17** could occur via the trinuclear dianion  $[\text{Co}_3(\text{CO})_6(\mu_3\text{-C}_7\text{H}_7)]^{2-}$ , which could have been formed in small amounts from  $[\mathbf{4}]^-$ . However, a direct attack of the ruthenium reagent on the  $\text{Co}_4$  cluster in  $[\mathbf{4}]^-$  or **14**, followed by extrusion of a cobalt vertex, cannot be ruled out.

## 6. A heteronuclear cluster where cot caps a $\text{Co}_2\text{Ni}$ face

The heteronuclear cluster complex  $[(\text{C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_9]$  **18** has a similar structure and properties as **1**. Quite surprisingly, reaction with cot gave a very dissimilar product, the trinuclear cluster complex  $[\text{NiCo}_2(\text{CO})_6(\mu_3\text{-C}_8\text{H}_8)]$  **19** [10].



As a second product,  $[(C_5H_5)Co(CO)_2]$  was detected in the reaction mixture. This can be taken as an indication that the incoming cot molecule first pushes the  $C_5H_5$  ligand from Ni to a cobalt vertex, which is then expelled from the  $Co_3Ni$  cluster in the form of  $[(C_5H_5)Co(CO)_2]$ . Complex **19** is isoelectronic to the anion **13**. As

Table 1  
Geometric parameters pertinent to the  $\mu_3$ - $C_7H_7$  and  $\mu_3$ - $C_8H_8$  ligands

Complex	Coordination mode	$d(M-C)$ [Å]	$d(C-C)$ [Å]
$\mu_3$ - $C_8H_8$			
$[Co_4(CO)_6(C_8H_8)_2]$ <b>5</b>	$\eta^2:\eta^3:\eta^3$	2.054(5)···2.386(5)	1.402(7)···1.417(7)
$[Co_4(CO)_8(C_8H_8)]$ <b>6</b> <sup>a</sup>	$\eta^2:\eta^3:\eta^3$	2.059(7)···2.429(7)	1.399(9)···1.431(8)
	$\eta^2:\eta^3:\eta^3$	2.068(6)···2.491(7)	1.400(9)···1.431(9)
$[Co_4(CO)_6(C_6H_8)(C_8H_8)]$ <b>8</b> <sup>a</sup>	$\eta^2:\eta^3:\eta^3$	2.060(4)···2.460(4)	1.402(5)···1.430(5)
	$\eta^2:\eta^3:\eta^3$	2.052(4)···2.479(4)	1.402(6)···1.426(6)
$[Co_4(CO)_6(C_5H_5)(C_8H_8)]$ <b>11</b>	$\eta^2:\eta^3:\eta^3$	2.072(3)···2.460(4)	1.404(5)···1.431(5)
$[Co_4(CO)_5(H)(C_5Me_5)(C_8H_8)]$ <b>10b</b>	$\eta^3:\eta^3:\eta^3$	2.05(2)···2.49(1)	1.40(1)···1.43(1)
$[(C_5Me_5)RuCo_3(CO)_6(C_8H_8)]$ <b>16</b>	$\eta^2:\eta^3:\eta^3$	2.041(10)···2.383(11)	1.37(2)···1.45(2)
$[Co_3(CO)_6(C_8H_8)]^-$ <b>13</b>	$\eta^3:\eta^3:\eta^3$	2.080(5)···2.518(5)	1.405(4)···1.429(6)
$[NiCo_2(CO)_6(C_8H_8)]$ <b>19</b>	$\eta^2:\eta^3:\eta^{3b}$	2.088(5)···2.427(5)	1.396(8)···1.434(8)
$[Rh_4(CO)_6(C_8H_8)_2]$ <b>7</b>	$\eta^3:\eta^3:\eta^3$	2.197(7)···2.727(7)	1.40(1)···1.43(1)
$[Rh_4(CO)_8(C_8H_8)]^c$	$\eta^2:\eta^3:\eta^3$	2.20(1)···2.72(1)	1.38(2)···1.45(2)
	$\eta^2:\eta^3:\eta^3$	2.19(1)···2.60(1)	1.37(2)···1.45(2)
	$\eta^2:\eta^3:\eta^3$	2.19(1)···2.57(1)	1.40(1)···1.44(2)
	$\eta^2:\eta^3:\eta^3$	2.19(1)···2.57(1)	1.39(1)···1.43(2)
$[Rh_4(CO)_6(C_6H_8)(C_8H_8)]^a$	$\eta^2:\eta^3:\eta^3$	2.14(3)···2.51(3)	1.38(3)···1.46(3)
	$\eta^2:\eta^3:\eta^3$	2.18(3)···2.53(3)	1.37(3)···1.46(3)
$[Ni_3(CO)_3\{(CF_3)_2C_2\}(C_8H_8)]^d$	$\eta^3:\eta^3:\eta^3$	2.067(7)···2.585(8)	1.403(13)···1.426(12)
$\mu_3$ - $C_7H_7$			
$[Co_4(CO)_6(C_7H_9)(C_7H_7)]$ <b>4</b>	$\eta^2:\eta^3:\eta^3$	2.032(4)···2.467(4)	1.404(7)···1.428(6)
$[Co_4(CO)_6(C_5H_5)(C_7H_7)]$ <b>12</b>	$\eta^2:\eta^2:\eta^3$	2.040(3)···2.364(4)	1.388(4)···1.452(6)
$[\{Co_4(CO)_6(C_7H_9)(C_7H_7)\}_2]^{2-}$ <b>14</b>	$\eta^2:\eta^2:\eta^3$	2.031(6)···2.398(7)	1.40(1)···1.43(1)
$[Ru_3(CO)_6(S^tBu)(C_7H_7)]^e$	$\eta^2:\eta^3:\eta^3$	2.082(5)···2.451(5)	1.398(7)···1.434(7)

