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(Cyclopentadienyl) metal cluster complexes of the group 9 transition metals

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Abstract

Cluster complexes with metal frameworks built from $[(C_5R_5)(d^9\text{-}M)]$ units are reviewed (d^9-M = Co, Rh, Ir). The range of additional ligands which may be attached to the $[(C_5R_5)M]_n$ cores includes main group atoms such as H, O, S and Se, small inorganic molecules such as CO, CS, NO and NH as well as organic compounds such as isocyanides, alkynes, alkylidynes, arenes and others.

Syntheses, structures and reactivities of the known cluster complexes of this type are discussed. Special emphasis is given to the relationship of structure and chemical properties to the valence electron count in systems of similar composition.

Keywords: Cyclopentadienyl; Group 9 transition metals; Synthesis; Structure; Reactivity

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List of abbreviations

cod	1,4-cyclooctadiene
Cp	cyclopentadienyl
Cp′	methylcylopentadienyl
Cp*	pentamethylcyclopentadienyl
^{R}Cp	methoxycarbonylcyclopentadienyl
CVE	cluster valence electrons
Cy	cyclohexyl
Ind	indenyl
^{n}L	donor ligand L donating *n* electrons to the metal
thf	tetrahydrofuran

1. Introduction

The topic of this review is what, on first glance, seems to be a rather arbitrary selection out of the huge number of molecular transition metal cluster complexes. However, as will become very obvious on closer scrutiny, the cluster complexes to be discussed here are a rather special and unique class. Important issues associated with these complexes range from fundamental reactions such as carbon–carbon and carbon–hydrogen bond scission or CO hydrogenation to quite subtle details of the electronic structure which have a dramatic influence on the physical properties of the solids or in solution.

There are a number of factors which control the occurrence, stability and structural variety of metal cluster complexes. These have been summarized in the excellent book of Mingos and Wales [1]. We shall illustrate a few major points with a comparison of two families of cluster complexes, those with metal frameworks consisting of $[(\eta\text{-}C_5R_5)M]_n$ oligomers and the very large and diverse class of metal carbonyl cluster complexes.

Let us just concentrate on two important factors: the electronic and steric requirements of a cluster complex. Theory [2] and experience [3] tell us that every metal polyhedron of a particular geometry has a certain magic number of cluster valence electrons (CVEs) where it is most stable. This number if made up by the valence electrons (VEs) of the metals and contributions from the ligands.

Metal carbonyl cluster complexes may attain this magic number quite easily by a loss or uptake of an appropriate number of CO ligands. Cluster complexes with an $[(\eta\text{-}C_5R_5)M]_n$ framework are much less flexible. Considerable energy is needed to remove a C_5R_5 ligand from the metal (a total of five metal–carbon bonds have to be cleaved). In such an unlikely case, the corresponding metal site would be naked, hence extremely reactive, and missing a total of five electrons which were lost with the C_5R_5 ligand.

Another important point is the spatial requirements of the ligand shell of the cluster. When the nuclearity of the metal core is increased, the available space per metal atom on the "surface" decreases. Every metal ligand fragment ML_n has a certain spatial requirement, which can be quantified by its cluster cone angle [4]. Generally, because of ligand–ligand repulsions, any given fragment will not be able to oligomerize to give a metal polyhedron which has an ideal cluster cone angle smaller than that of the fragment itself. As can be seen from Table 1, metal carbonyl fragments may adjust to higher nuclearities by losing carbon monoxide, an option that is not open to a cyclopentadienyl metal moiety.

Thus, a cluster complex with an $[(\eta\text{-}C_5R_5)M]_n$ core will have a limiting nuclearity of six, $[(\eta\text{-}C_5H_5)M]_6$ being "sterically saturated". On the contrary, a complex $[(\eta\text{-}C_5H_5)M]_4$ is and may take up additional ligands. For example, $[(C_5H_5)Ni]_6$ (90 CVEs) is known and has an octahedral structure, although there are four electrons in excess of the magic 86 required for the octahedron. In contrast, octahedral metal carbonyl cluster complexes may attain the right electron count by adjusting the number of CO ligands, e.g. $[Co_6(CO)_{16}]$ or $[Ru_6C(CO)_{17}]$. The tetrahedral $[Co_4(CO)_{12}]$ (60 CVEs) is both sterically and electronically saturated. The unsaturated hypothetical complex $[\{(C_5^1H_5)Co\}_4]$ takes up additional ligands to give saturated complexes such as $[\{(C_5H_5)Co\}_4H_4]$ or $[\{(C_5H_5)Co\}_4(CO)_2]$.

Previously we have pointed out a number of factors which make the $[(C_5H_5)(d^9\text{-}M)]$ fragments unique as versatile building blocks for oligonuclear cluster

Table 1
Cluster cone angles (degrees) for some metal ligand fragments [4]

	Tetrahedron	Octahedron	Icosahedron
Ideal	109.5	90	63.9
$(\eta\text{-}C_5H_5)M$ [a]	97	92	82
$(CO)_3M$ [b]	114	108	96
$(CO)_2M$ [b]	68	64	54
$(CO)M$ [b]	36	34	30

$d(M-M) = 2.50$ Å. [a] $d(C-C) = 1.42$ Å, $d(C-H) = 1.08$ Å, $d(M-C) = 2.21$ Å. [b] $d(C-O) = 1.18$ Å; $d(M-C) = 1.82$ Å.

complexes [5]. In addition to the general properties of the $(C_5R_5)M$ fragments discussed above, the advantages of $[(\eta\text{-}C_5R_5)M]$ (M = Co, Rh, Ir) are as follows:

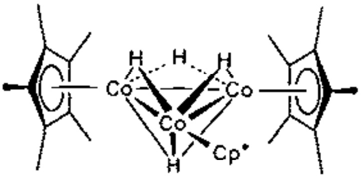
- the number of VEs (14) is neither too far from nor too close to 18;
- the even number of VEs enhances the probability of formation of diamagnetic products;
- the electronic and steric properties of the fragments can be modified to some extent by changing the substituents R;
- convenient-to-handle yet reactive sources are available from which the fragments can be generated.

A search in the Cambridge Structural Database reveals that of the about 250 structurally characterized cluster complexes with a $[(C_5R_5)M]_n$ frame some 100 (about 40%) are built up from the d^9 transition metals. These are the topic of this review. Metallaboranes and -carboranes will not be discussed here. For the sake of comparison, some of the borderline cases, metal-rich metallaboranes [6], which can be described as metal clusters with borane ligands, have been included in the appropriate sections. Also excluded are most "mixed-ligand" or "mixed-metal mixed-ligand" cluster complexes $[\{(C_5R_5)M\}_x(L_nM')_y]$ with cores not exclusively consisting of $[(C_5R_5)(d^9\text{-}M)]_n$ oligomers.

2. Hydrido cluster complexes

The most simple of the cluster complexes with a $[(C_5R_5)(d^9\text{-}M)]_n$ cluster core are some systems which have only hydrides as additional ligands. These are $[(Cp^*Co)_3H_4]$ **1**, $[(CpCo)_4H_4]$ **2** and $[(Cp^*Rh)_4H_4]^{2-}$ **3**. These compounds are good examples of the control of cluster nuclearity by the steric requirements of the $(C_5R_5)M$ fragments. In every case, cluster formation can formally be visualized as the oligomerization of $[(C_5R_5)MH_n]$ fragments. The Cp*Co group, with the largest cone angle, only aggregates to give the trimer. On the contrary, tetramers are obtained with either of CpCo and Cp*Rh, both having smaller cluster cone angles.

The $LiAlH_4$ reduction of $[\{Cp^*Co(\mu\text{-}Cl)\}_2]$ gave the cluster complex **1** and the dinuclear $[(Cp^*Co)_2H_3]$ in equal amounts [7]. The same products, together with



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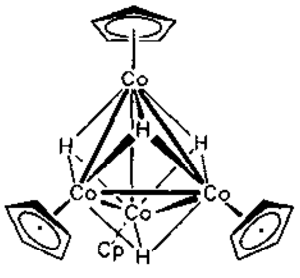

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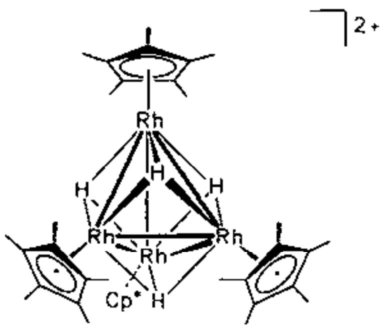

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$[Cp^*Co(\eta^4\text{-}C_5Me_5H)]$ and the tripledecker $[Cp_3^*Co_2]$, were also formed when Co atoms were cocondensed with Cp*H in methylcyclohexane at −120 °C [8,9].

In a crystal structure determination of **1** a nearly isosceles Co_3 triangle was found. The Cp* ligands are not perpendicular to the plane of the metal triangle, but are tilted to one face. This was attributed to the stereochemical influence of the hydrido ligands, which were not located in the X-ray study. From the spatial arrangement of the Cp* ligands one face-capping μ_3- and three edge-bridging μ_2-hydrides were assumed [7]. **1** is paramagnetic, electronically unsaturated and therefore very reactive. The very interesting chemistry of this complex is being extensively studied. Some published results will be discussed in other sections of this review (with CO, Section 3.2; with isocyanides, Section 5.1; with acetylene, Section 5.4.2).

In the presence of $AlCl_3$ the bridging NO ligands in $[\{CpCo(\mu\text{-}NO)\}_2]$ are reduced by $LiAlH_4$ to N_2, and the tetranuclear hydrido cluster complex **2** can be isolated after hydrolysis [10]. A tetrahedral core with four face-capping hydrido ligands was predicted for **2** [10] and later confirmed by an X-ray crystal structure analysis. Together with the vertices of the only slightly distorted Co_4 tetrahedron, the four hydrides form a cubane-like arrangement (Fig. 1) [11].

When dihydrogen is bubbled through an aqueous solution of the hydroxo-bridged dimer $[(Cp^*Rh)_2(\mu_2\text{-}OH)_3]^+$ **4** at 90 °C, the cluster cation **3** is formed and can be isolated as Cl^-, PF_6^-, BF_4^- or $PtCl_4^{2-}$ salts [12]. As apparent from the colour change (yellow–orange to deep red to dark green) the reaction proceeds via a trinuclear intermediate $[H_3(Cp^*Rh)_3(\mu_3\text{-}O)]^+$ **5** (see Section 7), which could be precipitated by adding KPF_6 to the red solution [13].

In the crystal, **3** $(BF_4)_2$ has a distorted Rh_4 tetrahedron with two shorter (2.655(1) Å) and four longer (2.829(1) Å) Rh–Rh bonds. The hydrido ligands were not located in the initial X-ray study; it was suggested that they bridge the four longer RhRh edges [12]. A neutron diffraction study, however, showed that the hydrides are in fact bridging the four Rh_3 faces [14]. Analysis of the ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra in solution showed that the Rh_4 tetrahedron must be symmetrical on the NMR time scale and that the hydrides do not take part in any major fluxional process [12,14].

The electronic structure of several cluster complexes $[(CpM)_4H_n]$ was studied

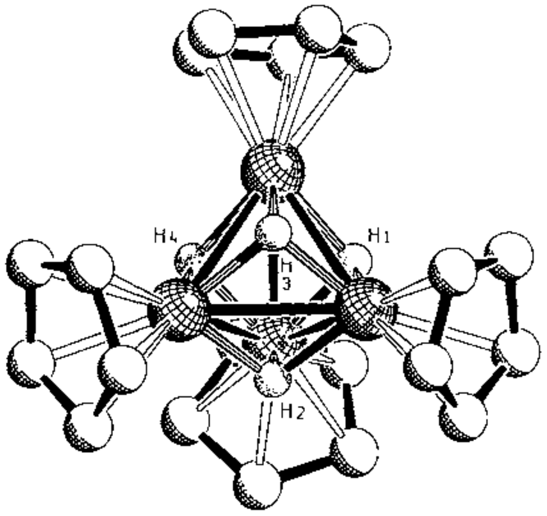


Fig. 1. Molecular structure of [$(CpCo)_4H_4$] **2**.

using the extended Hückel molecular orbital (MO) method [15]. **2** is a saturated 60 VE system with a set of three nearly degenerate orbitals as uppermost filled levels. A large preference for μ_3- over μ_2-hydride ligands was calculated for $[(CpFe)_4H_4]^{4-}$, which is isoelectronic to **2**. Part of the stabilization of the μ_3 sites was traced to an interaction with low-lying, occupied M_4 orbitals of (pseudo) t_2 symmetry. This argument should also be applicable to the electron-deficient complex **3** (58 VEs).

With a tetrahedral metal framework, **3**, which has two electrons less than **2** in the near-degenerate highest occupied MOs (HOMOs), should be paramagnetic. The observed diamagnetism can be explained by a Jahn–Teller distortion, which is indeed observed in the solid state structure.

3. $[C_5R_5)M]_n$ carbonyl cluster complexes

There are two different types of trinuclear $[(C_5R_5)(d^9\text{-}M)]_3$ carbonyl cluster complexes, namley $[\{(C_5R_5)M\}_3(CO)_3]$ and $[\{(C_5R_5)M\}_3(CO)_2]$. A few tetranuclear derivatives $[\{(C_5R_5)M\}_4(CO)_2]$ (M = Co, Rh) have also been reported. One hexanuclear cluster complex, $[(CpRh)_6(CO)_2]^{2+}$, was postulated, but little evidence for the existence and/or even structure of this compound was given [16].

3.1. *The cluster complexes* $[\{(C_5R_5)M\}_3(CO)_3]$

A number of oligonuclear complexes $[(CpM)_n(CO)_m]$ (n = 2, 3, 4) are formed when solutions of $[CpM(CO)_2]$ **6a** (M = Co) and **7a** (M = Rh) are irradiated with UV light [17,18]. In the first report on the cobalt system, only a very small yield of the trinuclear cluster complex $[(CpCo)_3(CO)_3]$ **8a** was isolated. Two fractions of this material were obtained; on the basis of the IR spectra the presence of two isomers was suggested [17]. Under conditions only slightly different from the original procedure, the μ_3-oxo complex $[(CpCo)_3(\mu_3\text{-}O)(\mu_3\text{-}CO)]$ **9a** was obtained in similarly low yield (see Section 4.2) [19].

Photolysis of **7a** gave $[\{CpRh(CO)\}_2(\mu\text{-}CO)]$ **10** [20] and two isomers of $[(CpRh)_3(CO)_3]$ **11A** and **11B** [18]. A mixture of these complexes and the tetranuclear $[(CpRh)_4(CO)_2]$ **12** is obtained when **7a** is heated in solution with addition of Me_3NO [21,22].

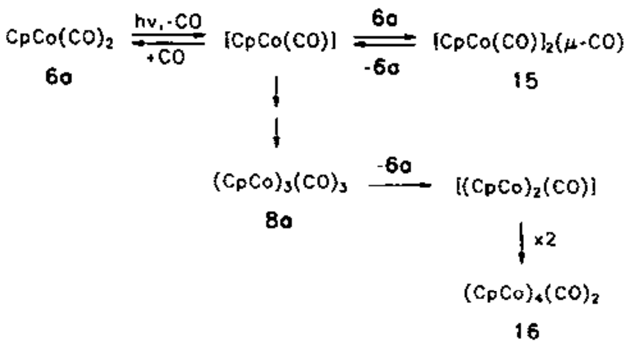
The triiridium cluster complex $[(CpIr)_3(CO)_3]$ **13** is the major decomposition product of the carbonyl hydride $[CpIr(CO)(H)_2]$ **14** in polar solvents. The minor reaction products were identified as $[(CpIr)_4(CO)_x]$ cluster complexes [23].

A mechanism for the photoreactions was proposed (Scheme 1) [24]. As the key intermediate the coordinatively unsaturated mononuclear $[CpM(CO)]$ [25] was postulated. This intermediate could recombine with CO, "trimerize" to $[CpM(CO)]_3$, or react with the starting material to give the dinuclear $[\{CpM(CO)\}_2(\mu\text{-}CO)]$ **15** (M = Co) [24] and **10** (M = Rh) [20] as the primary photoproducts. **15** was shown to be thermally unstable, releasing a molecule of **6a** and forming the trinuclear **8a**. **8a** is also unstable and decomposes around 130 °C with extrusion of **6a** to form the tetranuclear $[(CpCo)_4(CO)_2]$ **16** (see below) [24].

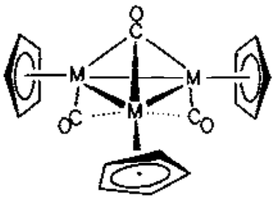
In these reactions, the direct trimerization of $[CpCo(CO)]$ seems unlikely, owing to its low concentration and high reactivity. The unsaturated dinuclear $[(CpCo)_2(\mu\text{-}CO)_2]$ **17a** is probably involved as an intermediate. The formation of **13** was suggested to involve trimerization of a "lightly stabilized" species $[CpIr(CO)\cdot\text{solvent}]$, which is formed by loss of H_2 from **14** in the coordinating solvent [23].

The Rh–Rh bond in **10** can also be activated by protonation to given the μ-hydrido cation $[\{CpRh(CO)\}_2(\mu\text{-}H)(\mu\text{-}CO)]^+$, which at room temperature slowly converts into a mixture of **11A** and $[CpRh(CO)_2]$ **7a** [26].

Several suggestions for the structure of **8a**, especially with respect to the positions (terminal, μ_2, μ_3) of the CO ligands were made, solely based on the IR spectra [17,24]. The problem was resolved for the crystalline solid by a structure analysis [27], which showed one triply bridging and two semibridging carbonyl ligands (**A**)



Scheme 1.



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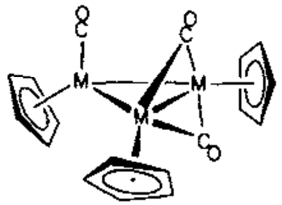

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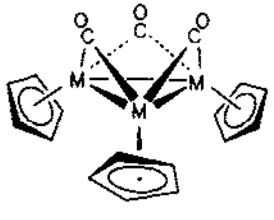

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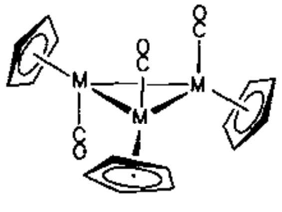


D

(Fig. 2, Table 2). Essentially the same structure was found for crystalline $[(Cp'Co)_3(CO)_3]$ **8b**, which was prepared by photolysis of $[Cp'Co(CO)_2]$ **6b** [27].

However, the IR spectra of **8a** and **8b** in solutions are very different from the solid state spectra, and they vary markedly from one solvent to another. In benzene, structure **B** seems to be present exclusively. In thf and chloroform, structure **B** is probably also present, but accompanied by one or more further isomers [27,35]. Apparently, the placement of the CO ligands on the $[(C_5R_5)Co]_3$ cluster is quite

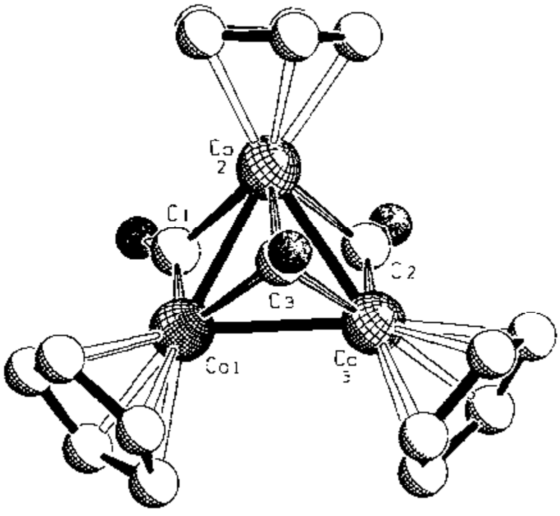


Fig. 2. Molecular structure of $[(CpCo)_3(CO)_3]$ **8a**.

Table 2
Structural data for some complexes of the type $[\{(C_5R_5)M\}_3(CO)_3]$

	$[(C_5R_5)M]_3$	Structure[a]		*d*(M−M)[b] (Å)	Ref.
		Solution	Crystal		
8a	$(CpCo)_3$	B[c]	A	2.438(1)[d], 2.457(1)[d], 2.519(1)	[27]
8b	$(Cp'Co)_3$	B[c]	A[e]	2.442(4)[d], 2.435(4)[d], 2.511(4) 2.416(4)[d], 2.447(4)[d], 2.498(4)	[27]
8c	$(CpCo)_2(Cp^*Co)$	A			[28]
8d	$(CpCo)(Cp^*Co)_2$	A			[28]
8e	$(Cp'Co)(Cp^*Co)_2$	A	A	2.444[d], 2.451[d], 2.566	[29]
11A	$(CpRh)_3$	C	C	2.617(3)[f], 2.622(3)[f]	[18a]
11A	$(CpRh)_3 \cdot$ acetone		C	2.6195[f]	[30]
11B	$(CpRh)_3$	B	B	2.620(2)[g], 2.663(2), 2.705(2)	[18b]
23	$(Cp^*Rh)_3$	A	A	2.675(1)[f], 2.678(1)[f], 2.792(1)	[31]
26	$(IndRh)_3$	C			[32]
	$(Cp^*Rh)(CpCo)_2$	A			[28]
	$(Cp^*Rh)_2(CpCo)$	A			[28]
13	$(CpIr)_3$	D	D	2.6693(7), 2.6697(6), 2.6876(6)	[23]
11	$(IndIr)_3$	C	C	2.6745(7)[f], 2.6757(7)[f], 2.6650(6)[f]	[141]
	$(IndIr)(IndRh)_2$	C			[141]
	$(IndIr)_2(IndRh)$	C			[141]
27A	$(Cp^*Ir)(CpCo)_2$	C	C	2.429(1)[d], 2.547(1)[f], 2.530(1)[f]	[33]
27B	$(Cp^*Ir)(CpCo)_2$	B[h]			[34]

[a] See text. [b] From X-ray crystallography. [c] Other isomers possible, dependent on the solvent (see text). [d] $Co(\mu_2\text{-}CO)Co$. [e] Two independent molecules. [f] $M(\mu_2\text{-}CO)M$. [g] $M(\mu_2\text{-}CO)_2M$. [h] $Co(\mu_2\text{-}CO)_2Co$.

sensitive to small changes in the environment of the molecule. Such extremely deformable molecules have been called "fictile" [35], but this term has not become general usage.

Interestingly, the slightly different packing forces in the crystals of **8b** did not impose a different structure as compared with **8a**. $[(Cp'Co)(Cp^*Co)_2(CO)_3]$ **8e**, prepared from $[(Cp^*Co)_2(CO)_2]$ **17d** and $[Cp'Co(CO)_2]$ **6b**, also has a solid state structure very close to that of **8a** and **8b** (Table 2). One μ_2-CO bridge is between the two Cp*Co groups and the other is between a Cp*Co and the Cp'Co group. However, as indicated by the IR and NMR data, structure **A** is also retained in solution. Therefore **8e** does not appear to be fictile [29].

The solid state molecular structure of the trirhodium tricarbonyl derivative $[(CpRh)_3(CO)_3]$ **11** was established soon after its discovery, using X-ray diffraction. The complex is obtained in two different crystalline forms **11A** and **11B**. The main product **11A** has a symmetric structure with the three CO ligands bridging the edges of an equilateral Rh_3 triangle (approximate molecular C_{3v} symmetry; Fig. 3, Table 2). The Cp ligands are all displaced to one face of the metal triangle, while the CO bridges are shifted to the other (structure **C**) [18a]. In the minor isomer **11B** one RhRh edge is bridged by two carbonyl ligands, the third CO ligand is terminally attached to the third rhodium atom (approximate C_s molecular symmetry.

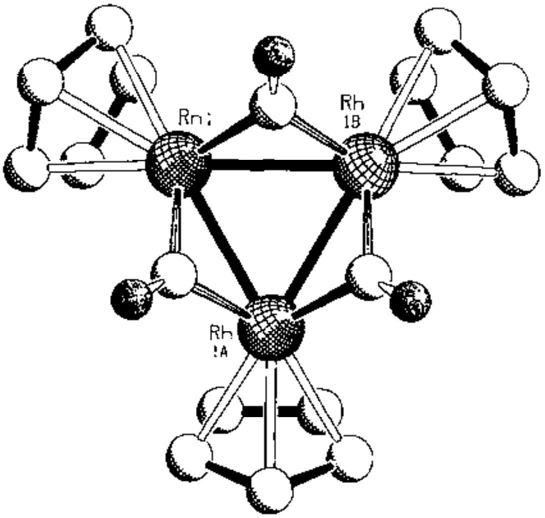


Fig. 3. Molecular structure of C_{3v}-[(CpRh)$_3$(CO)$_3$] **11A**.

structure **B**, Fig. 4). The Rh–Rh distances in this isomer are markedly different, the shortest being that bridged by the two CO ligands (Table 2) [18b].

The C_{3v} isomer **11A** can be more conveniently prepared by the above-mentioned oxidative decarbonylation of [CpRh(CO)$_2$] **7a** with Me_3NO. **11A** can be transformed into **11B** in high yield by UV irradiation [22]. The pentamethylcyclopentadienyl trirhodium cluster complex [(Cp*Rh)$_3$(CO)$_3$] **23** is formed in a similar way from [Cp*Rh(CO)$_2$] **7b**. However, in this case the main product is the dinuclear

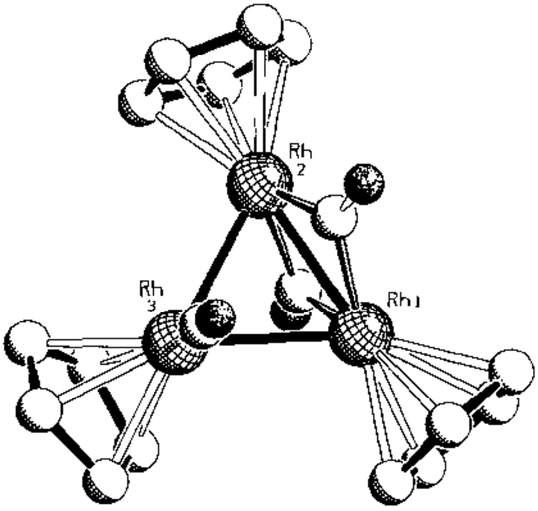


Fig. 4. Molecular structure of C_s-[(CpRh)$_3$(CO)$_3$] **11B**.

$[\{Cp^*Rh(CO)\}_2]$ **20d** [36]. **23** is only isolated in very small yield, together with some $[(Cp^*Rh)_3(\mu\text{-}CO)(\mu_3\text{-}O)]$ **24** [31]. In the solid, **23** attains structure **A**. Again, the Rh–Rh bonds, which are bridged by the μ_2-CO ligands, are the shortest in the molecule (Table 2). Structure **A** is retained in solution [31].

When treated with $PdCl_2$ or $PtCl_2$ in acetone, $[\{CpRh(CO)\}_2(\mu_2\text{-}CO)]$ **10** is nearly quantitatively transformed into **11A**, which crystallized as an acetone solvate. The structure of **11A** in this solvate is equal within experimental error to that of the acetone-free complex [30]. With $SnCl_2$, **10** reacts to give the complex $[\{CpRh(CO)(SnCl_2)\}]_3$ **25**. An Rh_3Sn_3 metallacyclic structure was assigned to **25** on the basis of analytical and spectroscopic data [30]. No Rh–Rh bonds are expected to be present in **25**.

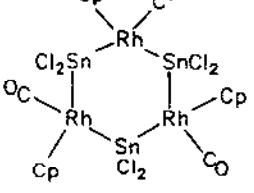
In marked contrast to $[CpRh(CO)_2]$ **7a** the indenyl derivative **7c** is readily transformed into $[(IndRh)_3(CO)_3]$ **26** when heated in heptane solution [32]. This behaviour is in line with the generally much greater lability of the ligands in indenyl complexes as compared with the cyclopentadienyl analogues. The IR spectrum of **26** indicates only μ_2-bridging CO ligands; thus a C_{3v} structure (**C**) can be assumed.

A structure with only terminal CO ligands, **D** is attained by the triiridium derivative **13**. An X-ray crystal structure analysis showed the CO ligands to be nearly perpendicular to the metal triangle (Fig. 5). Two CO groups and one Cp group are on one side and two Cp groups and one CO group are on the other side of the Ir_3 plane [23].

The heterotrinuclear cluster complex $[(Cp^*Ir)(CpCo)_2(CO)_3]$ **27A** was obtained as a side product from the reaction of $[Cp^*Ir(CO)_2]$ **28b** with $[CpCo(C_2H_4)_2]$ **29a** [33,37]. Although the mechanism of formation of **27** has not been investigated, it appears that the main product of this reaction, the dinuclear $[Cp^*Ir(\mu_2\text{-}CO)_2CoCp]$ **19b**, and probably $[(CpCo)_2(Cp^*Ir)(CO)_2]$ **43** (see below) are intermediates. **27A** belongs to the structural type **C** with all-*cis* edge-bridging CO ligands. This structure was established for the solid by an X-ray diffraction study; IR data indicate that it is retained in solution as well [33].

A second isomer **27B** is formed by carbon monoxide addition to the unsaturated cluster complex $[(CpCo)_2(Cp^*Ir)(CO)_2]$ **43** at room temperature. ^1H NMR and IR data support the structure **B** for **27B**, with the μ_2-ligands both bridging the Co–Co bond [34].

The intra- and intermolecular bonding of the cluster complexes $[\{(C_5R_5)M\}_n\text{-}\{(C'_5R_5)M\}'_{3-n}(CO)_3](M=Co,Rh,Ir;\ n=0\text{–}3)$ in the crystalline state has recently been examined in detail [142].



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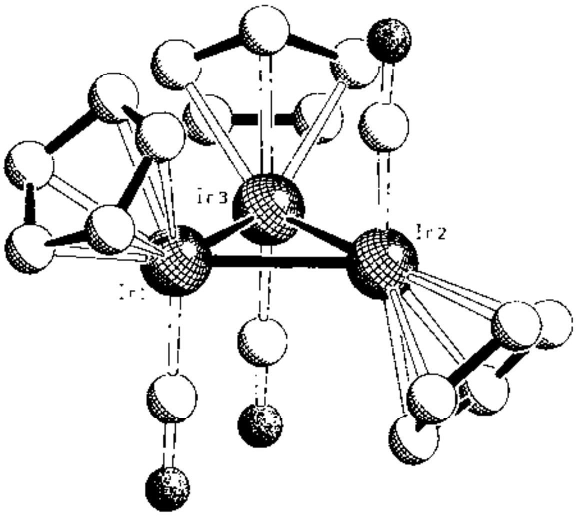
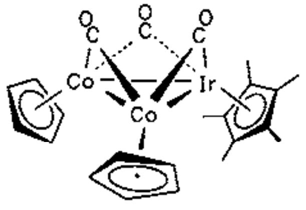
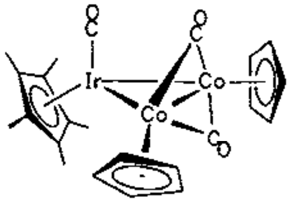


Fig. 5. Molecular structure of $[(CpIr)_3(CO)_3]$ **13**.



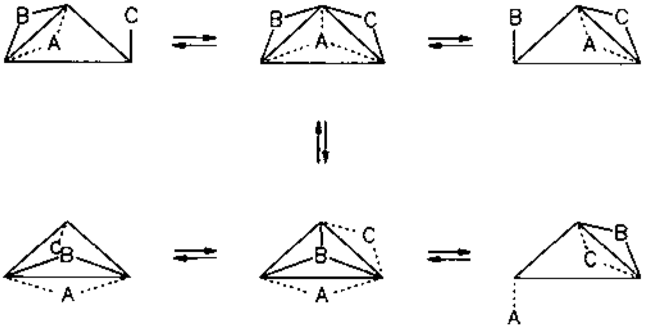
27A



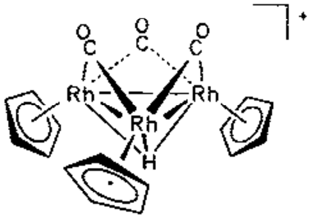
27B

The fluxional properties of both **11A** and **11B** were studied in solution [21,22]. Both were found to have the same structures in solution as in the solid state. As apparent from the quartet multiplicity of the ^{13}CO resonance, **11A** undergoes complete scrambling of the CO ligands over the Rh_3 framework at 26°C. At −65°C, the C_{3v} structure is frozen on the NMR timescale [21]. **11B** has considerably lower energy barriers to carbonyl migration. The ^{13}C NMR spectrum at −120°C (two quartets in a 2:1 intensity ratio) is consistent with a pairwise bridge opening and closing mechanism, which equilibrates the CpRh groups but not all the CO ligands [22]. At 25°C all carbonyls become equilibrated. A mechanism was proposed which accounts for the CO scrambling as well as the fact that **11A** and **11B** do not readily interconvert (Scheme 2). The key intermediate with one face- and two edge-bridging carbonyls (cf. structure **A**, analogous to the solid state structure of **8a**) was, however, not detectable by IR spectroscopy.

The observation of a triplet ($J(RhC) = 50.4$ Hz) for the carbonyl ligands in the room temperature ^{13}C NMR spectrum of **26** is consistent with a static C_{3v} structure of this complex. Thus, there is an interesting difference in activation energy for the



Scheme 2.



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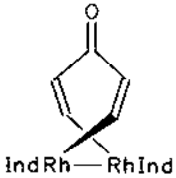


31

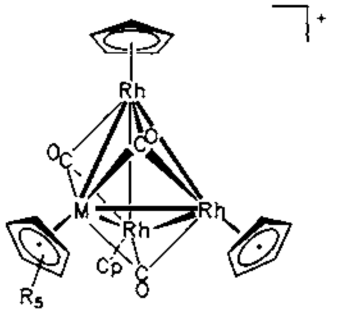
carbonyl site exchange process for the cyclopentadienyl (**11A**) and indenyl (**26**) derivatives [39].

At −50 °C, the triiridium derivative **13** is rigid in solution on the NMR time scale (structure **D**) [23].

The chemistry of the cluster complexes $[\{(C_5R_5)M(CO)\}_3]$ (M = Co, Rh) appears to be largely unexplored. The metal framework of both isomers of **11** is protonated by CF_3SO_3H. A very stable salt containing the hydrido cation $[(\mu_3\text{-}H)(CpRh)_3(\mu\text{-}CO)_3]^+$ **30** is formed in quantitative yield [38]. The indenyl complex **26** is cleaved by ethylene under forcing conditions (80 °C, 2 bar) to give the mononuclear $[IndRh(CO)(C_2H_4)]$, which in solution at room temperature gradually re-forms the cluster complex **26** [39]. With acetylene, **26** forms the dinuclear **31** with a fly-over type bridging pentadien-3-on-1,5-diyl ligand [39].

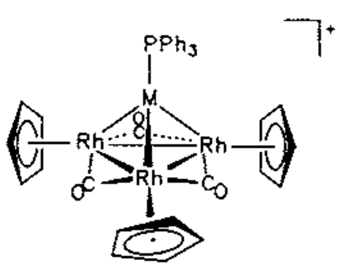
Several metal ligand fragments $[ML_n]^+$ containing 12 VEs add to **11** to give the tetranuclear cluster complexes **32**–**36**. μ_3-CO ligands were proposed for **32** and **33** on the basis of IR data. This was confirmed by an X-ray crystal structure analysis of **33b** [16]. With $[M(MeCN)_4]^+$ (M = Cu, Ag) the heptanuclear cluster complexes **37**, **38** with structures consisting of two tetrahedra sharing a common vertex (M) are obtained [40]. IR data suggest only μ_2-CO ligands for **34**–**38** [40]; crystal structures are not available.

Based on frontier orbital arguments, the reactions with $[(C_5R_5)M]^+$ (M = Fe, Ru) and the similar sizes of the Rh_3 and $(CH)_6$ cycles, it was proposed that **11A** should be isolobal to benzene [40]. For example, the arene in $[CpFe(arene)]^+$ (arene = C_6H_6, $C_6H_5NO_2$, $p\text{-}C_6H_4Me_2$) is substituted by the $[\{CpRh(CO)\}_3]$ moiety on



32, M = Fe a, R = H b, R = Me

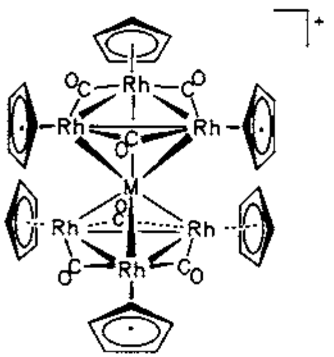
33, M = Ru; a, R = H; b, R = Me



34, M = Cu

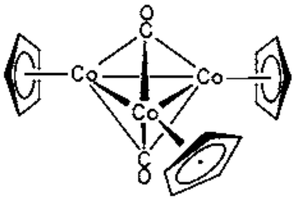
35, M = Ag

36, M = Au



37, M = Cu

38, M = Ag

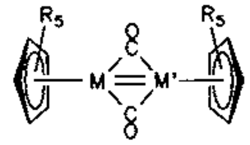


40a

treatment with **11A** to give **32a**. This reaction is reversible when **32a** is refluxed in an arene [16].

3.2. *The cluster complexes [{(C_5R_5)M}$_3$(CO)$_2$]*

The chemistry of a rather large class of cluster complexes with the general formula [{(C_5R_5)M}$_2${(C_5R_5)M}'(CO)$_2$] has been developed only fairly recently. Some of these complexes are formed in very small amounts during the photolysis of [Cp*Co(CO)$_2$] **6c** or a mixture of [{Cp*M(CO)}$_2$] **17d** (M = Co) and **20d** (M = Rh) [41]. A far better synthesis is by addition of the fragments [(C_5R_5)M], generated from the ethylene complexes [(C_5R_5)M(C_2H_4)$_2$] **29** (M = Co), **39** (M = Rh) to the unsaturated dinuclear [{(C_5R_5)M}{(C_5R_5)M}'(μ-CO)$_2$] **17**–**22** [28,33,34,42–46]. With this method, a large number of derivatives has been prepared (Table 3). A shorthand notion will be used for [{(C_5R_5)M}$_2${($C_5R'_5$)M'}(CO)$_2$], i.e. [M_2M'] for



	M	R	M'	R'
17a	Co	H	Co	H
17d	Co	Me	Co	Me
18d	Co	Me	Rh	Me
19b	Co	H	Ir	Me
c	Co	Me	Ir	H
d	Co	Me	Ir	Me
20d	Rh	Me	Rh	Me
21d	Rh	Me	Ir	Me
22d	Ir	Me	Ir	Me

Table 3
Syntheses and magnetic data for the complexes $[\{(C_5R_5)M\}_2\{(C_5R_5)M\}'(\mu_3\text{-}CO)_2]$

	R,M	(R,M)'	Synthetic method^{a}	Magnetism^{b}	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	Ref.
40a	H,Co	H,Co	Co=Co + Co; Co + 2Co	T			[43]
40b	H,Co	Me,Co	Co* + 2Co	S−T^{c}	10.56(5)^{c}	35(4)^{c}	[44]
40c	Me,Co	H,Co	Co*=Co* + Co	S−T^{c,d}			[44]
40d	Me,Co	Me,Co	Co*=Co* + Co; *hν*	S−T^{c}	18^{c}	50^{c}	[41,42]
41	Me,Rh	Me,Rh	Rh*=Rh* + Rh; Rh*=Rh* + Co*=Co*; *hν*	—^{e}			[41,45]
42a	H,Co	Me,Rh	Rh* + 2Co	S−T^{c}	20(2)^{c,f}	45(10)^{c,f}	[44]
43	H,Co	Me,Ir	Ir*=Co + Co; Ir* + 2Co	S−T^{c,d}			[34,44]
42b	Me,Co	Me,Rh	Co*=Rh* + Co*	—^{e}			[42]
44a	Me,Rh	H,Co	Rh*=Rh* + Co	S−T^{c}	8.2(1)^{c}	34(1)^{c}	[44]
44b	Me,Rh	Me,Co	Rh*=Rh* + Co*	—^{e}			[45]
45	Me,Ir	H,Co	Ir*=Ir* + Co	S−T^{c}			[44]
46	Me,Rh	Me,Ir	Rh*=Ir* + Rh*	—^{e}			[42]

[a] M = M', $[(C_5R_5)M\{(C_5R_5)M\}'(CO)_2]$; M, $[(C_5R_5)M(L)_2]$ (L = C_2H_4, CO); *hν*: photolysis of $[(C_5R_5)M(CO)_2]$; * denotes R = Me. [b] S, singlet; T, triplet; S−T, S ground state in solution in equilibrium with T isomer. [c] From solution NMR. [d] Solid state susceptibility measurement. [e] Diamagnetic from solution NMR at ambient temperature. [f] Different values were obtained from the Cp and Cp* resonances; given here is the average.

R = R′ = H, $[M_2^*M']$ for R = Me, R′ = H, $[M_2M'^*]$ for R = H, R′ = Me and $[M_2^*M'^*]$ for R = R′ = Me; cf. Table 3.

The two carbonyl ligands in these complexes are always in bridging positions. Two types of structures **E** and **F** are found in the solid state (Table 4). M_3 face-capping CO ligands (**E**) are only present in a few cases (Fig. 6). The alternative structure **F**, which is adopted by the majority of **40**–**46**, has semitriply bridging carbonyl groups (Fig. 7). This situation can be described using the angle Θ between

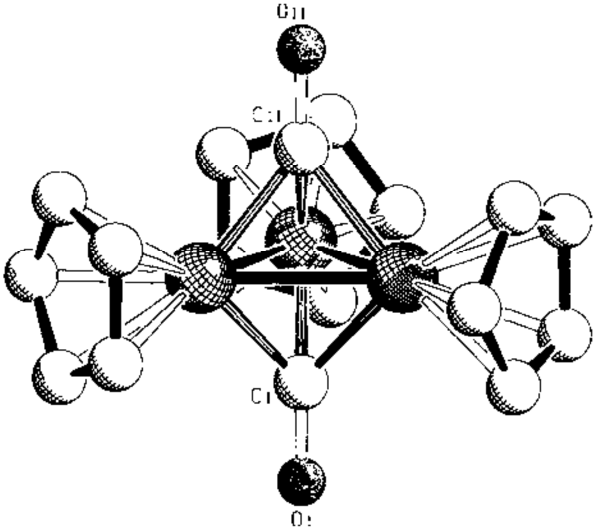


Fig. 6. Molecular structure of $[(CpCo)_3(CO)_2]$ **40a**.

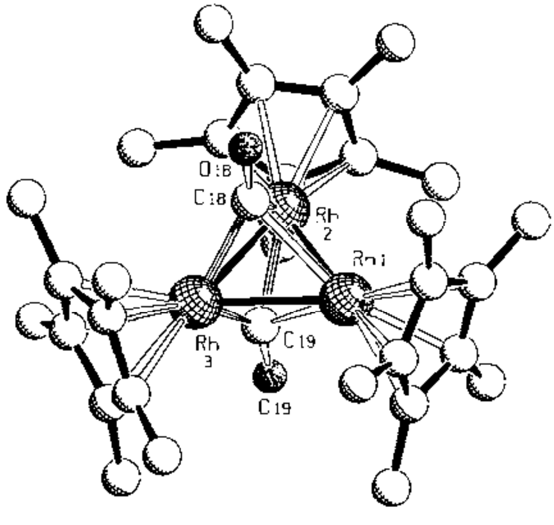
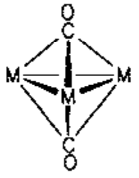
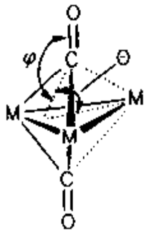


Fig. 7. Molecular structure of $[(Cp^*Rh)_3(CO)_2]$ **41**.



E



F

the M_3 and MC(O)M planes; a smaller Θ indicates a more μ_3-like carbonyl. With decreasing Θ, the carbonyl oxygen is also displaced from the MCM plane, away from the unique metal ($\varphi < 180°$). The very strongly distorted $[\mathrm{Ir}_2^*\mathrm{Co}]$ **45** is best described with two μ_2-CO ligands (Table 4).

In **F** the trimetal core may be formally divided into a dinuclear fragment with strong CO bridges and a mononuclear $(C_5R_5)M$ group. The dinuclear fragment is not necessarily identical with the dinuclear precursor from which it was actually prepared. There is strong bonding between the M_2 and M_1 units, as indicated by the short metal–metal bonds between these units. However, the M—M distance in the M_2 unit is lengthened as compared with the dinuclear precursor. The latter is also true for $[\mathrm{Co}_3]$ **40a** and $[\mathrm{Co}_2\mathrm{Co}^*]$ **40b** with μ_3-CO ligands (type **E**). In $[\mathrm{CoRh}_2^*]$ **44a** there is no noticeable difference (Table 4).

40–**46** have diamagnetic ground states. However, frequently there are thermally accessible equilibria between a singlet and a triplet isomer. In some cases thermodynamic data for these equilibria have been obtained from the analysis of the temperature-dependent NMR spectra (Table 3).

The unsaturated nature of **40**–**46** is seen in the reactions with two-electron donors. Many of the complexes react very readily with carbon monoxide to give the saturated tricarbonyl adducts [28,44].

The $[\mathrm{Rh}_3^*]$ complex **41** readily adds molecular hydrogen at ambient temperature and pressure. The resulting dihydride $[(\mathrm{Cp^*Rh})_3(\mu_3\text{-CO})(\mu_2\text{-CO})(\mu_2\text{-H})_2]$ **47** was characterized by an X-ray structure analysis. A structure with one face-bridging CO is attained. The other CO and the two hydrido ligands bridge the shorter and the two longer edges respectively of the isosceles Rh_3 triangle [42,46]. Reaction of H_2 with the heteronuclear derivatives $[\mathrm{Co^*Rh}_2^*]$ **44b** and $[\mathrm{Rh}_2^*\mathrm{Ir}^*]$ **46** gave a mixture of the corresponding isomeric dihydrides **48a,b** and **49a,b** respectively. On warming the solutions, hydrogen is evolved and **44b** and **46** are regenerated [42].

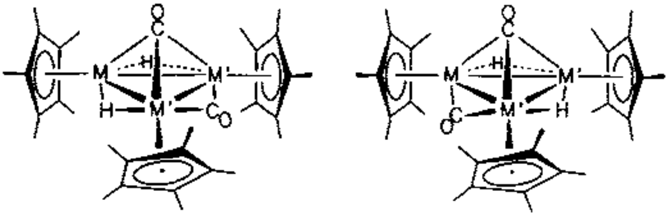
In contrast, the $[\mathrm{Co}_3^*]$ derivative **40d** was reported to be inert with respect to CO and H_2 [41]. The corresponding dicarbonyldihydride **50** can, however, be obtained from $[(\mathrm{Cp^*Co})_3\mathrm{H}_4]$ **1** and carbon monoxide [47]. With an excess of CO (1 bar, room temperature), **50** is smoothly transformed into the mononuclear $[\mathrm{Cp^*Co(CO)}_2]$ **6c**. On heating to 80 °C in a sealed tube, **50** loses H_2, and **40d** is formed [47].