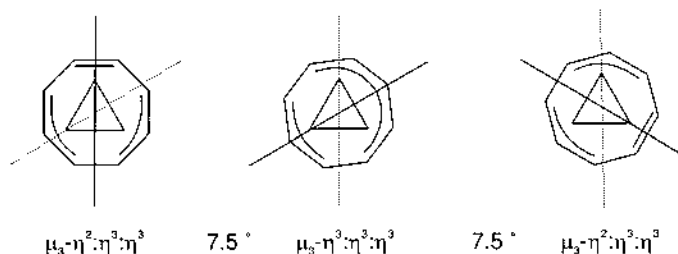
<sup>a</sup> Two independent molecules.

<sup>b</sup> Co and Ni not distinguishable.

<sup>c</sup> Four independent molecules.

<sup>d</sup> Reference 5c.

<sup>e</sup> Reference 5d.



Scheme 5.

expected, their molecular structures are quite similar (Figs. 4 and 9). In both cases, the  $M_3$  frame is greatly stabilised by the face-capping  $C_8H_8$  ligand.

Facial coordination of a  $C_nH_n$  ring to a heterotrimetallic face of a cluster complex is extremely rare. To our knowledge, there is only one other example of such a cluster-ligand interaction, viz.  $\mu_3$ -arene coordination to a  $Ru_2Pt$  face in  $[Ru_6Pt_3(CO)_{18}(\mu_3\text{-}C_6H_5(CH_2)_2Ph)(\mu_3\text{-}H)_4]$  [11].

## 7. Molecular structure and stereochemical nonrigidity

X-ray crystal structure determinations have been carried out on several tri- and tetranuclear  $\mu_3\text{-}C_7H_7$  and  $\mu_3\text{-}C_8H_8$  derivatives. Pertinent geometric parameters are collected in Table 1. Arrangement of a  $C_nH_n$  ring above an  $M_3$  plane is an interesting geometrical problem. For  $n = 6$ , the threefold symmetry of the metal site is matched by the arene ligand ( $C_{3v}$  is a subgroup of  $D_{6h}$ , the point group of free benzene). There are two highly symmetric orientations, with the  $C_6$  ring staggered and eclipsed, respectively, with respect to the  $M_3$  triangle. The ground state always corresponds to the staggered coordination, whereas the eclipsed structure is the transition state of the arene rotation parallel to the  $M_3$  face [12].

There is no such match of symmetry for  $n = 7$  and  $n = 8$ . Hence, the various possible orientations of a planar  $C_7H_7$  or  $C_8H_8$  ring parallel to a  $M_3$  face are not very different from each other. For example, only a  $7.5^\circ$  rotation suffices to transform the  $\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$  coordination of cot into a  $\mu_3\text{-}\eta^3\text{:}\eta^3\text{:}\eta^3$  arrangement (Scheme 5).

The actual bonding mode of the facial  $C_8H_8$  ligands in the crystalline complexes is best described as  $\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$  in most cases (Table 1, Fig. 10). There are only two exceptions, where the coordination is closer to  $\mu_3\text{-}\eta^3\text{:}\eta^3\text{:}\eta^3$  (Table 1). However, it must be stressed that the difference between the two orientations is only small, and the fully symmetrical orientation is rarely observed. In some crystal structures (e.g. of complex **8**) two independent molecules with somewhat different arrangement of the  $\mu_3\text{-}C_8H_8$  rings with respect to the basal plane are present. This is a clear indication of the presence of several energy minima of comparable depth.

A similar situation exists in the complexes with facial  $C_7H_7$  rings. The most highly symmetric orientation,  $\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$ , is found in complex **4**. The two  $\eta^3$ -enyl



systems in the seven-membered ring share a common carbon atom (Fig. 10), while in the  $\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3$  coordinated  $\text{C}_8\text{H}_8$  these are separated by a carbon–carbon bond.