Using electrochemical techniques, **40d** could only be reduced to a monoanion at a rather negative potential (−1.13 V vs. saturated calomel electrode (SCE)) [41]. This can be taken as an indication that the lack of reactivity with donor ligands is

Table 4
Structural data for the complexes $[\{(C_5R_5)M\}_2\{(C_5R_5)M\}'(\mu_3\text{-}CO)_2]$

R,M	(R,M)′	Bridge type[a]	Θ [b,c] (deg)	d(M−M) (Å)	d(M−M′) (Å)	d[M−(C)O] [c] (Å)	d[M′−C(O)] [c] (Å)	Δd(M−M) [d] (Å)	Ref.
H,Co	H,Co	E (CoCoCo)	64	2.390(1)	2.390(1)	1.973(4)	1.973(1)	+0.068	[43]
H,Co	Me,Co	F (CoCo)	77	2.405(1) [e]	2.305(1)	1.884(3)	2.160(3)	+0.083	[44]
Me,Co	H,Co	F (CoCo)	74	2.373(3) [e]	2.335(2)	1.89(1)	2.14(2)	+0.035	[44]
Me,Co	Me,Co	E (CoCoCo)	69	2.370(1)	2.370(1)	1.951(6)	1.951(6)	+0.032	[41]
Me,Rh	Me,Rh	F (RhRh)	77	2.639(2) [e]	2.572(2), 2.553(2)	1.99(2)	2.35(2)	+0.075	[42][f]
H,Co	Me,Rh	F (CoCo)	81	2.426(1) [e]	2.433(1), 2.431(1)	1.88	2.32	+0.104	[44]
H,Co	Me,Ir	F (CoIr)	85	2.359(1)	2.527(1) [e], 2.473(1)	1.90, 2.41	1.96	+0.067	[34]
Me,Rh	H,Co	E (RhRhCo)	60	2.560(1)	2.469(2)	2.12(1)	1.93(1)	−0.004	[44]
Me,Ir	H,Co[g]	μ_2 (IrIr)	84	2.658(2) [e]	2.132(4), 2.480(5)	2.02	2.44	+0.108	[44]
	—[g]	μ_2 (IrIr)	84	2.634(2) [e]	2.475(4)	1.98	2.43	+0.084	[44]
Me,Rh	Me,Ir	F (RhIr)	—[h]	2.589(1)	2.632(1) [e], 2.608(1)	2.05, 2.19	2.03	—[h]	[33]

[a] μ_2, edge-bridging CO; F, semi(face bridging) CO; E, face bridging. [b] See text. [c] Averaged if several equivalent values; given in parentheses is the standard deviation of the individual values. [d] Difference in bond length between the CO-bridged M−M bond in the complexes listed here and the free dinuclear complex corresponding to this fragment within each particular trinuclear complex. [e] CO bridged. [f] Ordered structure (at 200 K); a disordered structure at room temperature has also been reported (Ref. [41]). [g] Two independent molecules. [h] Data not available.



47, M = M' = Rh

48a, M = Co, M' = Rh **48b**, M = Co, M' = Rh

49a, M = Ir, M' = Rh **49b**, M = Ir, M' = Rh

50, M = M' = Co

not caused by purely kinetic factors, which should arise from the shielding of the metal core by the Cp* ligands.

Reaction of $[\{(C_5R_5)M\}_n\{(C_5H_5)Co\}_m(CO)_2]$ ($n = 0$–2, $n + m = 3$, M = Co, Rh, Ir) with ethylene causes fragmentation to $[CpCo(C_2H_4)_2]$ **29a** and the corresponding dinuclear species $[\{(C_5R_5)M\}(\mu\text{-}CO)\}_2]$ [43,44,48].

Exchange of dinuclear fragments has also been observed. For example, in the presence of a little ethylene the members of the $[M_2^*Co]$ series react with either of the dinuclear $[\{Cp^*M'(\mu\text{-}CO)\}_2]$ **17d** (M' = Co), **20d** (M' = Rh) to give an equilibrium mixture of the $[M_2^*Co]$, $[M_2'^*Co]$ clusters and the dinuclear $[\{Cp^*M(\mu\text{-}CO)\}_2]$, $[\{Cp^*M'(\mu\text{-}CO)\}_2]$. Two possible mechanisms, both involving the addition of ethylene to the trinuclear clusters as the first step, were suggested for this reaction, which does not proceed in the absence of the olefin [44].

In the $[M^*Co_2]$ series the exchange reactions are more complicated, and dinuclear metathesis products are also observed, together with some unexpected trinuclear complexes [44].

The $[Co_3]$ complex **40a** undergoes fragmentation in a variety of organic solvents, forming the dinuclear **17a** and tetranuclear $[(CpCo)_4(CO)_2]$ **16**. This reaction is much faster in thf than in benzene. From a kinetic investigation a mechanism was proposed which involves solvent-induced fragmentation of **40a** to give **17a** and an intermediate $[CpCo(solvent)_n]$. The latter then reacts with the educt **40a** to give **16** or, if the solvent is benzene, it can be trapped by **19b** to give **43** [48].

A complex related to **40a** can be obtained from the reaction of $[Cp_2Ti(CO)_2]$ and **29a**. The product **51** has a $[(CpCo)_3(\mu_2\text{-}CO)_2]$ core; both the carbonyl oxygen atoms are bonded to Cp_2Ti moieties (Fig. 8). The geometric parameters involving the carbonyl groups ($d(C{-}O) = 1.30(2)$ Å, $d(Ti\cdots O) = 1.90(1)$ Å; mean angle C—O···Ti, 162°), together with the magnetic moment of $3.7\mu_B$ (at 20 °C), were interpreted in terms of a one-electron reduction of each CO ligand [49,50]. Unfortunately, electron spin resonance (ESR) data which could substantiate the +3 oxidation state of the titanium atoms were not reported. The Cp_2Ti groups are replaced by $SiMe_3$ groups

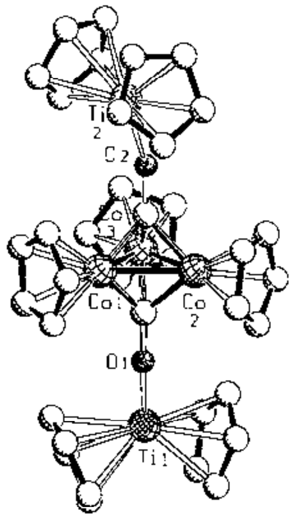
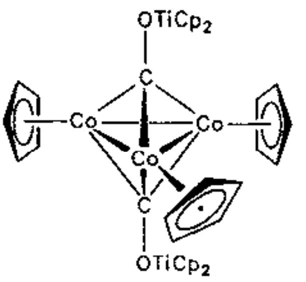


Fig. 8. Molecular structure of $[(CpCo)_3(COTiCp_2)_2]$ **51**.



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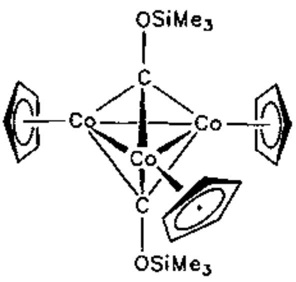


52

to give the bis(μ_3-silyloxycarbyne) cluster complex **52** when **51** is treated with $ClSiMe_3$ [50].

3.3. *Electronic structure of the cluster complexes* $[\{(C_5R_5)M\}_3(CO)_n]$ $(n=2,3)$

Several theoretical studies have appeared which deal with trinuclear cluster complexes of the type $[\{(C_5R_5)M\}_3(CO)_n]$ $(n=2,3)$. The reader is also referred to the discussion of the electronic structure of the cluster complexes $[\{(C_5R_5)M\}_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$ in Section 4.1 of this review.

Some useful generalizations may be made using the concept of isolobal relations [51,52]. Since $[(C_5R_5)(d^9\text{-}M)^2L]$ is isolobal to methylene, the dinuclear $[\{(C_5R_5)M\}\{(C_5R_5)M\}'(CO)_2]$ **17**–**22** can be related to ethylene. Addition of methylene to **17**–**22** to give the μ-methylene complexes $[\{(C_5R_5)M\}\{(C_5R_5)M\}'(CO)_2(\mu\text{-}CH_2)]$ **53** has therefore been called a cyclopropanation reaction [33]. Formally adding [$(C_5R_5)(d^9\text{-}M'')CO$] to **17–22** to generate the trinuclear tricarbonyl cluster complexes [$\{(C_5R_5)M\}\{(C_5R_5)M\}'\{(C_5R_5)M\}''(CO)_3$] amounts to an "organometallic cyclopropanation" [33]. The close similarity of [$\{(C_5R_5)Rh(CO)\}_2(\mu\text{-}CH_2)$] **53a** and C_s isomer of [$(CpRh)_3(CO)_3$] **11B** was indeed substantiated by extended Hückel MO (EHMO) calculations [53].

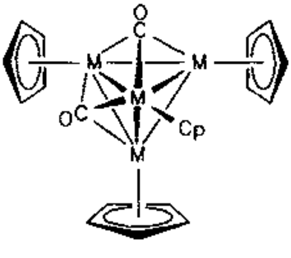
In the dicarbonyl cluster complexes [$\{(C_5R_5)(d^9\text{-}M)\}_3(CO)_2$] the metal centres do not reach the 18 VEs required for a "classical" structure. Of the total of 46 VEs, five electron pairs are available for cluster bonding, one less than required by polyhedral skeletal electron pair (PSEP) theory for a *closo* trigonal bipyramid. Hence, in both electron counting schemes the complexes are unsaturated.

Using the isolobal relationship between CH^+ and [$(C_5R_5)(d^9\text{-}M)$], the trinuclear dicarbonyl cluster complexes **40–46** can be related to the hypothetical [C_3H_5]$^+$ monocation, which is isolobal to the [C_3H_3]$^-$ monoanion by removal of two protons [41]. Like the antiaromatic D_{3h}-[C_3H_3]$^-$, the D_{3h}-[$(CpM)_3(\mu_3\text{-}CO)_2$] cluster complexes have triplet ground states and are Jahn–Teller unstable [41,53]. Several geometric distortions of the latter to remove the orbital degeneracy of the HOMO have been discussed [53]. One of them, the partial opening of the μ_3 bridges to a semi-μ_3 bridging geometry, is observed for most derivatives. In such a geometry the HOMO and lowest unoccupied MO (LUMO) are similar in energy, and this could explain the observed spin equilibria [44,53].

The crystal structure of the [Co_3^*] complex **40d** requires the cluster to have C_{3h} site symmetry. Unsymmetrical interactions of the Cp* ligands with the $Co_3(CO)_2$ core were proposed as the reason for the observed breakdown in HOMO–LUMO degeneracy, which leads to the observed singlet ground state for this complex [41].

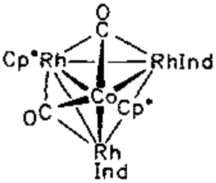
3.4. The cluster complexes [$\{(C_5R_5)M\}_4(CO)_2$]

Three tetranuclear carbonyl derivatives [$(CpM)_4(CO)_2$] **16** (M = Co), **12** (M = Rh) and [$(IndRh)_2(Cp^*Rh)(Cp^*Co)(CO)_2$] **54** have been reported. **16** [17,24] and **12** [21] are products of the thermal decomposition of the trinuclear tricarbonyl cluster complexes **8a** and **11A**. **16** was also formed during the decomposition of [$CpCo(CO)R$]$_2$ (R = Me, Et) [54] and as a product of the reaction of [$CpCo(C_2H_4)_2$] **29a** with formaldehyde or [$CpCo(CO)_2$] **6a** [55].



16, M = Co

12, M = Rh



54

The trirhodium cobalt complex **54** is formed when [(Cp*Co)(Cp*Rh)$(CO)_2$] **18d** is heated with [IndRh$(C_2H_4)_2$] **39c**. The trimetal dicarbonyl cluster complex [(Cp*Co)(Cp*Rh)(IndRh)$(CO)_2$] is believed to be an intermediate in this reaction [45], similar to the formation of **16** from **40a** and [CpCo(solvent)] [43,48].

In the crystal **16** has a slightly distorted tetrahedral Co_4 core. Two of the four faces of the Co_4 cluster are symmetrically bridged by the two carbonyl groups (Fig. 9) [51,55]. In solution, **16** appears to be rigid on the NMR time scale at room temperature [24]. The rhodium analogue **12**, however, displays fluxionality even below room temperature [21].

4. Trinuclear complexes of the type [$\{(C_5R_5)M\}_3(\mu_3\text{-}X)(\mu_3\text{-}Y)$]

The cluster complexes of the general composition [$\{(C_5R_5)M\}_3(X)(Y)$] form the largest subgroup of the title compounds of this review. Ideally, the M_3XY cluster cores are bicapped metal triangles; X and Y occupy the axial positions of a trigonal bipyramid. In several cases severe distortions of this ideal geometry are observed. Depending on the type of the capping groups and on the charge of the molecule, the valence electron count spans the range of 46 to 51. An overview of the known capping groups is given in Table 5.

According to PSEP theory and the 18 VE rule, the "correct" electron count for this class of complexes is 48. The "electron-deficient" [$\{(C_5R_5)M\}_3(CO)_2$] have already been discussed in detail. For reasons based on their chemistry, another

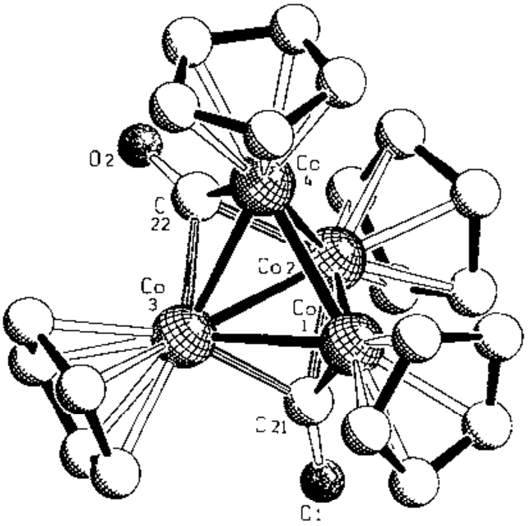


Fig. 9. Molecular structure of [$(CpCo)_4(CO)_2$] **16**.

Table 5
Complexes of the type $[\{(C_5R_5)M\}_3(\mu_3\text{-}^{n}L)(\mu_3\text{-}^{m}L)]^x$

n	^{n}L	m	^{m}L	x	VEs
2	CO	2	CO	0	46
2	CO	4	O	0	48
2	CO	4	S	0	48
2	CO	4	Se	0	48
2	CO	4	NR	1+, 0, 1−	47, 48, 49
2	BR	4	PR	0	48
2	CS	4	S	1+, 0, 1−	47, 48, 49
2	CS · L	4	S	0, 1+	48
2	CNR	4	S	0	48
2	CN(R)R′	4	S	1+	48
3	CN(H)(R)R′	4	S	2+	48
3	CR	3	CR	1+, 0, 1−	47, 48, 49
3	NO	3	NO	1+, 0	47, 48
3	NO	4	NR	1+, 0	48, 49
4	S	4	S	2+, 1+, 0, 1−	48, 49, 50, 51
4	S	4	NR	0	50

important series, the "electron precise" $[\{(C_5R_5)M\}_3(CR)_2]$, and a few related systems will be dealt with in the next section.

4.1. Molecular orbital treatments of $[(CpM)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$

MO calculations of cluster complexes $[\{(C_5R_5)M\}_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$ with VE counts ranging from 46 (e.g. M = Co, Rh, X = Y = CO) to 53 (M = Ni, X = Y = S) have been performed by several groups [41,44,53,56–59]. Only the salient features relevant to the systems under discussion in this and the preceding chapter will be summarized here.

As a starting point for the discussion an effective D_{3h} (or C_{3v} if $X \neq Y$) symmetry of the fragments or molecules is assumed. When three CpM fragments are combined to a $(CpM)_3$ triangle, the separation of the metal d orbitals into a lower lying "t_{2g}" set and higher-lying set is preserved. Only the latter orbitals, the metal–metal bonding e', a_2'' and antibonding a_2', e'' sets, in addition to a greatly stabilized a_1' combination of predominantly metal s, p character, are of primary importance for bonding to the μ_3 ligands (Fig. 10).

There are nine orbitals in the "t_{2g}" set, which have room for 18 electrons. The remaining 6 electrons of the three cobalt atoms (formally Co^{I}), together with the electrons donated by the μ_3 ligands, will be distributed among the combinations of the above-mentioned a and e sets of predominantly metal orbitals with the ligand σ and π orbitals.

Differences of the bonding schemes of various μ_3 ligands with the $(CpM)_3$ triangle arise, depending on their properties as π acceptors (such as CO or CR) or π donors (such as S). In the former case the metal e' and e'' are stabilized, while they are

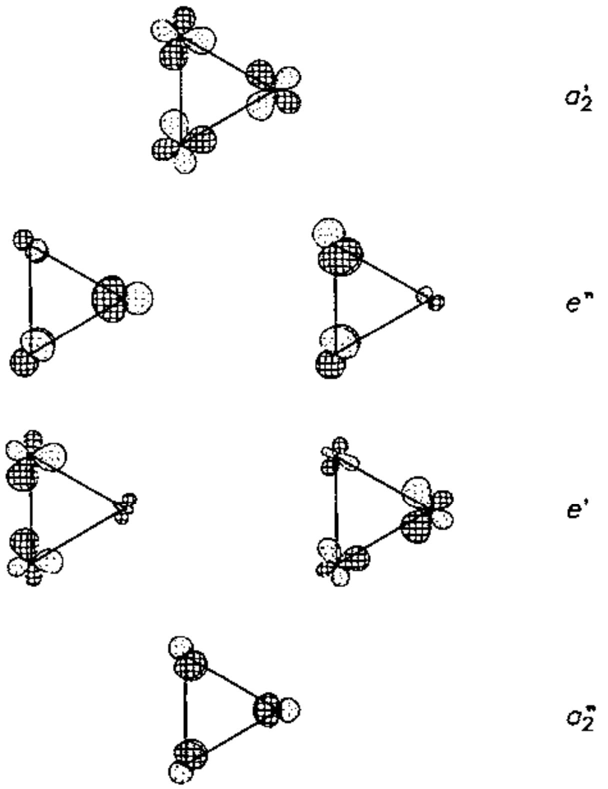
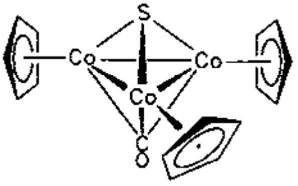


Fig. 10. Extended Hückel frontier orbitals of the D_{3h}-{Cp(d^9-M)}$_3$ cluster.

destabilized in the latter. Generally the metal–ligand interactions are much stronger than the metal–metal interactions [57].

For the systems with two π acceptor ligands, such as [(CpCo)$_3$(μ_3-CO)$_2$] **40a**, the Fenske–Hall (FH) method predicts a large stabilization (below t_{2g}) of the (CpCo)$_3$ e' and e'' orbitals which point towards the CO ligands [57]. Extended Hückel (EH) MO calculations suggest a higher energy of these sets (above t_{2g}) [56]. In any case, with 46 VEs these molecules are expected to have triplet ground states under D_{3h} symmetry.

The 48 VE systems have a total of 30 electrons (24 from the metals and 6 from the μ_3 ligands) in the pseudo-t_{2g} and a, e frontier orbitals. Again, for the mixed ligand system [(CpCo)$_3$(μ_3-CO)(μ_3-S)] **55** EH and FH calculations do not arrive at the same ordering of frontier orbitals. Here the orbitals in question are a set of e symmetry, derived from the now allowed mixing of the e' (D_{3h}) and e'' (D_{3h}) orbitals, which point towards the bridging CO ligand [56,57]. For **55** filled "t_{2g}" and stabilized e sets are predicted by both methods. This is in accord with molecular diamagnetism and a symmetric trimetal triangle. Filled HOMOs of e symmetry were also predicted for [(CpCo)$_3$(μ_3-CO)(μ_3-NH)] [60] and [(CpCo)$_3$(μ_3-CR)$_2$] [61,62].



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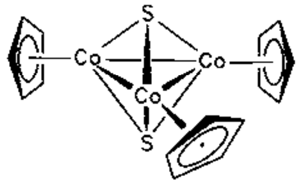


60a

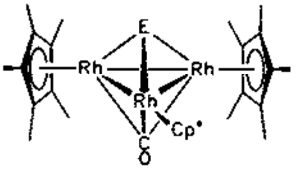
Various MO studies of [$(CpCo)_3(\mu_3\text{-}S)_2$] **60a** (50 VEs) do not agree with each other about the ordering of the frontier orbitals. In early studies close-lying a_2' and e' orbitals were proposed [58]. However, the number of electrons was incorrectly assigned to the frontier orbitals. FH calculations also resulted in a close spacing of these levels [57]. With 32 electrons to go into the frontier orbitals, the 50 VE species could be dia- or paramagnetic in the ground state, depending on whether the e' or a_2' orbital is lowest in energy. In contrast, a great destabilization of the e' orbital set was predicted by the EH method, leaving the a_2' orbital as the energetically isolated doubly occupied HOMO [56]. This is at variance with the observed magnetic behaviour of **60a** (see below).

Jahn–Teller distortions from the ideal D_{3h} symmetry may occur to lift the degeneracies of the HOMOs for the 46 and 50 VE clusters. Possible molecular distortions could involve a lengthening or contraction of one of the metal–metal bonds, a movement of a triply bridging ligand toward a doubly bridging position and/or a deformation of the Cp rings. The odd-electron systems (47, 49 or 51 VEs) may also be distorted for the same reason.

Discrepancies also exist about the orbital nature of the direct metal–metal interactions. In particular, in the FH MO study [57] the e' MOs were designated as trimetal bonding, owing to a major contribution of in-plane Co d_{xz} atomic orbitals (AOs). Based on a structural comparison of [$(Cp'Co)_3(\mu_3\text{-}S)_2$]$^{n-}$ ($n = 2, 1, 0$) with 48, 49 and 50 VEs and [$(CpCo)_3(\mu_3\text{-}S)_2$]$^{n+}$ ($n = 1, 0$) with 49 and 50 VEs with the e' set of orbitals was considered to be trimetal antibonding [63]. As an explanation it was assumed that the minor trimetal antibonding contributions of the diffuse and better overlapping Co 4s and 4p AOs dominate the metal–metal interactions in this orbital [63].

4.2. The cluster complexes [$\{(C_5R_5)M\}_3(\mu_3\text{-}^2L)(\mu_3\text{-}^4L)$]

A series of cluster complexes with $^2L = CO$ can be prepared from the mononuclear dicarbonyls [$(C_5R_5)M(CO)_2$] **6** (M = Co), **7** (M = Rh). [$(CpCo)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$] **9a** was obtained in very low yield as a product of the prolonged photolysis of **6a** [19]. The Cp*Rh analogue **61** is formed as a byproduct during the chemically induced decarbonylation (with Me_3NO) of **7b** to give [$\{Cp^*Rh(CO)\}_2$] **20d** [36]. thf solutions of the chalcogen-bridged dinuclear complexes [$\{Cp^*Rh(CO)\}_2(\mu\text{-}E)$] **62** (E = S), **63** (E = Se) slowly decompose at room temperature. The μ_3-thio- and

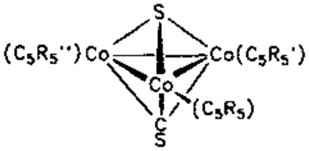


64, E = S

65, E = Se

μ_3-seleno-bridged cluster complexes [(Cp*Rh)$_3$(μ_3-CO)(μ_3-E)] **64** (E = S), **65** (E = Se) are isolated after 22 h in moderate yields [31].

Another thio-bridged complex, [(CpCo)$_3$(μ_3-CO)(μ_3-S)] **55a**, is one of the minor products (5%) of the reaction of bis(^{t}butyl)sulphurdiimide with [CpCo(CO)$_2$] **6a** [64,65]. The thiocarbonyl analogue of **55a**, [(CpCo)$_3$(μ_3-CS)(μ_3-S)] **56a**, was first obtained in high yield from the η^2-carbon disulphide complex [Cp(PR$_3$)Co(η^2-CS$_2$)] **66a** (R = Me) and [Cp(PMe$_3$)Co(μ-CO)$_2$Mn(CO)Cp′], a source of the [Cp(PMe$_3$)Co] fragment [66,67]. **56a** is also formed together with mononuclear products when [CpCo(CO)(PR$_3$)] (R = alkyl, aryl) is heated with CS$_2$ in toluene. In this reaction, the source of **56a** appears to be also **66a** which, when R = Ph, decomposes to it in 35% yield after 4 h in refluxing toluene [68].



56a, R = R′ = R″ = H

b, R = R′ = H, R$_5$″ = H$_4$Me

c, R = H, R$_5$′ = R$_5$″ = H$_4$Me

d, R$_5$ = R$_5$′ = R$_5$″ = H$_4$Me

Treatment of **66c** (PR$_3$ = PMePh$_2$) with two molar equivalents of **6a** in refluxing benzene also gave **56a** in high yield [69]. Variations of the reaction employ the Cp′ ligand instead of Cp in either of the two or both reagents. Thus, products that analysed for [(Cp′Co)(CpCo)$_2$(μ_3-CS)(μ_3-S)] **56b**, [(Cp′Co)$_2$(CpCo)(μ_3-CS)(μ_3-S)] **56c** and [(Cp′Co)$_3$(μ_3-CS)(μ_3-S)] **56d** were obtained. However, the mass spectra of the first two products indicated the presence of various mixed Cp′Cp-containing clusters. This leaves an interesting possibility of (C$_5$R$_5$)M group redistribution occur-ring at the high temperatures (above 200 °C) which were used to obtain the mass spectra [69].

The cleavage of a C—S bond in CS_2 by [CpCoLL′] (L, L′ = CO, PR_3) to give $(CpCo)_3$ cluster coordinated μ_3-S and μ_3-CS ligands can be extended to isothiocyanates. Thus a considerable number of complexes $[(CpCo)_3(\mu_3\text{-}CNR)(\mu_3\text{-}S)]$ (R = alkyl, aryl) **67** are obtained from the reactions of [CpCoLL′] [LL′ = (CO)(PPh_3), $(PPh_3)_2$, $(C_2H_4)_2$] with RNCS [70–72].

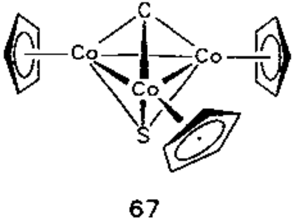
The carbonyl and imido (nitrene) bridged cluster complexes $[\{(C_5R_5)Co\}_3(\mu_3\text{-}CO)(\mu_3\text{-}NR)]$ **57**, **58** are obtained from $[(C_5R_5)Co(CO)_2]$ **6** and Me_3SiN_3 [73,74]. The range of products and their yields markedly depend on the substituents on the cyclopentadienyl ligands. $[CpCo(CO)_2]$ **6a** gives $[(CpCo)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)]$ **57a** in high yield [73]. In contrast, the reaction of $[Cp'Co(CO)_2]$ **6b** gives, in addition to the expected **57b** (24% yield), $[(Cp'Co)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ **58b** (60%) and the formamidonitrene cluster **59** (5%) [73]. Finally the major product of the analogous reaction with $[Cp^*Co(CO)_2]$ **6c** is the dinuclear $[\{Cp^*Co(CO)\}_2]$ **17d**; the nitrene cluster $[(Cp^*Co)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ **58c** is formed in 10%–15% yield [73].

The mixed Cp*Cp′ derivatives $[(Cp^*Co)_x(Cp'Co)_{3-x}(\mu_3\text{-}NSiMe_3)]$ ($x = 0, 1, 2$) **57b–d** and $[(Cp^*Co)_x(Cp'Co)_{3-x}(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ ($x = 1, 2$) **58d,e** can be isolated in 1%–4% yield from the reaction of an equimolar mixture of **6b** and **6c** with Me_3SiN_3 [60]. A high yield preparation of the trirhodium cluster complex $[(CpRh)_3(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)]$ **68** was reported, starting from $[(CpRh)_3(CO)_2]$ and using the trimethylsilylazide method [74]. This might be in error since the starting material $[(CpRh)_3(CO)_2]$ does not appear to be a known compound.

The *N*-silylated nitrene capped cluster complexes **57a,b** can be transformed into the μ_3-NH derivatives by cleavage of the N−Si bond with fluoride ion [73].

The redox chemistry of some derivatives $[\{(C_5R_5)Co\}_3(\mu_3\text{-}L^2)(\mu_3\text{-}{}^4L)]$ has been studied. The 47 VE monocations and 49 VE monoanions of $[\{(C_5R_5)Co\}_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ **56** are reversibly accessible by cyclic voltammetry [75]. The neutral $[(Cp^*Co)_x(Cp'Co)_{3-x}(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ **58c** ($x = 3$), **58e** ($x = 2$) and **58d** ($x = 1$) are oxidized by silver ion to give the 47 VE monocations [60].

A comprehensive electrochemical study of the series of cluster complexes $[\{(C_5R_5)Co\}_3(\mu_3\text{-}X)(\mu_3\text{-}NR')]$ (X = CO, NO^+) has appeared [76]. Their redox behaviour is summarized in Table 6. Each of the carbonyl complexes with Cp and Cp′ ligands exhibits one two-electron oxidation to a 46 VE species and one two-



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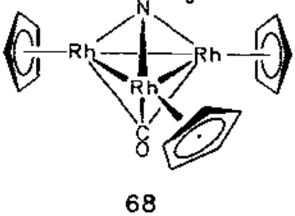

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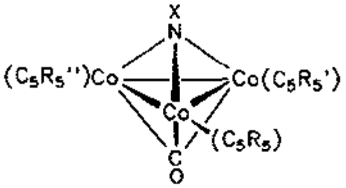


	X	C_5R_5	C_5R_5'	C_5R_5''
57a	$SiMe_3$	Cp	Cp	Cp
b	$SiMe_3$	Cp'	Cp'	Cp'
c	$SiMe_3$	Cp*	Cp'	Cp'
d	$SiMe_3$	Cp*	Cp*	Cp'
58a	H	Cp	Cp	Cp
b	H	Cp'	Cp'	Cp'
c	H	Cp*	Cp*	Cp*
d	H	Cp*	Cp'	Cp'
e	H	Cp*	Cp*	Cp'
59	$C(O)NH_2$	Cp'	Cp'	Cp'

Table 6
Electrochemical data [76] for some cluster complexes $[\{(C_5R_5)Co\}_3(\mu_3\text{-}X)(\mu_3\text{-}NR')]$

	R/R'	−2/0	−1/0	0/+1	0/+2
X = CO					
57a	Cp/$SiMe_3$	−1.60	—	—	+0.40
57b	Cp'/$SiMe_3$	−1.68	—	—	+0.33
59	Cp'/$C(O)NH_2$	−1.73	—	—	+0.22
58a	Cp/H	−1.63	—	—	+0.31
58b	Cp'/H	−1.76	—	—	+0.25
58c	Cp*/H		−2.03	−0.07	
58c	Cp*/H [a]			−0.21	+0.75[b]
X = NO					
75a	Cp/H [c]		−1.49	−0.53	
75b	Cp'/H [c]		−1.58	−0.60	

Volts vs. SCE; in thf unless stated otherwise.
[a] In CH_2Cl_2. [b] +1/+2. [c] In MeCN.

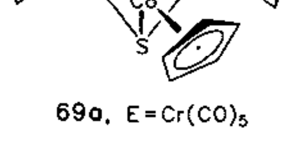
electron reduction to a 50 VE complex. In sharp contrast, the Cp* complex undergoes two sequential one-electron oxidations to the 47 VE and 46 VE mono- and dications and a one-electron reduction to the 49 VE monoanion. The behaviour of the Cp and Cp′ derivatives was explained by a much greater stabilization in the 50 VE dianions and the 46 VE dications relative to the 49 VE and 47 VE systems. A combined effect of the steric and electron-donating properties of the Cp* ligands was made responsible for the one-electron redox reactions of **58c**. This was presumed to stabilize the filled HOMOs of both the neutral and the dianion relative to the corresponding half-filled HOMOs of the monoanion and monocation respectively.

The nitrene ligands in **58a,b** do not react with strong bases and hydrogen abstraction reagents [73]. There is, however, electrochemical evidence that the triply bridging NH group in the dication [**58a**]$^{2+}$ can be reversibly deprotonated. The product is thought to have a "naked" exposed pyramidal-like nitrido ligand capping the three cobalt atoms [76].

The sulphur atom of the μ_3-CS ligand in $[(CpCo)_3(\mu_3\text{-CS})(\mu_3\text{-S})]$ **56a** is very basic, and a wide range of adducts $[(CpCo)_3(\mu_3\text{-CS} \rightarrow E)(\mu_3\text{-S})]$ **69** are obtainable with electrophiles E (E = alkyl$^+$ [66,67,69], I$^+$ [69], Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag$^+$ [68,69], $Cr(CO)_5$ [66,67]). The $Cr(CO)_5$ adduct **69a** has been characterized by X-ray crystallography (Fig. 11). As expected, the μ_3-(CSCr) unit is non-linear (angle C—S—Cr, 121°). The C—S bond distances are about the same in **56a** and **69** [67].

The μ_3-CNR ligand in $[(CpCo)_3(\mu_3\text{-CNR})(\mu_3\text{-S})]$ **67** is also basic. With HBF_4 the salts $[(CpCo)_3(\mu_3\text{-CN(H)R})(\mu_3\text{-S})]^+$ **70** are obtained when R = aryl. For R = Et diprotonation takes place to give $[(CpCo)_3(\mu_3\text{-CN(H)}_2\text{R})(\mu_3\text{-S})]^{2+}$ **71** [70]. **70** is also formed when **67** is treated with $[Ph_3C]BF_4$. Deuterium is not incorporated in **70** when the reaction is carried out in deuterated solvents, which suggests that the protons do not arise from the solvent [70]. Alkyl or aryl halides R′X only give the monoalkylation products $[(CpCo)_3(\mu_3\text{-CN(R')R})(\mu_3\text{-S})]^+$ **72**. The methyl–ethyl derivative can be further protonated to give the dication $[(CpCo)_3(\mu_3\text{-CN(H)(Me)Et})(\mu_3\text{-S})]^{2+}$ **73**. When R or R′ is an aryl group, **72** does not react with protons [70].

The crystal structures of many of the 48 VE cluster complexes mentioned have been determined using X-ray crystallography (Figs. 12–14, Table 7). Structural information is also available for some 47 VE ions. A detailed comparison of the structures of several 47 and 48 VE systems was made in the series



69a, E = $Cr(CO)_5$

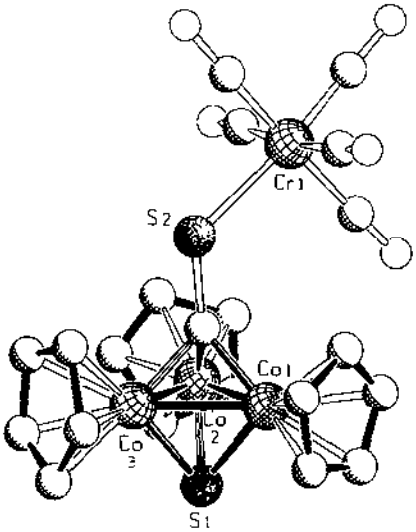


Fig. 11. Molecular structure of $[(CpCo)_3(S)\{CS \cdot Cr(CO)_5\}]$ **69a**.

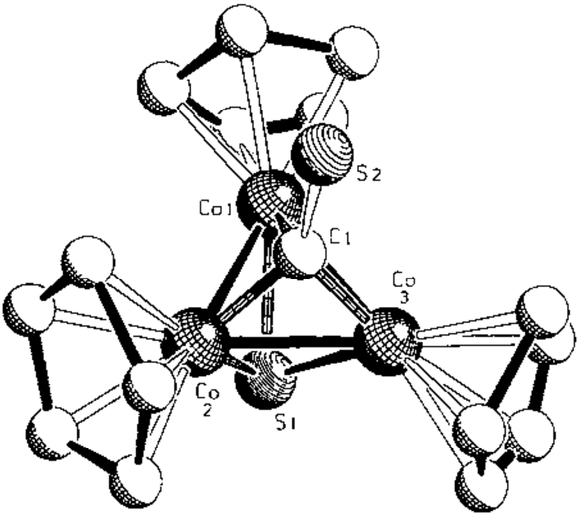


Fig. 12. Molecular structure of $[(CpCo)_3(S)(CS)]$ **56a**.

$[(Cp^*Co)_{3-x}(Cp'Co)_x(\mu_3\text{-}CO)(\mu_3\text{-}NH)]^{n+}$ **58c** ($x = 0$), **58e** ($x = 1$) and **58d** ($x = 2$), $n = 0, 1$. The tricobalt cores in the 48 or 47 VE clusters **58c** and **58c**$^+$ approximate equilateral triangles. The mean cobalt–cobalt distance is only slightly shortened after removal of an electron from **58c**. This is consistent with relatively little tricobalt antibonding character of the degenerate HOMOs. Several reasons are given for the absence of a pronounced Jahn–Teller distortion of the cations, including the possi-

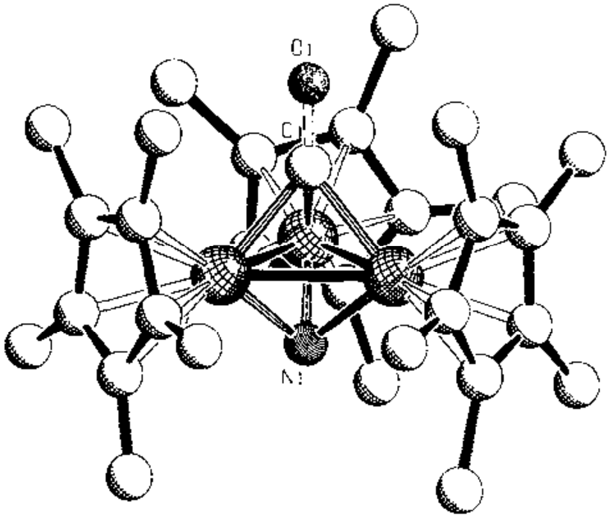


Fig. 13. Molecular structure of [(Cp*Co)$_3$(CO)(NH)] **58c**.

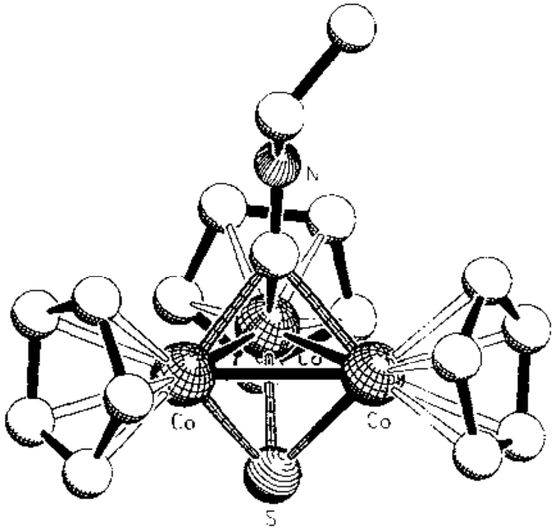


Fig. 14. Molecular structure of [(CpCo)$_3$(S)(CNEt)] **67a**.

bility of a threefold disorder of an asymmetric molecule in the solid state. Replacement of a Cp* by a Cp′ ligand only has an influence on the capping carbonyl ligand which, because of $d_\pi(Co)-\pi^*(CO)$ back bonding, forms stronger (shorter) bonds to the Cp*Co groups with more electron density on the Co [60].

Table 7
Structural data for some complexes of the type $[\{(C_5R_5)M\}_{3-n}\{(C_5R_5)M\}'_n(\mu_3\text{-}X)(\mu_3\text{-}Y)]$

		X	Y	VEs	Symmetry[a]	d_{mean}(M—M)[b] (Å)	d_{mean}(M—X)[b] (Å)	d_{mean}(M—Y)[b] (Å)	Ref.
58c$^+$	$[(Cp^*Co)_30]^+$	CO	NH	47	C_{3v}	2.409[9,3]	1.98[1,2]	1.81[1,1]	[60]
58e$^+$	$[(Cp^*Co)_2(Cp'Co)]^+$	CO	NH	47	C_s	2.443[—,2][c], 2.363[4,2][d]	2.10[—,1][e], 1.947[5,11][f]	1.820[—,8][e], 1.809[1,8][f]	[60]
58d$^+$	$[(Cp^*Co)(Cp'Co)_2]^+$	CO	NH	47	C_s	2.408[1,2][d], 2.350[—,2][g]	1.945[19,9][e], 1.875[—,10][f]	1.784[2,9][e], 1.793[—,8][f]	[60]
58c	$(Cp^*Co)_3$	CO	NH	48	C_{3v}	2.428[6,3]	1.93[1,2]	1.83[1,1]	[73]
58d	$(Cp^*Co)(Cp'Co)_2$	CO	NH	48	C_s	2.395[0,1][d], 2.375[—,1][g]	1.957[0,6][e], 1.935[—,7][f]	1.815[0,5][e], 1.812[—,7][f]	[60]
59	$(Cp'Co)_3$	CO	$NC(O)NH_2$	48	C_{3v}	2.400[13,1]	1.953[10,3]	1.835[5,3]	[73]
9a	$(CpCo)_3$	CO	O	48	C_{3v}	2.365[—,4]	1.78[—,2]	2.00[—,2]	[19]
55a	$(CpCo)_3$	CO	S	48	C_{3v}	2.452[—,2]	—[h]	—[h]	[77]
65	$(Cp^*Rh)_3$	CO	Se	48	C_{3v}	2.709[3,2]	2.11[2,2]	2.380[3,2]	[31]
56a	$(CpCo)_3$	CS	S	48	C_{3v}	2.42[2,2][i] 2.44[0,1][i]	1.77[9,7][i] 1.91[0,3][i]	2.17[2,3][i] 2.04[0,10][i]	[67]
69a	$(CpCo)_3$	$CS\cdot Cr(CO)_5$	S	48	C_s	2.405[5,5], 2.517[—,5][j] 2.393[12,5], 2.497[—,5][j] 2.403[4,5], 2.509[—,5][j] 2.406[0,5], 2.499[—,5][j]	1.87[1,3], 1.91[—,3][j] 1.96[1,3], 1.94[—,3][j] 1.91[1,3], 1.92[—,3][j] 1.90[1,3], 1.93[—,3][j]	2.131[5,9], 2.130[—,9][j] 2.114[4,9], 2.095[—,9][j] 2.116[5,9], 2.124[—,9][j] 2.113[9,9], 2.127[—,9][j]	[67]
67b	$(CpCo)_3$	CNCy	S	48	C_{3v}	2.450[30,5][i], 2.455[5,4][i]	1.96[7,3][i], 1.95[4,3][i]	2.125[7,7][i], 2.126[21,7][i]	[71]
67a	$(CpCo)_3$	CNEt	S	48	C_s	2.483[—,1], 2.450[2,1]	1.912[—,6], 2.027[13,6]	2.131[—,2], 2.113[1,2]	[70]
75b$^+$	$[(Cp'Co)_3]^+$	NO	NH	48	C_{3v}	2.406[16,3]	1.869[18,11]	1.835[13,10]	[73]
74a	$(CpCo)_3$	NO	NO	48	D_{3h}	2.399[—,3]	1.843[—,9]	1.843[—,9]	[78]
74b	$(Cp'Co)_3$	NO	NO	48	D_{3h}	2.403[8,1]	1.864[5,4]	1.863[4,4]	[78]

75b	$(Cp'Co)_3$	NO	NH	49	C_s	2.420[6,3], 2.554[—,3]	1.875[15,12], 1.880[—,11]	1.812[8,12], 1.833[—,11]	[79]
60b^{2+}	$[(Cp'Co)_3]^{2+}2(SbF_6)^-$	S	S	48	D_{3h}	2.521[26,3]	2.125[3,5]	2.117[5,5]	[63]
60a$^+$	$[(CpCo)_3]^+I^-$	S	S	49	C_{2v}	2.649[0,1], 2.474[—,2]	—[k]	—[k]	[77]
60a$^+$	$[(CpCo)_3]^+(SbF_6)^-$	S	S	49	C_{2v}	2.64[0,—[k]], 2.52[—,—[k]]	2.15[—[k]] 2.14[—[k]]	2.15[—[k]] 2.14[—[k]]	[63]
60b$^+$	$[(Cp'Co)_3]^+(PF_6)^-$	S	S	49	C_{2v}	2.491[5,1], 2.873[—,1]	2.153[2,2], 2.163[—,2]	2.154[5,2], 2.149[—,2]	[63]
60a	$(CpCo)_3$[l]	S	S	50	D_{3h}	2.687[—,3]	—[k]	—[k]	[77]
60a	$(CpCo)_3$[l]	S	S	50	D_{3h}	2.691[—,4]	2.168[—,4]	2.168[—,4]	[80]
60a	$(CpCo)_3$[m]	S	S	50	C_{2v}	2.625[5,10], 2.76[—,1]	2.24[4,1], 2.14[—,1][n]	2.11[1,1], 2.18[—,1][n]	[80]
60b	$(Cp'Co)_3$	S	S	50	C_{2v}	2.495[3,2], 3.151[—,2][i] 2.473[16,2], 3.221[—,2][i]	2.168[2,3], 2.174[—,3][i] 2.167[1,3], 2.171[—,3][i]	2.166[5,3], 2.179[—,3][i] 2.179[3,3], 2.183[—,3][i]	[63]
76c	$(^RCpCo)_3$	S	N^{t}Bu	50	C_{2v}	2.599[12,1], 2.537[—,1]	2.157[3,2], 2.153[—,2]	1.874[8,4], 1.883[—,5]	[81]

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[a] Idealized symmetry of the $M_{3-n}M'_nXY$ core. [b] Values in the form mean[σ(mean), σ], where σ is the standard deviation. [c] Cp*Co—Cp*Co. [d] Cp'Co—Cp*Co. [e] Cp'Co—X[Y]. [f] Cp*Co—X[Y]. [g] Cp'Co—Cp'Co. [h] X,Y disordered. [i] Two independent molecules. [j] Four independent molecules. [k] Data not available. [l] Room temperature. [m] 130 K. [n] Value corrected according to entry CYPCOS12 in the Cambridge crystallographic database.

4.3. *The cluster complexes* $[\{(C_5R_5)M\}_3(\mu_3\text{-}^3L)(\mu_3\text{-}^3L)]$ *and* $[\{(C_5R_5)M\}_3(\mu_3\text{-}^3L)(\mu_3\text{-}^4L)]$

The 48 VE complexes $[(CpCo)_3(\mu_3\text{-}X)_2]$ are known for X = CR and X = NO. The bis(carbyne) cluster complexes $[(CpM)_3(\mu_3\text{-}CR)(\mu_3\text{-}CR')]$ (M = Co, Rh, Ir) will be discussed in detail in the next section of this article. No species exist with two $\mu_3\text{-}^3L$ ligands of different types. The only examples of the ^3L,^4L combination are a series of complexes with capping NO and NH ligands.

The dinitrosyl cluster complex $[(CpCo)_3(\mu_3\text{-}NO)_2]$ **74a** was first observed when $[\{CpCo(\mu\text{-}NO)\}_2]$ was heated in the ion well of a mass spectrometer. On a preparative scale **74a** is obtained in about 90% yield when $[\{CpCo(\mu\text{-}NO)\}_2]$ is refluxed in thf for several days [82]. The Cp′Co derivative **74b** can be prepared in the same way [82]. Small quantities of **74a** are also formed when $[CpCo(CO)_2]$ **6a** is slowly added to a photolysed solution of $[\{CpFe(NO)\}_2]$ [78].

74a and **74b** exhibit very similar electrochemical behaviour. There are reversible one-electron oxidations and reductions to the 47 and 49 VE ions. Consistent with the enhanced electron-donating properties of the Cp′ ligands, **74b** is easier to oxidize (0.70 vs. 0.80 V (vs. SCE)) but more difficult to reduce (−1.14 vs. −1.05 V) than **74a** [78].

In the crystal, **74a** has crystallographically imposed C_{3h} site symmetry (Fig. 15). The $Co_3(NO)_2$ core in **74b**, which is not constrained by crystal symmetry, has essentially the same geometry (cf. Table 7) [78].

The 49 VE monoanion $[\mathbf{74b}]^-$ exhibits an increased (by 0.045 Å) mean Co−Co bond length with no marked geometrical distortion of the cluster core. The mean Co−N(O) bond length of 1.86 Å is the same in both the 48 VE and the 49 VE systems [60].