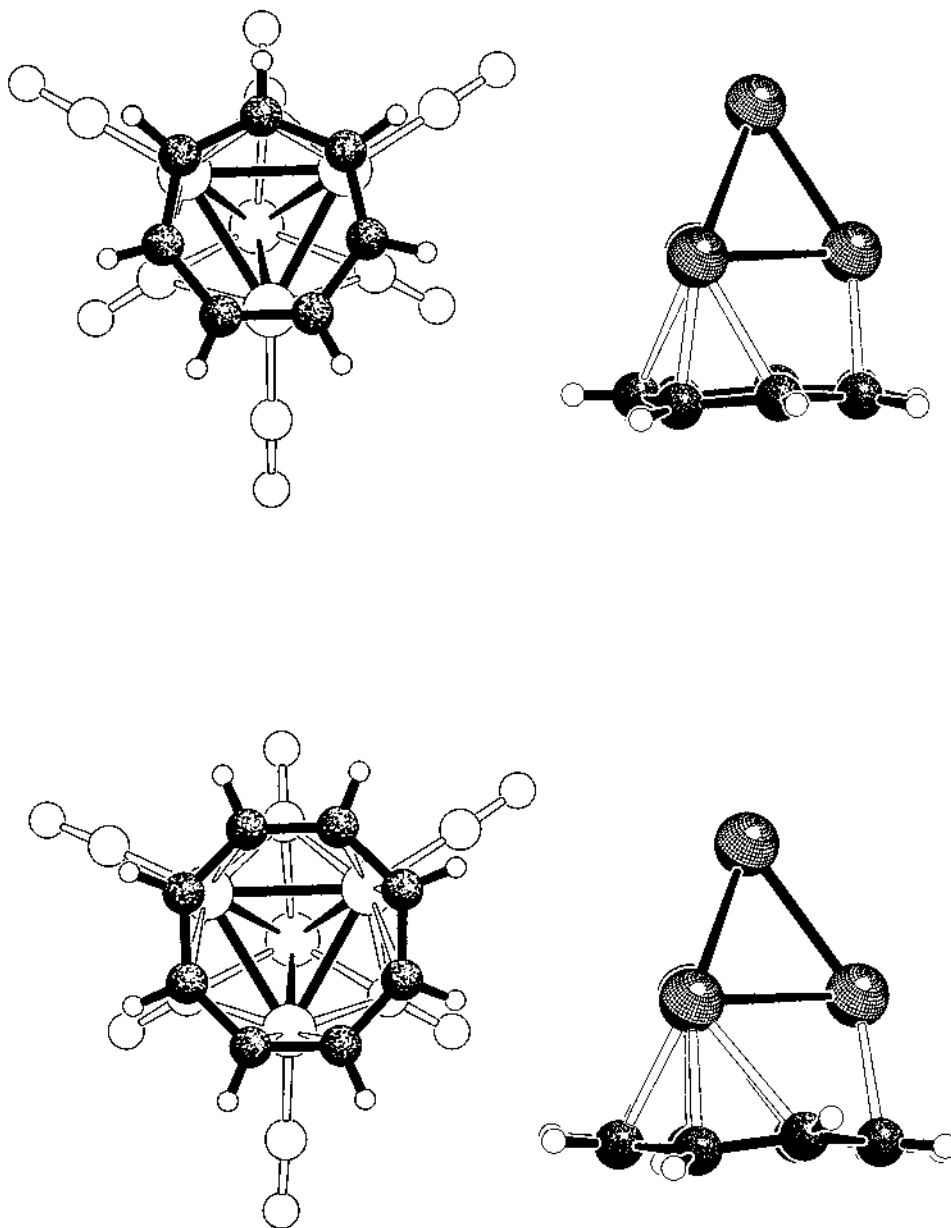


Fig. 10. Projections on and perpendicular to the basal plane of the  $\text{Co}_4$  tetrahedron showing the coordination geometry of the facial  $\text{C}_7\text{H}_7$  and  $\text{C}_8\text{H}_8$  ligands. Top: complex 4; bottom: complex 5. Some of the ligands are omitted for clarity.

As a rule, the facial  $C_7H_7$  and  $C_8H_8$  rings are not planar but slightly puckered towards a chair conformation. The best planes through all ring carbons are however still parallel to the basal  $M_3$  plane. There appears to be no regular pattern of longer and shorter endocyclic carbon–carbon bond lengths around the  $M_3$  rings, in contrast to the  $\mu_3$ -arene derivatives [1,12]. The carbon–carbon distances and endocyclic bond angles are largely leveled (1.40–1.43 Å; 125–130° in the  $\mu_3$ - $C_7H_7$  rings and 132–137° in the  $\mu_3$ - $C_8H_8$  rings, respectively).

Not surprisingly, a very low barrier to rotation exists for the facial  $C_7H_7$  and  $C_8H_8$  ligands in solution. This is evident from the NMR spectra, where only one sharp resonance is observed for these ligands down to 200 K.

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