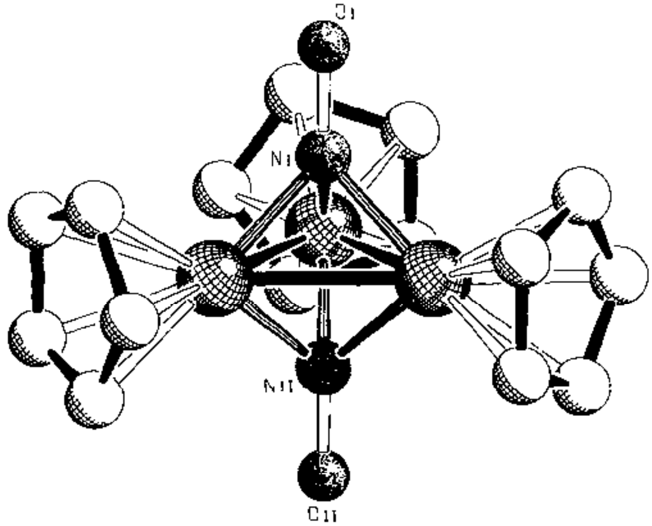
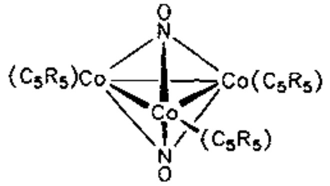


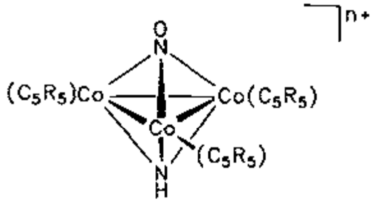
Fig. 15. Molecular structure of $[(CpCo)_3(NO)_2]$ **74a**.



74a, R = H

b, $R_5 = H_4Me$

c, R = Me



75a, R = H;

b, $R_5 = H_4Me$

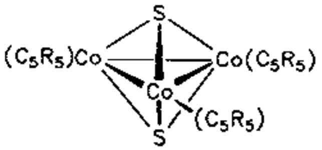
A μ_3-CO ligand is substituted by a μ_3-NO$^+$ when the nitrene, carbonyl capped cluster complexes [$\{(C_5R_5)Co\}_3(\mu_3\text{-CO})(\mu_3\text{-NR}')$] **57a**, **57b**, **58a**, and **58b** are treated with $NOBF_4$ [73]. If R′ = $SiMe_3$, desilylation to give the μ_3-NH species occurs at the same time. The resulting 48 VE cluster cations [$\{(C_5R_5)Co\}_3(\mu_3\text{-NO})(\mu_3\text{-NH})$]$^+$ [**75a**]$^+$ (R = H), [**75b**]$^+$ ($R_5 = MeH_4$) are quantitatively reduced by cobaltocene to the neutral 49 VE **75a,b** [79].

The X-ray crystal structures of the pair **75b**, [**75b**]$^+$ have been determined. The overall configuration of the monocation [**75b**]$^+$ roughly conforms to C_{3v} symmetry. Although the $Co_3(NO)(NH)$ core appears to be slightly distorted, the observed variations are not large (Table 7) [73]. In contrast, the neutral **75b** has an idealized C_s geometry with one much longer and two slightly enlarged Co—Co distances (Table 7) [79]. The reduction-induced geometrical changes are believed to result from a first-order Jahn–Teller distortion of the molecule which has the unpaired electron in the doubly degenerate HOMO of *e* symmetry (in C_{3v}). From a comparison of Co—Co, Co—N(H) and Co—N(O) distances it can be assumed that the HOMO containing the unpaired electron in **75b** is largely composed of in-plane Co_3 d AO components and essentially localized on the two cobalt atoms associated with the longer Co—Co distance [79]. The observed geometrical distortion requires this orbital to be antisymmetric with respect to the mirror plane (a'' in C_s) [79].

4.4. The cluster complexes [$\{(C_5R_5)M\}_3(\mu_3\text{-}^4L)_2$]

Tris(cyclopentadienyl)disulphur **60a** in about 20% yield was first obtained as one of the products of the reaction of *N,N′*-(^{t}BuN)$_2$S with [$CpCo(CO)_2$] **6a** [64,65]. The ^{t}BuN fragments are trapped by CO, giving urea [65]. In the absence of CO and using [^{R}CpCo(cod)] (^{R}Cp = C_5H_4COOMe) as a source of ^{R}CpCo fragments, the cluster complex [$(^RCpCo)_3(\mu_3\text{-S})(\mu_3\text{-N}^tBu)$] **76** is formed in 44% yield as the sole isolable product [81]. Alternative synthetic routes to **60** use **6a**, **6b** or [$CpCo(C_2H_4)_2$] **29a** and the solvent CS_2 as the source of sulphur [63,72].

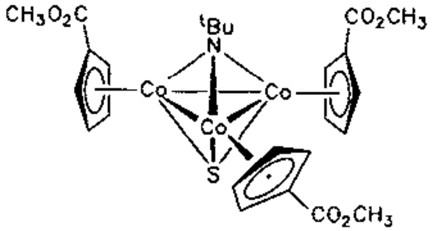
Both **60** and **76** have 50 valence electrons. In the cyclic voltammetry experiment, **60a,b** undergo two one-electron oxidations to form the 49 VE mono- and 48 VE dications and a one-electron reduction to form the 51 VE monoanion. [**60a**]$^+$,



60a, R = H

b, $R_5 = H_4Me$

c, $R_5 = H_4(COOMe)$



76

$[\mathbf{60b}]^+$, $[\mathbf{60b}]^{2+}$ were also prepared by chemical oxidation using I_2 or Ag^+ as oxidants [63,77].

In the solid state, **60b** is paramagnetic at room temperature, with a magnetic moment characteristic of two unpaired electrons. Curie–Weiss behaviour was observed from 340 to 196 K [63,77] or above 215 K [58a]. The molar magnetic susceptibility reached a maximum at 196 K [63,77] or 215 K [58a]. Below its maximum the susceptibility and the effective magnetic moment μ_{eff} dropped; the latter was calculated to be $0.93\mu_B$ at 98 K [63,77] or zero at 130 K [58a]. Anomalies in the temperature dependence of the heat capacity were attributed to a phase transition at 192.5 ± 0.1 K with an unusually large entropy value [58].

Solid **60b** is diamagnetic from 6 to 280 K [63]. In solution, μ_{eff} for this complex is temperature dependent ($1.05\mu_B$ at 21 °C, $0.86\mu_B$ at 0 °C).

Solid **60a** gives a broad ESR resonance that considerably narrows when the temperature is decreased to 220 K. At low temperature (e.g. 160 K) no ESR signal is detected. Solutions and frozen solutions of **60a** and **60b** do not give ESR spectra [63]. In contrast both complexes give ^{1}H NMR resonances with very temperature-dependent chemical shifts.

The magnetic, ESR and NMR data can be explained by spin equilibria in solution between diamagnetic ($S = 0$) and paramagnetic ($S = 1$) isomers. Thermodynamic data for these equilibria, obtained from the temperature dependence of the NMR shifts in solution, are given in Table 8. The positive values for ΔH indicate that the ground states of the complexes **60b,c** are singlets in solution [77].

Two independent X-ray studies established a crystallographically imposed C_{3h} site symmetry for **60a** at room temperature. The reported Co–Co bond lengths (2.687(3) Å [77], 2.691(4) Å [80]) are equivalent within experimental error. At

Table 8
Thermodynamic data for spin equilibria in solution of some cluster complexes $[\{(C_5H_4R)Co\}_3(\mu_3\text{-}S)(\mu_3\text{-}X)]$

	R, X	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	Ref.
60b	Me,S	18.1	48	[63]
60c	CO_2Me,S	19.0	60	[81]
76	CO_2Me,N^{t}Bu	−23.2	−72.9	[81]

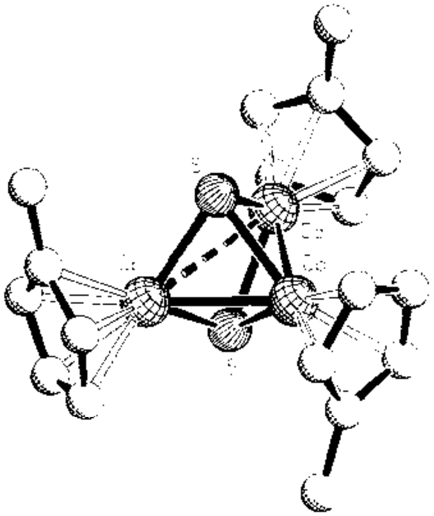


Fig. 16. Molecular structure of $[(Cp'Co)_3S_2]$ **60b**.

130 ± 5 K the Co_3S_2 cluster is a scalene bipyramid with two shorter (2.63(1) Å) and a longer (2.76(1) Å) CoCo edges [80]. The Cp′ derivative **60b** crystallizes with two independent molecules in the unit cell. Each independent Co_3S_2 core closely conforms to C_{2v} symmetry with one non-bonding and two bonding Co—Co distances (Fig. 16, Table 7).

The undistorted D_{3h} trigonal bipyramid found in the room temperature structure of **60a** is thought to represent the true geometry of the triplet spin state isomer, which has a degenerate HOMO [63]. In the other cases, the HOMO of the cluster (which contains the 2 electrons in excess of the 48 required for a "saturated" structure) must be non-degenerate, antibonding, localized along the non-bonding edge of the Co_3 triangle and antisymmetric with respect to the vertical mirror bisecting the long CoCo edge. Therefore it was concluded that the HOMO is the antisymmetric b_1 (C_{2v}) descendent of the doubly degenerate in-plane e' (D_{3h}) MOs [63].

The $Co_3(\mu_3\text{-}S)(\mu_3\text{-}N^tBu)$ cluster complex **76** also exhibits an anomalous temperature dependence of the solid state magnetic susceptibility, with a maximum at 90 K. This was explained with a model where a triplet excited state lies very close to a singlet ground state. The magnetic moment at 300 K of $2.74\mu_B$ indicates that solid **76** has two unpaired electrons at this temperature [63]. However, the analysis of the temperature-dependent NMR shifts points to a paramagnetic isomer as the ground state of **76** in solution (Table 8, $\Delta H < 0$).

The room temperature crystal structure analysis of **76** reveals a small C_{2v}-type deformation of the $Co_3(\mu_3\text{-}S)(\mu_3\text{-}N)$ core, with one shorter and two longer Co—Co bonds. It was pointed out that according to the magnetic susceptibility data the observed structure in the solid must be that of the triplet isomer, despite the isosceles C_{2v} distortion from an equilateral Co_3 triangle [63]. The mean Co—Co distance (2.58 Å) is shorter than in the isoelectronic **60a** (2.69 Å) and **60b** (2.72 Å); Table 7.

This was attributed to the geometrical effect of formally substituting a smaller μ_3-NR ligand in place of μ_3-S and an electronic effect of the electron-withdrawing COOMe substituents [63,81].

The 48 VE dication $[(Cp'Co)_3(\mu_3\text{-}S)_2]^{2+}$ $[\mathbf{60b}]^{2+}$ is diamagnetic in solution. In the crystal, the Co_3S_2 core of $[\mathbf{60b}]^{2+}$ is considered to conform ideally to D_{3h} symmetry, despite some variations in the Co—Co distances.

The 49 VE cluster cation $[\mathbf{60b}]^+$ has a virtually temperature-independent magnetic moment of $1.75\mu_B$, consistent with one unpaired electron. In frozen solution it gives an axial ESR spectrum without resolved ^{59}Co hyperfine structure.

The crystal structures of three salts $[\{(C_5R_5)Co\}_3(\mu_3\text{-}S)_2]^+X^-$ have been determined. The Co_3S_2 cluster cores of the cyclopentadienyl derivatives $[\mathbf{60a}]^+$ have two longer and one shorter Co—Co edges. In contrast, there are two shorter and one longer Co—Co bonds in the Cp′ derivative $[\mathbf{60b}]^+$ (Table 7). The same argument that was used to explain the structure of the 49 VE cluster $[(Cp'Co)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]$ **75b** also applies to the bis(sulphur) bridged monocations $[\mathbf{60}]^+$. A Jahn–Teller distortion splits the doubly degenerate HOMO of e' symmetry (under D_{3h}) into non-degenerate MOs of a_1 and b_1 symmetry (under C_{2v}).

The different distortions are caused by the different nature of the HOMO containing the unpaired electron in $[\mathbf{60a}]^+$ and $[\mathbf{60b}]^+$. In the former case, the HOMO must conform to the a_1 representation (which is symmetric with respect to the vertical mirror bisecting the isosceles Co_3 triangle), whereas in the latter case the HOMO belongs to the antisymmetric b_1 representation [63].

4.5. Comparison of the 46–50 valence electron cluster complexes $[\{(C_5R_5)M\}_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$

From the large body of experimental evidence a relatively clear picture of the structure of and bonding in the bis-μ_3-capped cluster complexes can be drawn. Under idealized C_{3v} (or D_{3h} for $X = Y$) symmetry, the electronically "saturated" 48 VE systems are configurationally stable and diamagnetic. With C_{3v} (or D_{3h}) symmetry, both the "electron-deficient" 46 VE and "excess electron" 50 VE clusters are triplets with degenerate ground states and therefore prone to Jahn–Teller distortions. Several modes of distortion were identified in various systems, such as a movement of the μ_3-capping ligands to μ_3-semibridging or even μ_2 geometry, the lengthening or shortening of one metal–metal bond with respect to the other two and unsymmetrical interactions of the metals with the C_5R_5 ligands.

The first type of distortion is commonly found in the 46 VE dicarbonyl cluster complexes. Capping chalcogen, nitrene and NO ligands are usually symmetrically bonded. In such systems, Jahn–Teller distortions affect metal–metal and metal–(C_5R_5) interactions.

Regardless of the variations in the individual metal–metal distances, their mean values normally agree well within a series of electronically equivalent complexes with capping atoms of similar sizes and sterically innocent ligands (i.e. Cp and Cp′). This was attributed to a balancing of charge densities on the metal atoms [59].

There is a striking correlation of the mean metal–metal distances with the size of the larger of the μ_3-X, μ_3-Y groups. This can be related to the fact that the metal–(μ_3 ligand) interactions are much stonger than the direct metal–metal interactions in these systems. As long as the μ_3 ligands are the same or similar in size, the mean metal–metal distances increase when the electron count increases from 46 to 50 VE. This is an indication that metal–metal antibonding orbitals are populated by the additional electrons. However, starting from various 48 VE bicapped tricobalt clusters, on reduction to the 49 VE systems much larger changes in the Co–Co bond lengths occur than on oxidation to a 47 or 46 VE system.

Important conclusions about the type and symmetry of the HOMO(s) can be drawn when the direction of the Jahn–Teller distortions is analysed. Some examples of this "experimental quantum mechanics" [60] have been given in this and the previous sections of this review.

5. Cluster complexes with μ-alkyne and μ-alkylidyne ligands

The complexes to be discussed in this section have the general composition $[\{(C_5R_5)(d^9\text{-}M)\}_n(CR')_m(L)_x]$ with $n = 3, 4$ and $m = 1{,}2$. These complexes may be viewed as $\{(C_5R_5)M\}_n$ clusters with bridging alkyne (two adjacent CR′ groups) or carbyne ligands (only one CR′, or two CR′ groups separated from each other), or as polyhedral metal carbon clusters with M_nC_m cores.

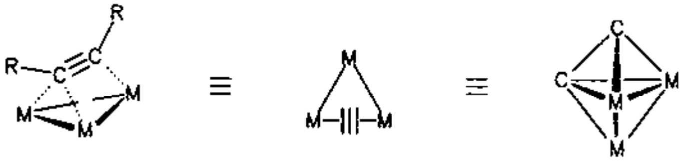
Most abundant are trimetallic systems. In the cases with two adjacent CR′, CR″ groups, the alkynes R′CCR″ can be placed parallel to a metal–metal vector, η^2-$\parallel$ [84], **G**, or perpendicular, η^2-$\perp$, **H**. The η^2-$\parallel$ coordination mode of the alkyne (**G**) is most commonly found. For only a very small number of complexes the η^2-$\perp$ structure **H** has been reported.

In the polyhedral cluster scheme **G** and **H** have respectively *nido* and *closo* M_3C_2 cores. According to PSEP theory, 7 and 6 cluster bonding electron pairs are needed for **G** and **H** respectively. Thus, with $(C_5R_5)(d^9\text{-}M)$ metal fragments (which donate one electron pair each for cluster bonding) and the composition $[\{(C_5R_5)M\}_3(\text{alkyne})]$, the correct electron count is attained only for **H**. The *nido* cluster **G** needs two more electrons for cluster bonding. These may be furnished by additional ligands, such as one CO or two hydrides, resulting in a stoichiometry $[\{(C_5R_5)M\}_3(^2L)(\text{alkyne})]$ or $[\{(C_5R_5)M\}_3(^1L)_2(\text{alkyne})]$.

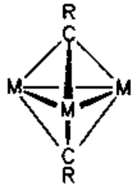
In terms of the more classical 18 VE rule, a complex $[\{(C_5R_5)(d^9\text{-}M)\}_3(^2L)(\eta^2\text{-}\parallel\text{-alkyne})]$ with structure **G** is fully saturated, while a complex $[\{(C_5R_5)(d^9\text{-}M)\}_3(\eta^2\text{-}\perp\text{-alkyne})]$ with structure **H** is unsaturated (formally either one metal with 16 VE, or two metals with 17 VE each). The alkyne is considered to be a four-electron ligand in each case.

Isomers and formal rearrangement products of $[\{(C_5R_5)(d^9\text{-}M)\}_3(\text{alkyne})]$ are the bis(carbyne) (or bis(alkylidyne)) cluster complexes **I**. Here the two cluster carbon atoms are now separated from each other in the two apical sites of a trigonal bipyramid. Since there is no carbon–carbon bond any more, the two carbyne fragments of the former alkyne now donate three electrons each to the metals. **I** is electron precise in terms of both the 18 VE rule and PSEP theory.

G



H



I

Synthetically, the CR′, CR″ groups in the cluster complexes **G**, **H** and **I** are most commonly derived from alkynes, although other sources are possible. Reactions of sources of $(C_5R_5)M$ (M = Co, Rh, Ir) with alkynes have been reported by several groups. Initially there had been some confusion about the correct structures of the trinuclear products, but with the increase in the available experimental evidence (particularly ^{13}C NMR spectroscopy) a clear picture emerged.

5.1. Cluster complexes with μ-(η^2-$\|$-alkyne) ligands: the alkyne complexes $[\{(C_5R_5)M\}_3(CO)(R'CCR'')]$ and related systems

When the complexes $[CpM(CO)_2]$ **7a** (M = Rh) and **28** (M = Ir) were heated with certain alkynes, the cluster complexes $[(CpM)_3(\mu\text{-}CO)(\mu\text{-}RCCR')]$ **77** (M = Rh) and **78** (M = Ir) respectively were isolated together with several mono- and dinuclear complexes and very minor amounts of "$[(CpM)_3(RCCR)]$" (see below) [85–87]. In these reactions the yields of the trinuclear cluster complexes are very low, the main products being hexasubstituted benzenes. The dinuclear intermediates appear to be the dimetallacyclobutenes $[\{Cp(CO)M\}_2(\mu\text{-}RCCR')]$ **79** (M = Rh) and **80** (M = Ir), which were isolated together with **77** and **78**. **79** gives a good yield of **77** when treated with additional **7a** [86].

In contrast, the more unsaturated dirhodium complex $[(CpRh)_2(\mu_2\text{-}CO)\{\mu_2\text{-}(CF_3)_2C_2\}]$ **81** [88] slowly adds **6a,b** or **7a,b** to give two isomers of the tricarbonyl complexes $[(CpRh)_2\{(C_5R_5)M\}(CO)_3\{(CF_3)_2C_2\}]$ (M = Co, Rh). Spectroscopic data reveal the presence of three types of carbonyl groups: terminal, μ_2 and acyl. The structure of the isomer **82** was determined by X-ray crystallography; this indicates a V-shaped arrangement of the three rhodium atoms. Several possible structures were discussed for the other isomer [83].

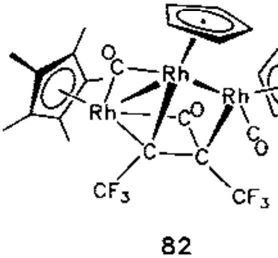
From **81** and $[(C_5R_5)Rh(CO)PR'_3]$ ($PR'_3 = PPh_3$, $PMePh_2$, $P(OMe)_3$) the cluster complexes **77c** and $[(Cp^*Rh)(CpRh)_2(CO)(\{(CF_3)_2C_2\})]$ **83** are obtained, together with dinuclear products resulting from addition of CO or PR_3 to **81**. **83** can also be prepared by oxidative decarbonylation of **82** with Me_3NO [83].

77 can also be obtained from the saturated tricarbonyl cluster complex $[(CpRh)_3(CO)_3]$ **11** and the corresponding alkynes [86,89]. When the unsaturated $[(Cp^*Rh)_3(\mu_3\text{-}CO)_2]$ **41** is treated with acetylene at room temperature, a CO ligand is displaced and the cationic hydrido cluster complex **84a** is formed. Apparently the likely intermediate $[(Cp^*Rh)_3(CO)(\mu\text{-}HCCH)]$ **85** is immediately protonated by the acetylene [46]. Another hydrido cation, **84b**, is formed on protonation of the neutral **77c** with strong acids [86].

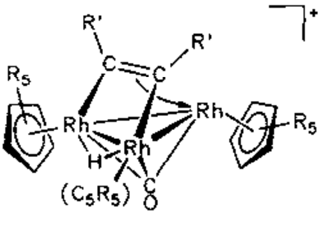
The cobalt analogues of **77** and **78** cannot be prepared directly from **6a** and alkynes. The complex **86a** was isolated in very low yield as one of many products of the reaction of cobalt atoms with cyclopentadiene and hexafluorobut-2-yne [90]. The source of the carbon monoxide is unknown.

Alkynes can be introduced into the trinuclear framework of the unsaturated cluster complexes $[(CpCo)_3(\mu_2\text{-}CO)_2]$ **40**. A wide variety of cluster complexes **86** with monoalkynes, diynes and functionalized alkynes have been prepared (Table 9) [91].

The cobalt and rhodium complexes **86** and **77** can exist as two isomers, **J** with a μ_2 edge bridging carbonyl ligand and **K** with the CO ligand capping the trimetal face which is not occupied by the bridging alkyne. The crystal and molecular structures of **77a** (type **K**, Fig. 17) and **77b** (type **J**, Fig. 18) have been determined [95]. It has been argued [95] that the type of geometry (**J** or **K**) which is adopted by **77** is mainly governed by its HOMO. It can be assumed that the change from a doubly bridging towards a symmetrically triply bridging CO group is dominated by the electronic π*(CO) effect (back donation d(Rh)→π*(CO)). In **K** both the alkyne and the carbonyl ligands compete for the back bonding from the unique rhodium atom Rh1. Electronegative substituents greatly enhance the π accepting properties



82



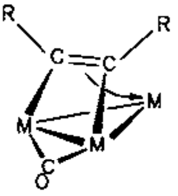
84a, R = Me, R' = H

b, R = H, R' = CF_3

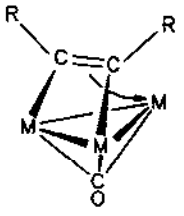
Table 9
IR (ν_{CO}) and structural data for some complexes of the type $[\{(C_5R_5)M\}_3(CO)(R'CCR'')]$ with monoalkynes as bridging ligands

	$[(C_5R_5)M]_3$	R′	R″	ν_{CO} (cm^{-1})	Structure	Fluxionality[a]	Ref.
86a	$(CpCo)_3$	CF_3	CF_3	1698 [c]	K	+	[90]
86b	$(CpCo)_3$	H	H	1680 [b]	K	+	[91]
86c	$(CpCo)_3$	Me	Me	1669 [b]	K	+	[91]
86d	$(CpCo)_3$	Et	Et	1671 [b]	K [d]	+	[91]
86e	$(CpCo)_3$	H	^{t}Bu	1672 [b]	K	+	[91]
86e	$(CpCo)_3$	H	^{t}Bu	1803 [b]	J	–	[91]
86f	$(CpCo)_3$	H	Ph	1680 [b]	K	+	[91]
86g	$(CpCo)_3$	Ph	Ph	1682 [b]	K	+	[91]
86h	$(CpCo)_3$	CH_2OH	CH_2OH	1684 [b]	K	+	[91]
86i	$(CpCo)_3$	CO_2Me	CO_2Me	1694 [b]	K	+	[91]
86k	$(CpCo)_3$	$SiMe_3$	$SiMe_3$	1700 [f]	K	+	[93]
94	$[(CpCo)_3H]^+$	H	H	1845 [d]	J	–	[94]
77a	$(CpRh)_3$	Ph	Ph	1675 [e]	K [d]	+	[85,95]
				1797, 1693, 1678 [b]			[89]
				1847 [e] (1808)[e,h]			[96]
77b	$(CpRh)_3$	C_6F_5	C_6F_5	1810 [c]	J [d]		[85,95]
77c	$(CpRh)_3$	CF_3	CF_3	1710 [c]	K	+	[86]
77c	$(CpRh)_3$	CF_3	CF_3	1820, 1720 [g]	J, K		[86]
77d	$(CpRh)_3$	Me	Me	1680 [c], 1674 [g]	K	+	[86]
77e	$(CpRh)_3$	C_6Cl_5	C_6Cl_5	1810 [c]	J	–	[87]
77f	$(CpRh)_3$	Ph	C_6Cl_5	1680 [c]	K	+	[87]
77g	$(CpRh)_3$	Ph	*p*-Tol	1851, 1794, 1691, 1676 [b]	K	+	[89]
83	$(CpRh)_2(Cp^*Rh)$	CF_3	CF_3	1693 [b], 1711 [i]	K		[83]
84a	$[(Cp^*Rh)_3H]^+$	H	H				[46]
84b	$[(CpRh)_3H]^+$	CF_3	CF_3	1880 [c]	J	–	[86]
78a	$(CpIr)_3$	Ph	Ph	1736 [c]	j	–	[89]
78b	$(CpIr)_3$	C_6F_5	C_6F_5	1760 [c]	j	–	[85]

[a] Fluxional (+) or rigid (–) in solution at ambient temperature. [b] In CH_2Cl_2. [c] In KBr. [d] Crystal structure determined. [e] No solvent given. [f] In hexane. [g] In $CHCl_3$. [h] ^{13}CO. [i] In MeCN. [j] See text.



J



K

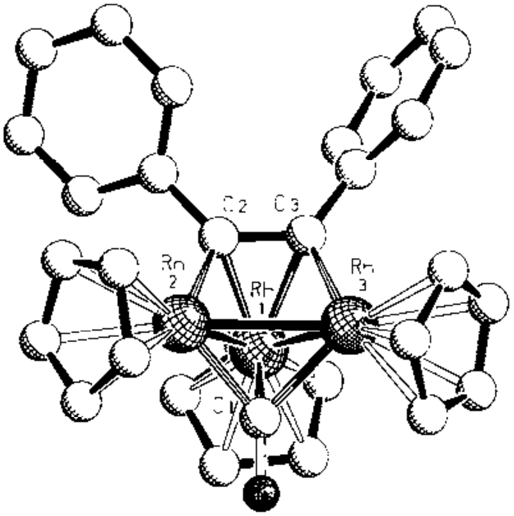


Fig. 17. Molecular structure of [(CpRh)$_3$(CO)(PhCCPh)] **77a**.

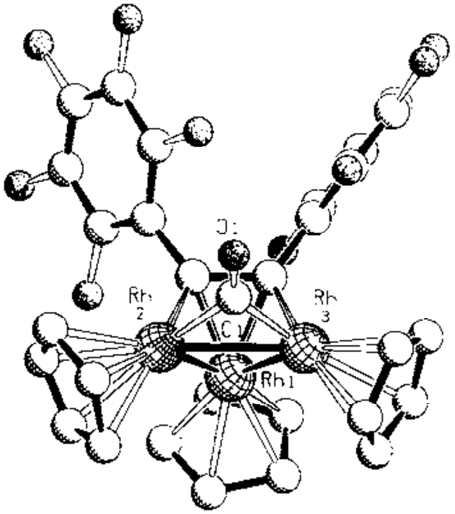


Fig. 18. Molecular structure of [(CpRh)$_3$(CO){(C$_6$F$_5$)CC(C$_6$F$_5$)}] **77b**.

of an alkyne, which therefore dominates the back bonding from **Rh1**. In this case, the Rh1—CO bond is destabilized and consequently geometry **J** will be favoured.

The structures of other derivatives are in line with the above arguments. As judged from their IR spectra **77d** and **77f** adopt structure **K**, while structure **J** is attained for **77e**. For hexafluorobutyne as a ligand the difference in energy between the two alternative structure types is small. **77c** has structure **K** in the solid [86]. In solution, the concentration of form **J** increases with solvent polarity (Table 9). The simultaneous presence of both species in acetone solution was confirmed by the observation of a quartet ($J_{RhC} = 36.8$ Hz) and a triplet ($J_{RhC} = 46.0$ Hz) in the carbonyl region of the ^{13}C spectrum. From the ^{19}F spectrum the relative concentrations of **K**:**J** were estimated as 45:55 at room temperature [86]. **84b**, the protonation product of **77c**, also has structure **J** in solution [86].

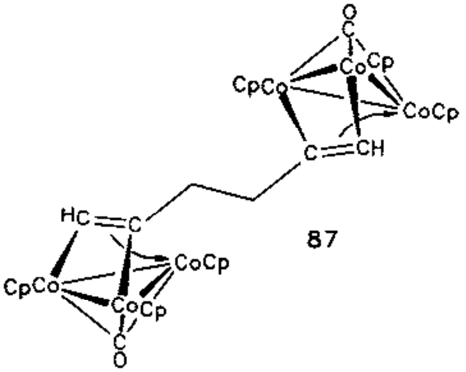
The $(CpRh)_2(Cp^*Rh)_{25}$ complex **83** has structure **K** in CH_2Cl_2 or acetonitrile solution. As judged from the $^{13}CO-^{103}Rh$ coupling constants the carbonyl might be more closely associated with the two CpRh groups than with the Cp*Rh [83]. Since Cp*Rh is a stronger electron donor than CpRh, the difference between **77c** (μ_3-CO in equilibrium with μ_2-CO) and **83** (μ_3-CO) is in accord with the electronic arguments outlined above.

The structure of the cationic **84a** is related to **K**. A crystal structure determination of the tetrafluoroborate reveals a face-capping CO and an edge-bridging hydrido ligand [46].

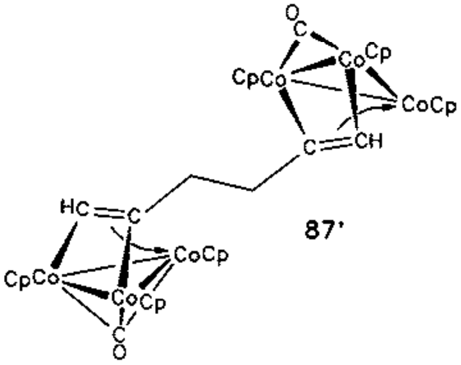
As indicated by the IR and NMR data most of the tricobalt complexes **86** adopt structure **K** in solution (Table 9) [91,93]. In the case of the 3-hexyne derivative **86d** this was confirmed also in the solid state by an X-ray crystal structure determination [91]. However, the *tert*-butylacetylene complex **86e** is first obtained from **6a** and ^tBuCCH as the isomer with structure **J**, and it can then be irreversibly transformed into type **K** by a first-order process at 80–100 °C. Addition of one $[(CpCo)_3(CO)]$ cluster fragment to diynes always results in structure **K**. The second addition yields as coordination geometry either **J** or **K**, depending on the bulk and proximity of the substituents on the triple bond. For example, both the type **K**—type **K** isomer **87** and type **K**—type **J** isomer **87′** have been isolated [91].

The structures of $[(CpIr)_3(CO)(\mu\text{-}RCCR)]$ **78** are not clear. The CO stretches of the diphenyl and the bis(pentafluorophenyl) derivatives lie between the values generally found for complexes of types **J** and **K** (Table 9).

The cluster complexes of type **J** and **K** exhibit distinctly different fluxionality. Generally the μ_2-CO clusters **J** are rigid at room temperature. However, the two Cp resonances in both the ^1H and the ^{13}C NMR spectra of **77b** ($R' = R'' = C_6F_5$) coalesce at +87 °C [96]. From the coalescence of two of the three ^1H resonances of the Cp ligands in the type **K** isomers of **86e** ($R = H$, $R' = {}^tBu$) an energy barrier of



87



87′

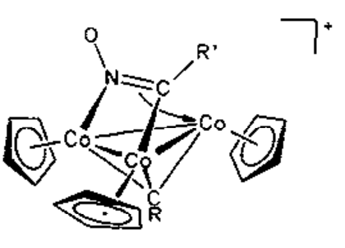
17.5 kcal mol^{-1} was estimated [91]. These observations are consistent with a "windscreen wiper" movement of the alkyne between two CoCo edges of the Co_3 triangle with synchronous movement of the CO ligand between the same two edges. From the observation of nuclear Overhauser effect enhancements between the two exchanging Cp resonances and the ^{t}Bu group in **86e** (type **K**) it can be deduced that only the unsubstituted end of the alkyne is involved in the dynamic process.

At $-87\,°C$ **77a** ($R' = R'' = C_6H_5$) gives a 2:1 pattern for the Cp protons, and the carbon resonance of the Ph^{13}CCPh ligand is an eight-line multiplet, owing to coupling to three inequivalent Rh nuclei [96,97]. This is consistent with a rigid structure on the NMR time scale. The carbon resonance of the Cp rings of this complex at $-90\,°C$ was, however, reported to be a singlet [96], which could only be due to accidental degeneracy.

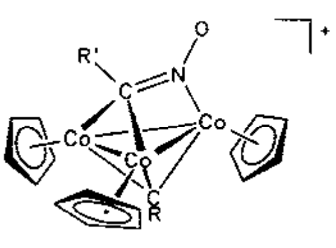
77c ($R' = R'' = CF_3$) in CS_2 gives a sharp singlet for the Cp protons down to $-100\,°C$, indicative of a very high fluxionality of the μ_3-CO isomer. In the Cp region of the low temperature ^{1}H NMR spectrum of **77c** in acetone there are two further peaks in addition to the 2:1 pattern of the μ_2-CO isomer and the sharp resonance of the μ_3-CO complex. The surplus resonances were assigned to a partial freezing out of the μ_3 form to a static conformation stabilized by the polar solvent [86].

A number of very interesting tricobalt clusters with alkyne or heteroalkyne ligands can be obtained from the bis(carbyne) cluster complexes $[(CpCo)_3(\mu_3\text{-}CR)(\mu_3\text{-}CR')]$ **88** (see below). NO^+ inserts into a cobalt–C(carbyne) bond to give the alkanenitrile oxide cluster complexes **89**. With unsymmetrically substituted educts **88** this reaction is completely regiospecific, the NO^+ apparently seeking the more electron-rich cobalt–carbon bond. The crystal structure of **89a** shows a η^2-∥ coordination of the heteroalkyne to the tricobalt cluster, the other face of which is still μ_3 bridged by the remaining carbyne ligand (Fig. 19). In crystalline **89b** the nitrile oxide ligand adopts an alternative conformation, which results in a coordination geometry more like η^2-⊥ (Fig. 20). In solution, the molecules appear to be fluxional down to at least $-80\,°C$ [98].

On attempted deprotonation, NO is expelled and carbyne–carbyne coupling takes place to give an η^2-∥-alkyne ligand. The deinserted NO moves to the metal framework, **90**. As evident from a single ^{1}H NMR resonance for the Cp ligands at $-80\,°C$, **90** is fluxional in solution. On the basis of IR data ($\nu_{NO} = 1420\ cm^{-1}$) a μ_2 bridging position was assigned to the NO ligand [98]. However, in the light of the very good



89a, R = R' = *n*-Bu



89b, R = H, R' = *n*-Pr

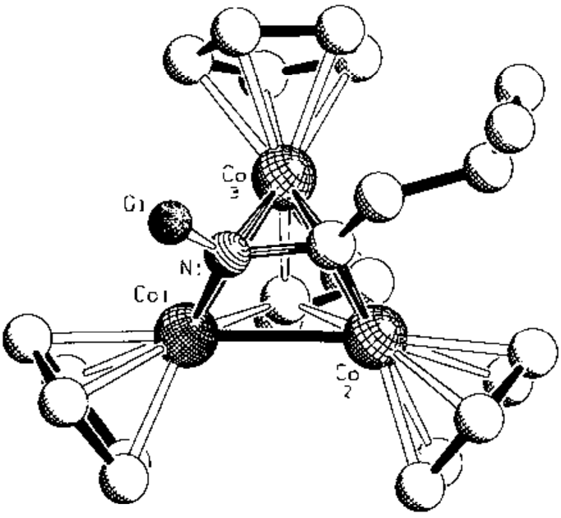


Fig. 19. Molecular structure of $[(CpCo)_3(C^nBu)\{N(O)C^nBu\}]^+$ **89a**.

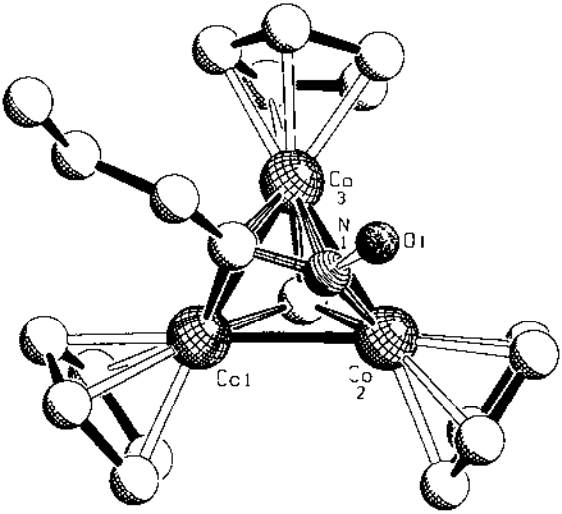
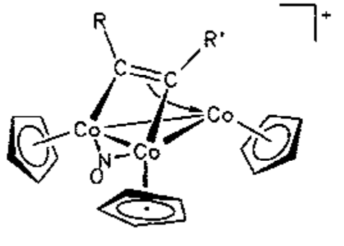


Fig. 20. Molecular structure of $[(CpCo)_3(CH)\{N(O)C^nPr\}]^+$ **89b**.

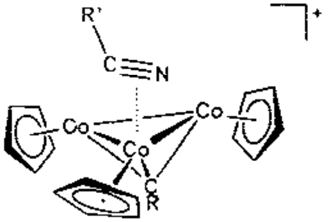
acceptor properties of NO, the positive charge of the complex and the scarcity of reliable vibrational data for bridging NO ligands, a μ_3-NO should also be considered.

When exposed to CO (10 bar), the complexes **90** are deoxygenated. Structure **91** with a μ_3-nitrile ligand was assigned to the products on the basis of IR and ^{13}C NMR spectra. The complexes are also fluxional at room temperature [98].

The protonated bis(methylidyne) tricobalt hydrido cluster cation $[H(CpCo)_3(\mu_3\text{-}CH)_2]^+$ **92a** (c.f. section 5.4.1.2) undergoes CO insertion in one of the



90



91

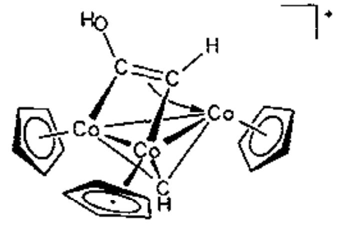
cobalt–C(methylidyne) bonds. For this reaction, coupling of HOC^+ with a cluster-coordinated methylidyne was suggested. The resulting (μ_3-ethynol)(μ_3-methylidyne) complex **93** is non-rigid in solution. In the solid state, the ethynol ligand adopts the η^2-∥ coordination mode (Fig. 21). The molecular structure is quite similar to that of **89a** [94].

In a reaction related to the deinsertion of NO from the alkanenitrile oxide ligand in **89**, CO deinsertion and carbyne–carbyne coupling occur when **93** is treated with CO under pressure. The product **94** was formulated as a Co_2 edge-protonated cluster cation of type **J**. As in the case of the rhodium analogue **84b**, the hydride resonance was not observed in the ^1H NMR spectrum [94].

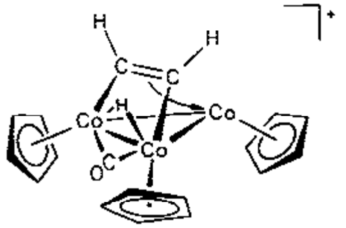
Another interesting complex **95** with a heteroalkyne-like bridging formimidoyl ligand is formed when the unsaturated tetrahydride [$(Cp^*Co)_3H_4$] **1** is heated with *tert*-butyl isocyanide. A transient intermediate was detected when the reaction was carried out at −80 to −35 °C. Structure **96** with one face- and one edge-bridging isocyanide and two edge-bridging hydrides was assigned to the intermediate, which should then undergo insertion of one isocyanide into a Co—H bond, followed by expulsion of the other ^{t}BuNC ligand to give **95**. In the crystal, **95** exhibits a η^2-∥ orientation of the HCN^tBu ligand. The bridging hydride is intermediate between μ_2 and μ_3. A "windscreen wiper" type motion of the formimidoyl ligand with concurrent hydride migration was found to take place in solution [47].

5.2. The alkyne hydrido cluster complexes [$H_2(CpCo)_3(\mu_3\text{-}RCCR')$]

1,2 double CH activation of olefins is another route to cluster-coordinated alkynes. Thus a number of ring-substituted styrenes give the μ-alkyne dihydrido cluster



93



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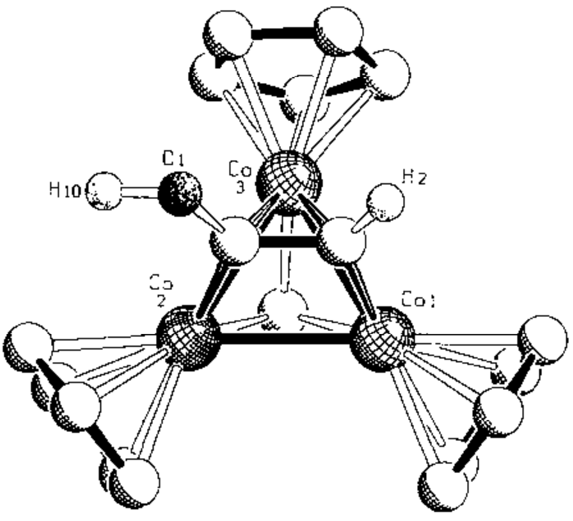
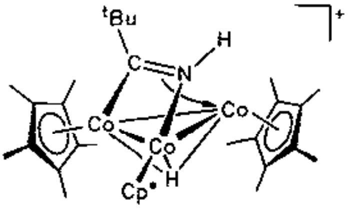


Fig. 21. Molecular structure of $[(CpCo)_3(CH)(HCCOH)]^+$ **93**.



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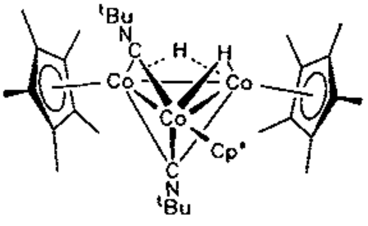
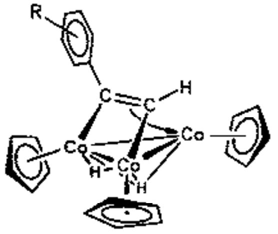
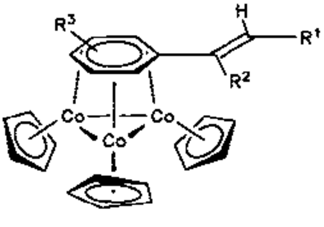


96

complexes **97** when treated with sources of the CpCo fragment [99]. This formally amounts to a twofold oxidative addition of the olefin to a $(CpCo)_3$ cluster. It is not clear at what stage of the cluster formation from the mononuclear CpCo fragments the CH activation takes place. In some cases the isomeric cluster complexes $[(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-arene})$ **98** with face-capping arene ligands are formed together with **97**; in others **98** are the sole products (see below).



97



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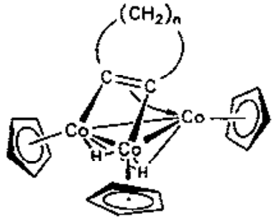
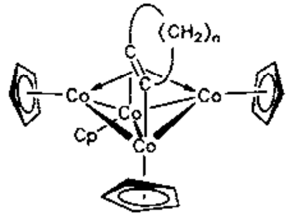


99a, n = 3
b, n = 4
c, n = 5
d, n = 6



100a, n = 3
b, n = 4
c, n = 5
d, n = 6

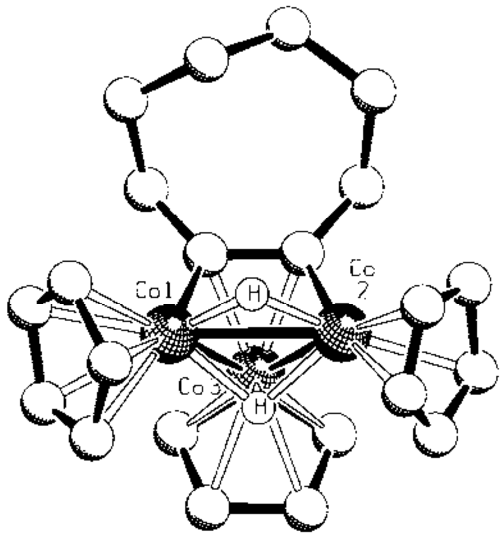


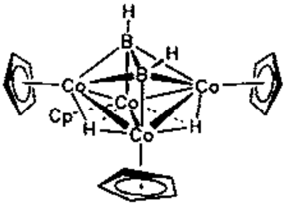
Fig. 22. Molecular structure of [$H_2(CpCo)_3$(*cyclo*-octyne)] **99d**.

The μ-cycloalkyne complexes **99** ($n = 3, 4, 5, 6$) could also be prepared, either from the cycloolefines and [$CpCo(C_2H_4)_2$] **29a** or by using the reductive cleavage of cobaltocene with potassium [100] as a source of CpCo fragments [101]. The tetranuclear μ-cycloalkyne complexes **100** ($n = 3, 4, 5, 6$) are minor products in most of these reactions. In crystalline **97** and **99** the alkyne or cycloalkyne ligands adopt the μ_3-$\|$ coordination mode to the tricobalt clusters. In several X-ray studies the hydrides could be located, one in a μ_3 position on the face of the Co_3 triangle, which is not occupied by the alkyne, the other bridging the unique CoCo edge (Fig. 22) [5,99,101].

In solution **97** and **99** are fluxional. Low energy dynamic processes involve rotation of the alkyne on top of the tricobalt cluster (probably in a "windscreen wiper" fashion) with concurrent shifts of the μ_2-hydride along the Co_2 edges. To explain qualitatively the observed temperature dependence of the NMR spectra, only one of the two processes is required to slow down on lowering the temperature. Therefore no conclusion could be reached as to whether hydride migration and alkyne rotation are independent dynamic processes or are coupled to each other. Another process, detectable on the NMR time scale above 300 K, interconverts μ_2- and μ_3-hydrido ligands [99,101].

X-ray crystal structure analyses showed **100** to have tetracobalt butterfly frameworks with $\mu_4-\eta^2$ ($\sigma-\pi-\sigma-\pi$) coordination [102] of the cycloalkynes (Fig. 23) [101,103]. Alternatively, this structure can be viewed as a *closo* octahedral 1,2-C_2Co_4 polyhedral cluster.

A metal-rich cobaltaborane [$H_2(CpCo)_4(\mu_4$-η^2-HBBH)] **101** has been reported [104], which is closely related to **100**. **101** is obtained in low yield from [$CpCo(PPh_3)_{2-x}(C_2Et_2)_x$] ($x = 0, 1$) and excess $BH_3 \cdot$thf. The Co_4 butterfly frameworks of **101** and **100** are quite similar. In an X-ray crystallographic study two hydrides were found bridging the two Co_3 faces of the Co_4B_2 octahedron (Fig. 24). Unlike in other metallaboranes the borane fragment is not hydrogen bridged. This structure is retained in solution. Thus the borane ligand may be formally considered $(B_2H_2)^{2-}$, isoelectronic to an alkyne.



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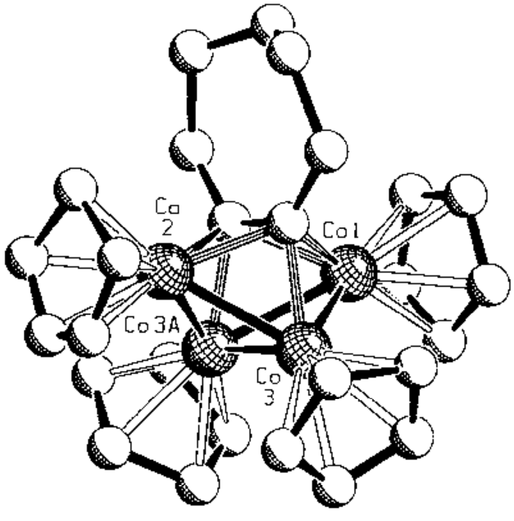


Fig. 23. Molecular structure of [$(CpCo)_4$(*cyclo*-heptyne)] **100c**.

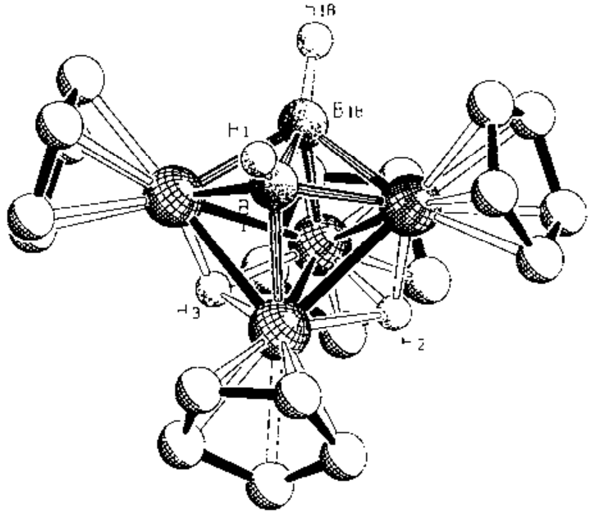


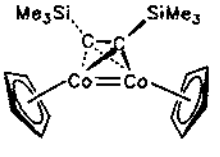
Fig. 24. Molecular structure of $[(CpCo)_4(H)_2(HBBH)]$ **101**.

5.3. *Cluster complexes with μ-(η²-⊥-alkyne) ligands*

There are only a very few cluster complexes in the literature where structure **H** (η^2-⊥-alkyne) has been proven unequivocally by spectroscopic data or a crystal structure analysis [105]. Some claims for such cluster complexes, based on the analogy with the crystallographically characterized $[\{(CO)_3Fe\}_3(\eta^2\text{-}\perp\text{-}Ph_2C_2)]$ [106], later turned out to be incorrect, the complexes in question belonging to the bis(μ_3-carbyne) clusters of type **I**. For example, the complexes originally formulated [85] as $[(CpM)_3(\mu RCCR)]$ (M = Rh, R = Ph; M = Ir, R = C_6F_5) had to be reformulated [89,107] as $[(CpM)_3(\mu_3\text{-}CR)_2]$ on the basis of their ^{13}C NMR spectra.

When the Jonas reagent $[CpCo(C_2H_4)_2]$ **29a** was treated with excess $(Me_3Si)_2C_2$ the transient mononuclear complex $[CpCo(\eta^2\text{-}C_2H_4)\{\eta^2\text{-}(Me_3Si)_2C_2\}]$ was formed, which on removal of solvent transformed into the dimetallatetrahedrane **102** [93]. The X-ray crystal structure of this unsaturated complex revealed a very short Co—Co distance, consistent with a cobalt–cobalt double bond, as expected from the 18 VE rule. **102** takes up another CpCo group from **29a** to give the trinuclear cluster complex **103**. At room temperature, **103** only gave ^1H NMR resonances of equivalent Cp and $SiMe_3$ groups, indicating a fluxional $(Me_3Si)_2C_2$ ligand. The low temperature ^1H and ^{13}C NMR spectra (2:1 patterns for the Cp rings) are consistent with the η^2-⊥-alkyne structure **H**, although only one of the two expected sp carbon resonances could be detected, and an apparent hindered rotation of one $SiMe_3$ group complicates the spectrum.

When heated, **103a** slowly converts into the bis(carbyne) cluster complex $[(CpCo)_3(\mu_3\text{-}CSiMe_3)_2]$ **88a**. CO is readily added to give the monocarbonyl μ-alkyne cluster complex **86k**. As judged from its CO stretch (1700 cm^{-1}) **86k** has structure **K** with a μ_3-CO ligand [93].



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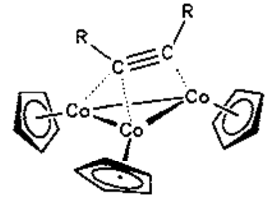


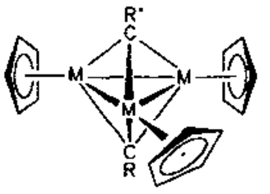
103a, R = $SiMe_3$
b, R = CF_3

From the above-mentioned reaction of Co atoms, cyclopentadiene and hexafluorobut-2-yne some material of the composition $[(CpCo)_3\{(CF_3)_2C_2\}]$ was obtained together with many other products and, quite significantly, $[(CpCo)_3(\mu_3\text{-}CO)(F_3CC_2CF_3)]$ **86a** [90]. From the NMR data (only one singlet in the room temperature ^1H and ^{19}F spectra; a 2:1 pattern in the ^1H NMR spectrum at −78 °C) structure **103b** is likely for the carbonyl-free cluster complex. As explained above, **103** is similar to a Co_3C_2 trigonal bipyramid with the carbon atoms in an apical and an equatorial site, in contradiction with the formulation given in the original publication (the two carbon atoms in equatorial sites) [90].

5.4. Cluster complexes with μ_3-alkylidyne ligands

5.4.1. Systems which are mainly derived from alkynes: the bis(alkylidyne) cluster complexes $[\{(C_5R_5)M\}_3(\mu_3\text{-}CR')(\mu_3\text{-}CR'')]$

5.4.1.1. Syntheses and structures. The most common CpM clusters with μ_3-carbyne ligands are of the type $[(CpM)_3(\mu_3\text{-}CR)(\mu_3\text{-}CR')]$ (M = Co, Rh, Ir) **I**. In most cases, but not exclusively, the carbyne (alkylidyne) ligands stem from the cleavage of an alkyne at some stage of the assemblage of the metal cluster. This can be achieved by reaction of the alkynes with $[CpM(CO)_2]$ **6a** (M = Co), **7a** (M = Rh), **28a** (M = Ir) under forcing conditions. For M = Rh, Ir and non-activated alkynes RCCR the cluster complexes $[(CpM)_3(\mu_3\text{-}CR)_2]$ **104** (M = Rh) and **105** (M = Ir) were obtained in low yields [85,89]. From $(Et_2N)_2C_2$ and **6a** and **7a** the bis(aminocarbyne) tricobalt and trirhodium cluster complexes **88b** (R = R′ = NEt_2) or **104a** (R = R′ = NEt_2) respectively could be prepared in moderate yields [108]. Later it was discovered that the yields of **88** can be improved dramatically when the reactants are added very slowly to boiling decalin under nitrogen purge [109]. The reaction is relatively



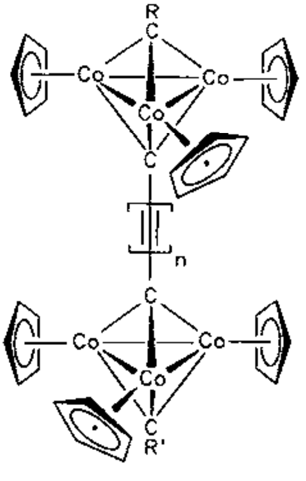
88, M = Co
104, M = Rh
105, M = Ir

general, and some functionalized alkynes can be used. For example, from mono- and bis(ferrocenyl)acetylene the ferrocenyl-substituted derivatives **88c** (R = Fc, R′ = H) and **88d** (R = R′ = Fc) were obtained [62]. The tricobalt clusters **88** are also formed when neat mononuclear (CpCo(PPh$_3$)(η^2-RCCR′)] is heated just above the melting point [110].

Silylated alkynes are transformed in many ways during the reaction with **6a** [92,109]. For example, in neat (Me$_3$Si)$_2$C$_2$ only traces of the cluster complex **88e** (R = SiMe$_3$, R′ = C$_2$SiMe$_3$) are formed. Mononuclear cyclobutadiene complexes are the main products, together with appreciable amounts of tetrakis(trimethylsilyl)butatriene.

Using the infusion method in decalin, one and two (CpCo)$_3$ clusters are formally inserted into the carbon–carbon triple bonds of bis(trimethylsilyl)butadiyne (products **88e** (R = SiMe$_3$, R′ = C$_2$SiMe$_3$) and **106a**). In addition, small amounts of 107 and as many as four other trinuclear cluster complexes are formed as the products of alkyne coupling and decoupling, dimerization and hydrolysis [109].

Other systems with two bis(carbyne)(CpCo)$_3$ clusters, which are linked via an (oligo) acetylenic chain, could be prepared by CuCl · TMEDA-catalysed self-coupling of mono[(CpCo)$_3$(μ_3-carbyne)(μ_3-carbynyl)]-substituted precursors. The butadiyne linked system **108** was obtained from **88f** (R = SiMe$_3$, R′ = C$_2$H) which was generated in situ from **88e** (R = SiMe$_3$, R′ = C$_2$SiMe$_3$) and 1% KOH. Similarly the unstable **109** was prepared from **88g** (R = SiMe$_3$, R′ = (C$_2$)$_2$SiMe$_3$) [111].



106a, n = 0, R = R′ = SiMe$_3$

b, n = 0, R = SiMe$_3$, R′ = C$_2$SiMe$_3$

107, n = 1, R = R′ = SiMe$_3$

108, n = 2, R = R′ = SiMe$_3$

109, n = 4, R = R′ = SiMe$_3$

Flash vacuum pyrolysis (FVP) of some unsymmetrically substituted derivatives of **88** resulted in carbyne–carbyne coupling with re-formation of the free unsymmetrical alkynes without scrambling of the individual carbyne units [112]. In the double-deck system **106b** (R = $SiMe_3$, R′ = C_2SiMe_3) with one "internal" and one "terminal" $(CpCo)_3$ deck, a very remarkable "deck shift" reaction takes place on heating (FVP (500–550 °C, approximate $E_A = 41$ kcal mol^{-1}) or pristane solution (290 °C)). The product is **107** with two "terminal" $(CpCo)_3$ decks. Using the methylcyclopentadienyl or pentadeuterocyclopentadienyl and triethylsilyl derivatives, it could be shown by cross-over experiments that the deck shift is intramolecular. The rearrangement is reversible, **107** being thermodynamically more stable. As a side product, the "single deck" cluster **88h** (R = R′ = C_2SiMe_3) is formed, presumably via $(CpCo)_3$ deck extrusion from **107** followed by a deck shift to the "internal" position [112].

The X-ray crystal structures of several derivatives of **88** have been determined (Table 10). Usually, the planes of the Cp rings are nearly perpendicular to the Co_3 plane, and the axis $R-C_{apex}$ is also at a right angle to that plane (Fig. 25). In **88c** (R = H, R′ = Fc) the ferrocenyl substituent is tilted back such that the bond which connects it to the apical cluster carbon atom is bent away by 10° from the pseudo-threefold axis of the Co_3C_2 cluster. The C_5H_4 ring plane of the ferrocenyl substituent is at 173° to that bond. An electronic interaction between the ferrocenyl and the cluster centres was proposed as the reason, the former behaving as a π donor [115]. This would lead to a removal of the degeneracy of the two carbyne π orbitals, thus facilitating the observed distortion [115].

The μ-tolan and μ-phenyl-*p*-tolylacetylene monocarbonyl trirhodium and triirid-

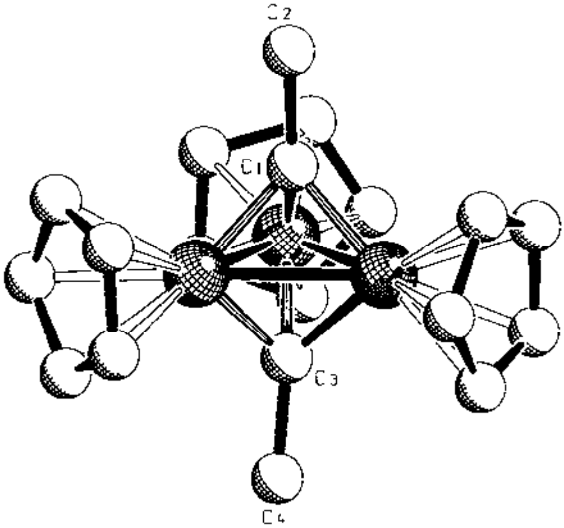


Fig. 25. Molecular structure of $[(CpCo)_3(CMe)_2]$ **88l**.

Table 10
Structural data for some complexes of the type $[\{(C_5R''_5)Co\}_3(CR)(CR')]$ and related systems

	R″	R	R′	*d*(Co—Co) (Å)	*d*[Co—C(R)] (Å)	*d*[Co—C(R′)] (Å)	Ref.
88m	H	H	H	2.35	1.84	1.84	[113]
88l	H	Me	Me	2.354(1)–2.389(1)	1.838(4)–1.861(8)	1.812(9)–1.897(9)	[114]
88t	H	Me	CO_2Me	2.366(1)–2.393(2)	1.873(8)–1.881(7)	1.865(5)–1.869(8)	[110]
88e	H	$SiMe_3$	C_2SiMe_3	2.383(9,14)[a]	1.873(9,16)[a,b]		[92]
108	H	$SiMe_3$	$C_4[C(CpCo)_3C]SiMe_3$	2.366(4)–2.380(4)	1.85(2)–1.89(2)	1.85(2)–1.88(2)	[111]
88c	H	H	Fc	2.365(2)–2.394(2)	1.842(4)–1.858(4)	1.870(3)–1.880(4)	[115]
118	Me	Me	Me	2.437(1)	1.873(3)	1.873(3)	[116]
51	H	$OTiCp_2$	$OTiCp_2$	2.385(2)–2.404(2)	1.87(1)–1.91(1)	1.87(1)–1.89(1)	[50]
112	H	Ph[c]	Ph[d]	2.473(2)–2.561(1)	2.018(8)–2.065(8)[e]	2.082(2)–2.100(2)[f]	[117]
111	Me	H[c]	H[c]	2.507(1)	2.013(8)[c,g]	1.985(6)[c,g]	[118]

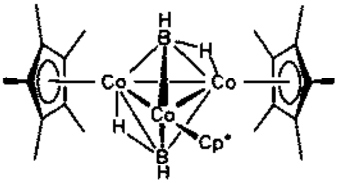
[a] Mean value, with average and maximum deviations in parentheses. [b] *d*[Co—C(R)] and *d*[Co—C(R′)]. [c] μ_3-BR. [d] μ_3-PR′. [e] Co—B. [f] Co—P. [g] Hydrogen bridged.

ium cluster complexes **77** and **78** are cleanly converted into the dialkylidyne cluster complexes **104** and **105** respectively by FVP at 500–560°C [89]. These reactions proceed without fragmentation of the trimetallic frameworks and without exchange of the CR fragments. A theoretical analysis of various possible reaction pathways using the EHMO method ruled out the unsaturated $[(\mathrm{CpIr})_3(\eta^2\text{-}\perp\text{-alkyno}$l **110** as an intermediate. Instead, rearrangement of **77** to give another intermediate with the alkyne bridging a dimetal edge of the cluster was proposed. In this reaction channel the CO ligand remains coordinated until the alkyne is cleaved [89]. However, as shown by the transformation of **103a** into **88a** ($\mathrm{R = R' = SiMe_3}$), the presence of an additional donor ligand is not a prerequisite for the cleavage of an alkyne on a $(\mathrm{CpM})_3$ cluster.

It is interesting to compare the structures of $[\{(\mathrm{C_5R_5})\mathrm{Co}\}_3(\mu_3\text{-CR})_2]$ with those of two isoelectronic heteroboranes, the tricobalta- and tricobaltaphosphapentaboranes(5), $[(\mathrm{Cp^*Co})_3(\mu\text{-H})_2(\mu_3\text{-BH})_2]$ **111** and $[(\mathrm{CpCo})_3(\mu_3\text{-BPh})(\mu_3\text{-PPh})]$ **112**. $\mathrm{LiBH_4}$ reduction of $[(\mathrm{Cp^*CoCl})_2]$ proceeds smoothly, via a transient intermediate, to give 30% of **111** as the major boron-containing product [118]. **112** is obtained from $[\mathrm{CpCo(PPh_3)_2}]$ and $\mathrm{BH_3 \cdot thf}$ in low yield [117]. Compared with **88** the two three-electron ligands CR have been replaced by two two-electron ligands BR (in **111**) or by a BR ligand and a four-electron ligand PR (in **112**). In **111** the two additional electrons needed to make up the 48 VEs required for the saturated structure are furnished by two CoB edge or $\mathrm{Co_2B}$ face bridging *endo* hydrogen atoms.

The molecular geometry of both heteroborane cages was determined by crystal structure analyses. As expected, *closo* trigonal bipyramids with all the cobalt atoms in the equatorial sites were found (Figs. 26 and 27). Unfortunately, the bridging hydrogen atoms in **111** were not located and would necessarily be disordered. The mean Co–Co distance in **112** is 0.15 Å longer than that in the bis(carbyne) complexes. This is another example of the control of metal–metal distances by the larger of the two capping ligands (compare Section 4.5). Co–(μ_3-B) and Co–(μ_3-C) distances also differ by more than expected. This is probably related to **112** being more polar and to the presence of the *endo* hydrogen atoms in **111**.

5.4.1.2. Electrochemistry, electronic structure and reactivity of bis (μ_3-alkylidyne) cluster complexes. The electrochemistry of a number of derivatives $[(\mathrm{CpCo})_3(\mathrm{CR})(\mathrm{CR'})]$ **88** has been investigated [61,62,114]. The current–voltage response was found to depend on the working electrode material. On mercury, complicated cyclic voltammograms were obtained, indicative of strong interactions



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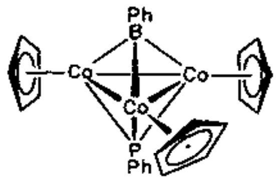

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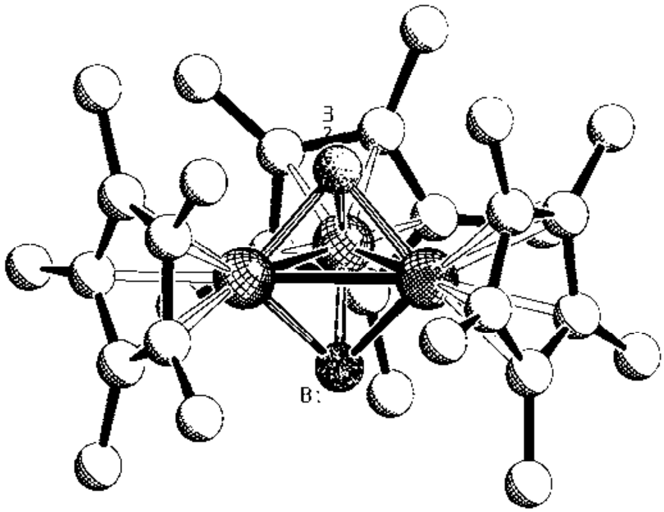


Fig. 26. Molecular structure of $[(Cp^{*}Co)_3(H)_2(BH)_2]$ **111**.

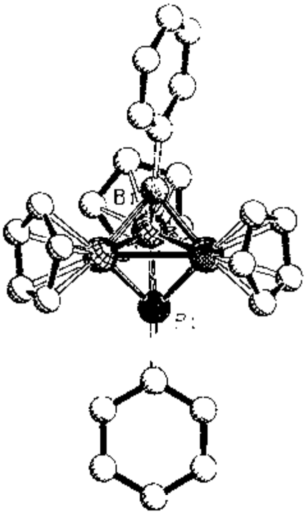


Fig. 27. Molecular structure of $[(CpCo)_3(BPh)(PPh)]$ **112**.

of the generated species with the electrode. On platinum, reversible one-electron oxidations are generally found at potentials around +0.3 V (vs. SCE). Preparative oxidation (with electrochemical methods, or addition of silver ion) of **88i** (R = H, R′ = Me_3Si), **88j** (R = H, R′ = Ph) and **88k** (R = R′ = Ph) gave the corresponding cations $[\mathbf{88}]^{+}$, which could be isolated as air-stable hexafluorophosphates [62].

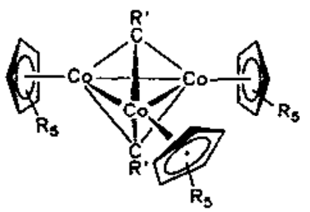
Reduction of some neutral cluster complexes at potentials around −1.1 to −1.9 V was reported to be irreversible even at −70 °C [62]. However, a reversible one-electron wave was found in the cyclic voltammogram of **88l** ($R = R' = Me$) at -1.95 V [114]. Also, the radical anion $[(CpCo)_3(CPh)_2]^-$ [**88k**]$^-$, generated by potassium reduction, was stable for weeks in solution at room temperature [61]. An attempt has been made to correlate the oxidation and reduction potentials of various derivatives with the electron donating and accepting properties of the apical substituents R and R′ [62].

The ESR spectrum of [**88k**]$^-$ ($R = R' = Ph$) has been analysed in some detail [61]. An axial g tensor is observed in frozen solution ($g_\parallel = 2.129$, $g_\perp = 1.987$). The unique axes of the g and hyperfine splitting tensors (three magnetically equivalent ^{59}Co nuclei) are parallel to each other. From the large magnitudes of the ^{59}Co hyperfine coupling constants, the large deviation of g from the free electron value and the line shape it was concluded that the odd electron orbital of [**88k**]$^-$ is non-degenerate and of predominantly metal character. A qualitative MO scheme for **88** with D_{3h} symmetry was suggested which had a non-degenerate LUMO (a_2') above the degenerate e' combination of metal d orbitals (see the general bonding scheme for cluster complexes of the type $[(CpM)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$, as discussed in Section 4.1). In the cation radical [**88**]$^+$ there would be three electrons in a degenerate set of orbitals (e'), leading to a Jahn–Teller distortion. This expectation is consistent with the ESR spectra of several cationic derivatives [**88**]$^+$ (very broad signals at $g = 2.2$) [61,62].

The cationic species exhibit transitions in the near-IR region. These could be explained using the same qualitative MO scheme [62].

As expected, reduction as well as oxidation of the cluster complexes becomes easier on going from the trinuclear **88l** to the tetranuclear $[H(CpCo)_4(CCH_3)]$ **113a** (see Section 5.4.2) (-1.68 V and -0.28 V respectively) [114].

A number of derivatives of **88** with redox-active organometallic substituents at the apical carbon atom were synthesized, and their redox properties studied [62,111,115]. The alkyne-linked bis(Co_3C_2–cluster) systems **107** and **108** both give two oxidation waves in the cyclic voltammogram, separated by about 140 mV. This behaviour and intense bands at 610–635 nm (the latter causing a green as opposed to the normal purple colour) point to an electronic interaction between the cluster units (delocalized mixed-valence monocations) [111].



88l, $R = H$, $R' = Me$

88l', $R_5 = H_4Me$, $R' = Me$

88s, $R = H$, $R' = CH_2Ph$

Two and three reversible one-electron oxidation waves were observed for the ferrocenyl-substituted bis(carbyne) clusters **88c** (R = H, R′ = Fc) and **88d** (R = R′ = Fc) respectively. This behaviour was interpreted as resulting from an oxidation of the cluster followed by an oxidation of one or two ferrocenyl substituent(s). The fact that the two ferrocenyl groups in the symmetrical **88d** are oxidized at two distinct potentials (300 mV apart) is considered evidence that the two equivalent ferrocenyl centres are strongly interacting in the mixed-valence ions. While **88c**$^+$ and **88c**$^{2+}$ could be isolated after Ag^+ oxidation of **88c** (R = H, R′ = Fc), the three possible cations of **88d** (R = R′ = Fc), namely **88d**$^+$, **88d**$^{2+}$ and **88d**$^{3+}$, were only obtained as an equilibrium mixture and identified by optical spectroscopy. From the near-IR transitions class II (according to Robin and Day [119]) mixed valence behaviour of the monocations was inferred [62].

The carbyne carbon atoms in **88** are formally nucleophilic. For example, **88m** (R = R′ = H) can be halogenated with IBr to give a mixture of all five possible halogenated derivatives (R, R′ = H, Br, I) [120]. With I_2 at 0 °C **88m** forms a precipitate, presumably a charge transfer complex [62,120]. At higher temperatures and in the presence of oxygen and water, the mono- (R = H, R′ = I) and diiodo (R = R′ = I) derivatives are formed [120]. The diphenyl and di(*n*-butyl) derivatives **88k** and **88n** could not be iodinated. Silver ions in MeOH remove iodide from **88o** (R = H, R′ = I); a quantitative yield of the methoxycarbyne complex **88p** (R = H, R′ = OMe) was isolated. This reaction probably proceeds via an electrophilic attack by silver ion, and not by an oxidation of the cluster complex followed by nucleophilic attack by OMe^- [62]. Refluxing the bis(*n*-butyl) derivative **88n** (R = R′ = ^{n}Bu) in air-flushed C_6H_{12}—EtOH for several weeks resulted in the oxidation of one butyl group to give the alcohol **88q** (R = ^{n}Bu, R′ = CH(OH)^{n}Pr) and the ketone **88r** (R = ^{n}Bu, R′ = C(O)^{n}Pr) [120].

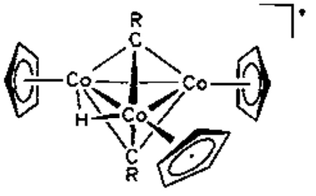
Some derivatives of **88** (R = R′ = Me, ^{n}Bu, H) are protonated by strong acids [94,120,121]. The methylidyne hydrogen atoms are rapidly exchanged when **88m** (R = R′ = H) or **88i** (R = $SiMe_3$, R′ = H) is treated with CF_3COOD. Therefore, protonation at the apical carbon atom was initially assumed [109]. However, the observation of temperature-independent ^1H resonances at very high field is more consistent with the association of the proton with the metal framework, **92**. The hydrido cations are strong acids and very fluxional in solution, with the protons probably moving around the three CoCo edges of the cluster. Any cationic species with protonated apical carbon atoms or Co—C(apex) bonds [122] are not detectable and may exist only as reactive intermediates.

The diphenyl derivative **88k** (R = R′ = Ph) was reported to give benzene and toluene on treatment with hot CF_3SO_3H [109]. In marked contrast to the isoelectronic **88**, $[(Cp^*Rh)_3(\mu_3\text{-}CH)_2]$ **104b** is degraded when treated with acid. With CF_3COOH the mononuclear $[Cp^*Rh(O_2CCF_3)_2]$ is formed, and methane is released essentially quantitatively [123].

The protonated cluster complexes **92** are activated and may undergo further reactions. The insertions of the electrophiles NO^+ and HCO^+ into a cobalt–C(carbyne) bond of **88** have been already described above section 5.1. The latter reaction also makes use of the higher reactivity of **88** after protonation.

It was noted that an alkyne group adjacent to the C(CpCo)$_3$CR moiety (as in **88e** (R = Me$_3$Si, R′ = C$_2$SiMe$_3$) or **88f** (R = Me$_3$Si, R′ = C$_2$H)) does not react with [CO$_2$(CO)$_8$]. **88g** (R = SiMe$_3$, R′ = (C$_2$)$_2$SiMe$_3$) exclusively added the cobalt carbonyl at the thermal alkyne function to give **114**. The regiospecificity of this reaction was attributed to electronic rather than steric factors [111].

When exposed to elemental sulphur or selenium, the μ$_3$-carbyne ligands in **88** couple to give a series of cyclopentadienylcobaltdithiolenes **115** and -selenolenes **116** in almost quantitative yield. As a byproduct of the reactions with sulphur, the bis(sulphido) capped cluster complex **60** was formed in low yield [113,124]. By means of cross-over experiments an intramolecular course of the coupling reaction was established, and a possible participation of the free alkynes was ruled out [113]. However, the molecularity of this process with respect to the CpCo unit could not be established. A cross-over experiment using the Cp-labelled cluster complex [(Cp′Co)$_3$(μ$_3$-CC$_6$H$_5$)$_2$] and the carbyne-labelled cluster complex [(CpCo)$_3$(μ$_3$-CC$_6$H$_5$)(μ$_3$-CC$_6$D$_5$)] revealed complete scrambling of both labels. Unfortunately, this result is not conclusive, since it could be shown that exchange



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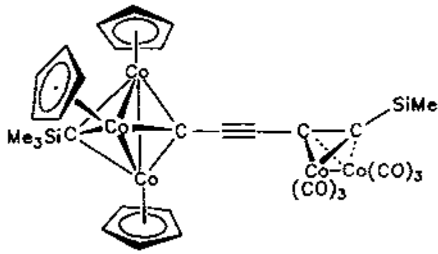

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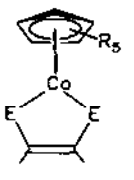
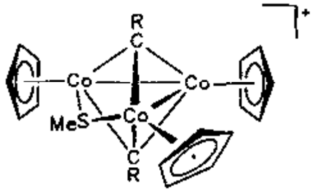


115, E = S

116, E = Se



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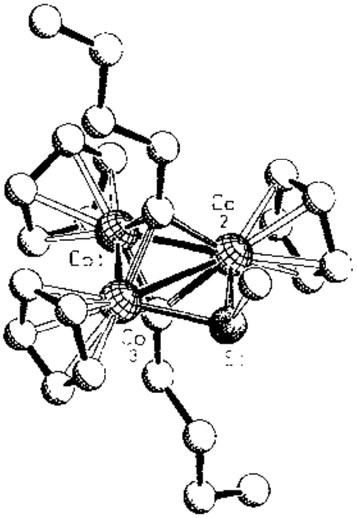


Fig. 28. Molecular structure of $[(CpCo)_3(C^nBu)_2(SMe)]^+$ **117**.

of the Cp labels takes place on the level of the cobaltadithiolenes [113]. Sulphur is thought to attack **88** electrophilically. Indeed, SMe^+ attacks a Co—Co bond in **88**. The Co_2-edge-bridged cation **117** [113] is formed in these reactions. This reaction is similar to the above-mentioned protonation of **88**, where hydrido cations with μ_2-hydrides are obtained.

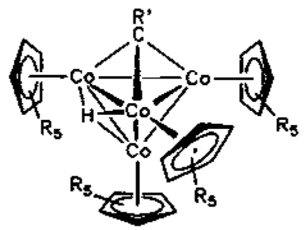
As is evident from a crystal structure determination the SMe-bridged Co—Co bond has been opened in **117** (d(CoCo) = 2.738 Å [113], compared with about 2.35–2.40 Å in the parent systems) (Fig. 28). Like **88**, **117** is converted to **115** when heated with sulphur [113].

5.4.2. Systems which are derived from olefins: μ-alkylidyne hydrido cluster complexes

An alternative source of ethylidyne fragments to be incorporated into a $[(C_5R_5)Co]_n$ cluster can be ethylene. When the Jonas reagent **29a** is heated above 50 °C [51,55], or treated with dihydrogen at 0–20 °C [114], transformation of some of the coordinated ethylene into ethylidyne takes place and a series of mono- and bis(ethylidyne) cluster complexes is formed. The main product of these reactions is the tetranuclear cluster complex **113a**, which still contains both fragments (ethylidyne and H) of the former ethylene in its coordination sphere. Minor products are the trinuclear **88l** (R = R′ = Me), the tetranuclear $[(CpCo)_4(CMe)_2]$ and the pentanuclear $[H(CpCo)_5(CMe)]$, the last two could not be isolated but were detected by field desorption mass spectroscopy [114]. The gases present at the end of the thermal reaction were only ethylene with traces of H_2 [55].

During the hydrogenation of $[Cp'Co(C_2H_4)_2]$ **29b** the trimetallic **88l′** is formed in higher yield but the tetrametallic **113b** is still the main product. No cluster complexes of a nuclearity higher than four were detected [114].

Both **113a** (Fig. 29) and **88l** (Fig. 25) were structurally characterized by X-ray



113a, R = H, R' = Me

b, R_5 = H_4Me, R' = Me

121, R = H, R' = CH_2Ph

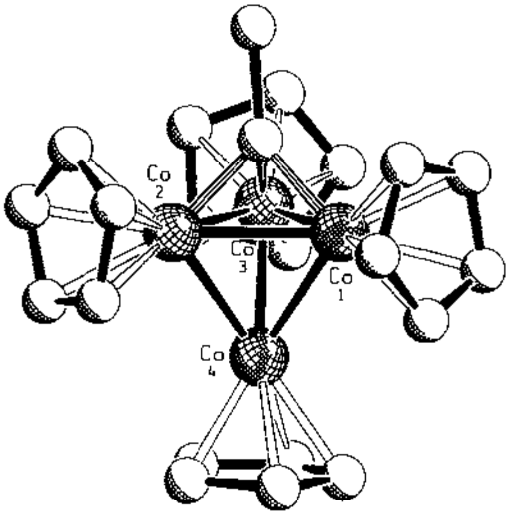


Fig. 29. Molecular structure of [$H(CpCo)_4(CMe)$] **113a**.

crystallography [51,114]. As expected from PESP theory, their cluster cores are *closo* trigonal bipyramids, with the quarternary ethylidyne carbon atom(s) in apical positions, thus putting the carbon atoms in the sites with lowest connectivity. The hydride ligand in **113a** could not be located in the X-ray studies, but from geometrical arguments and potential energy calculations [114] a μ_3-Co_3 face-capping site can be assumed.

The complexes **113a,b** are fluxional in solution. The dynamic process, which involves migration of the hydride ligand across all the three open tricobalt faces of the cluster core, can be slowed down at low temperature ($\Delta G^{\ddagger}(225\ K) = 46\ kJ\ mol^{-1}$ for **113a** [121]) [114].

With strong Brønsted acids stepwise protonation of **113a** to give the mono- [**113a** + H]$^+$ and dication [**113a** + 2H]$^{2+}$ takes place. This reaction exhibits a strong normal kinetic deuterium isotope effect. As apparent from the ^1H NMR spectra, the additional protons occupy hydridic Co_3 face-capping sites in the cations. The crystal structure of $[\mathbf{113a}+X]^+[(CF_3COO)_2X]^-$ ($X = H$, D) was determined. However, only one of the two hydrido ligands could be located unambiguously [121].

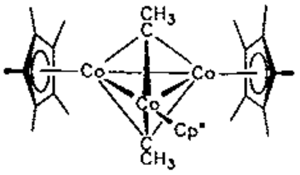
As **113a**, $[\mathbf{113a}+H]^+$ exhibits hydride mobility in solution ($\Delta G^{\ddagger}(203\ K) = 41\ kJ\ mol^{-1}$). In contrast, $[\mathbf{113a}+2D]^{2+}$ appears to be non-fluxional. Therefore it was concluded that the hydride migration processes operative in **113a** and $[\mathbf{113a}+H]^+$ seem to need at least one "open" tricobalt face [121].

$[Cp^*Co(C_2H_4)_2]$ **29c** was reported [125] to give the trinuclear bis(ethylidyne) cluster complex **118** on heating at 110 °C (the gases released were ethane and C_4, C_6, C_8 and C_{10} monoolefins). Recently it was proven that the product of this reaction is in fact the paramagnetic mono(ethylidyne) tricobalt hydride **119** [116]. In the crystal the molecules of **119** are disordered, resulting in a pseudomirror plane through the cobalt atoms [116], which led to the wrong assignment of the structure in the first X-ray study [125]. With excess acetylene **119** is slowly converted to genuine **118** at 80 °C [126].

118 is also formed on prolonged heating of the tetrahydride $[(Cp^*Co)_3H_4]$ **1** with acetylene at 100 °C. Two intermediates were detected during the course of the reaction, **119** and the diamagnetic trihydride **120**. As judged from their ^1H NMR chemical shifts, the hydrido ligands in **120** bridge the CoCo edges of the cluster. On heating **120** slowly loses H_2 to form reversibly the more stable **119**.

Crystals of **118** and **119** are isomorphous. The pseudomirror in the structure of **119**, which relates two half μ_3-CCH_3 and two half μ_3-H ligands, is a genuine crystallographical mirror plane in the structure of **118**, this time relating two μ_3-CCH_3 groups (Fig. 30). The shapes of the two molecules are very similar [116].

During the aforementioned "decomposition" of $[CpCo(C_2H_4)_2]$ **29a**, ethylene is readily CH activated and rearranged to give μ-ethylidyne (and in some cases μ-hydrido) ligands. This reaction cannot easily be extended to other olefins. For example, when **29a** is heated in neat styrene, several mostly mononuclear products



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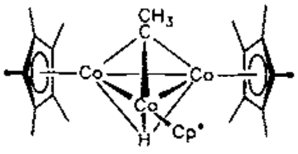

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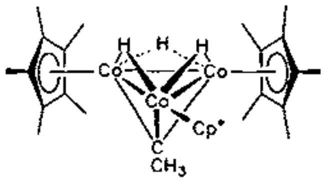

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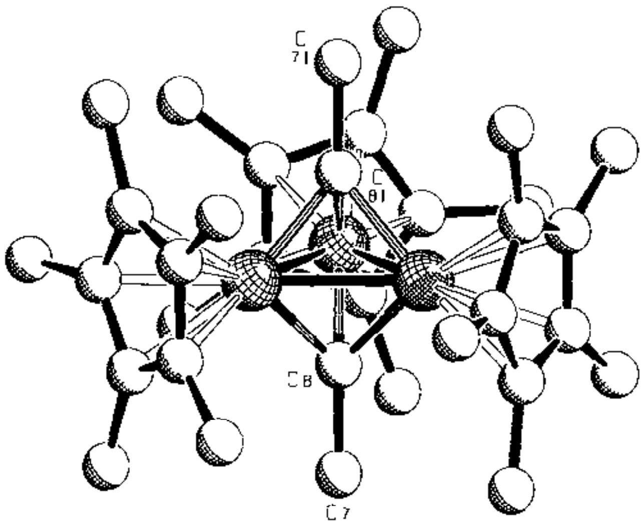


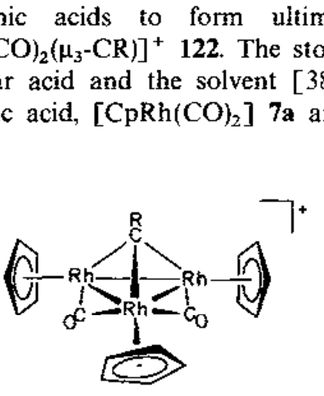
Fig. 30. Molecular structure of $[(Cp^*Co)_3(CMe)_2]$ **118**.

are formed. The phenylethylidyne cluster complexes **88s** ($R = R' = CH_2Ph$) and **121** are only obtained in very minor quantities [127]. On the contrary, ring or side chain substituted styrenes react with **29a** to give μ_3-alkyne and/or μ_3-arene tricobalt cluster complexes, which are discussed elsewhere in this review.

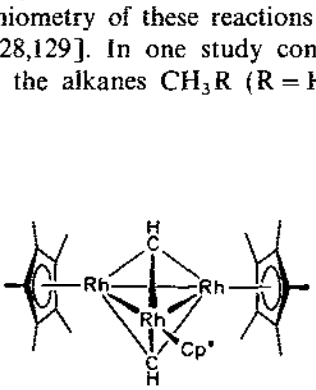
5.4.3. Systems which are derived from methylene or methyl groups

In certain cases, alkylidyne-bridged cluster complexes are obtained from dinuclear methylene- or methyl-bridged complexes. Such reactions are of great interest because of their potential relationship to Fischer–Tropsch chemistry.

The μ-alkylidene complexes $[(CpRhCO)_2(\mu\text{-}CHR)]$ **53** ($R = H$, Me) react with protonic acids to form ultimately the cationic cluster complexes $[(CpRh)_3(\mu\text{-}CO)_2(\mu_3\text{-}CR)]^+$ **122**. The stoichiometry of these reactions depends on the particular acid and the solvent [38,128,129]. In one study conducted with trifluoroacetic acid, $[CpRh(CO)_2]$ **7a** and the alkanes CH_3R ($R = H$, Me) were



122a, R=H
b, R=Me



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identified as additional products. No hydrogen is generated [38,128]. With HBF_4 etherate a high conversion appeared to occur without formation of **7a** [128].

The mechanism of formation of the methylidyne derivative **122a** was studied in some detail. Using HBF_4 in water–thf a nearly quantitative yield of **122a** was obtained. The only other products were **7a** together with large amounts of methane and hydrogen. In the first step of the reaction the electron-rich Rh—Rh bond in **53a** is protonated. The resulting μ-methylene μ-hydrido dinuclear cation $[\mathbf{53a}+H]^+$ could be isolated when the reaction was carried out at a lower temperature. From labelling experiments there is proof for a metal-centred hydrido methylene–methyl tautomerism in this complex, even though intermediates with methyl groups could not be detected by NMR spectroscopy. During the formation of **122a** partial deprotonation of $[\mathbf{53a}+H]^+$ takes place. It was suggested that methane is eliminated from methyl hydrido species while hydrogen could originate from cationic metal-bound methyl groups. The reaction sequence **53** → **122** is an interesting parallel to the proton-induced formation of the tricarbonyl trirhodium cluster complex $[(CpRh)_3(CO)_3]$ **11A** from $[\{CpRh(CO)\}_2(\mu\text{-}CO)]$ **10**, which differs from **53** only by the isolobal replacement of a CO for an alkylidene bridge [38].

The μ-methylidyne cluster complexes **122a** are thermodynamically very stable and, even in solution, do not react with air. Down to −80 °C there is only one ^{13}CO NMR resonance, indicating a rapid carbonyl migration process around the Rh_3 triangle. The crystal structures of the trifluoroacetate [38] and hexafluorophosphate [128] have been determined. In both cases the CO ligands were found semibridging two edges of the nearly equilateral Rh_3 triangles (Fig. 31).

The chloride-bridged dimer $[Cp^*RhCl_2]_2$ **123** is known to react with Al_2Me_6 to first give an intermediate $[Cp^*RhMe_2MeAlMe_xCl_{2-x}]$ **124**, which then transforms into the μ-methylene complexes *cis*- and *trans*-$[(Cp^*RhMe)_2(\mu_2\text{-}CH_2)_2]$

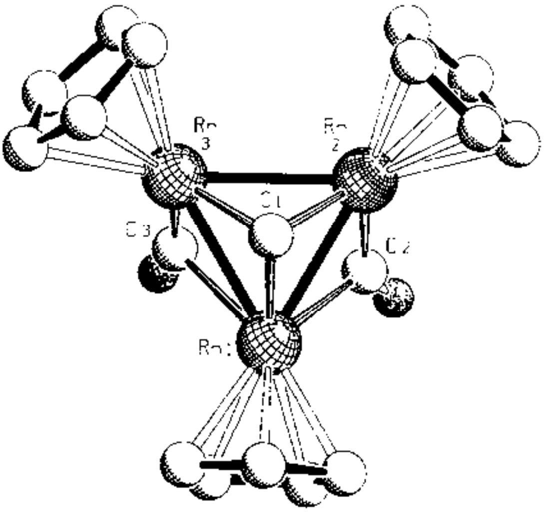


Fig. 31. Molecular structure of $[(CpRh)_3(CO)_2(CH)]^+$ **122a**.

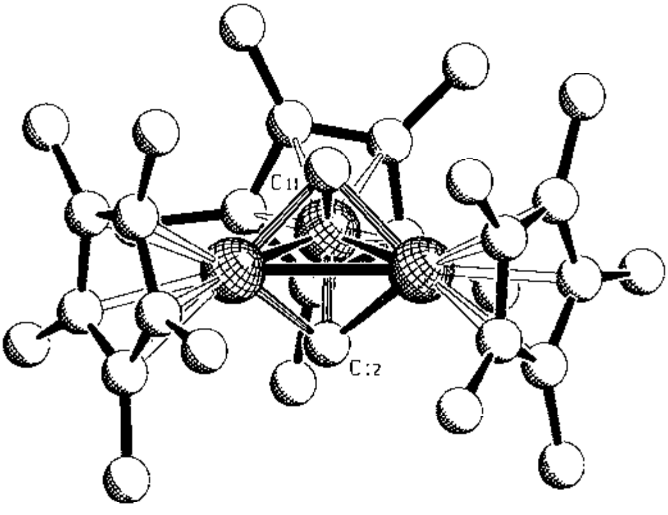


Fig. 32. Molecular structure of $[(Cp^*Rh)_3(CH)_2]$ **125**.

[130]. Under slightly different conditions the bis(methylidyne) cluster complex $[(Cp^*Rh)_3(\mu_3\text{-}CH)_2]$ **125** is obtained. Four mol of methane are evolved per mol of complex **125** [123]. Although **124** also gave some **125** with an excess of **123**, it was not possible to decide whether **124** is a direct intermediate in the formation of **125** from **123**.

The thermally very stable **125** was characterized by an X-ray crystal structure analysis (Fig. 32). The Rh–Rh and Rh—C(methylidyne) bonds were found to be quite similar in length to those in the monomethylidyne cluster complex **122a**. The former distances lie well within the fairly narrow range of all Rh–Rh contacts which are thought to be single bonds [38].

6. Cluster complexes with face-capping cyclopentadienyl and arene ligands

During the reaction of $RhCl_3$ with CpMgBr to give $[Cp_2Rh]$, the tetracyclopentadienyl trirhodium cluster complex $[H(CpRh)_3(\mu\text{-}Cp)]$ **126** is formed in small yield [131]. The X-ray crystal structure analysis of **126** revealed a $(CpRh)_3$ cluster core with the fourth Cp ligand capping the Rh_3 face (Fig. 33). The hydride ligand was not located in the structure analysis [132]. Although the precision of the structure is not very high, the carbon–carbon bond lengths in the μ_3-Cp ring may be interpreted in terms of an "allyl–ene" type distortion. The allyl part of the ring is bridging two CpRh groups, while the more localized double bond is coordinated to the third rhodium atom. In solution, there is rapid rotation of the face-capping Cp ring, as indicated by a quartet ($J(RhH) = 0.8$ Hz, μ-Cp) and a doublet ($J(RhH) = 0.3$ Hz, $(\eta^5\text{-}Cp)_3$) in the ^1H NMR spectrum [132a].

$(CpRh)_3$ cluster complexes **127** with face-capping arenes were recently prepared from $[CpRh(C_2H_4)_2]$ **39a** and benzene or hexamethylbenzene. The dinuclear com-

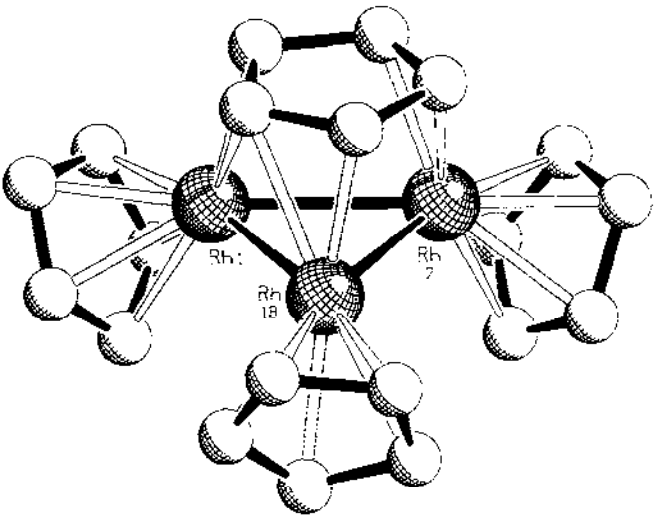
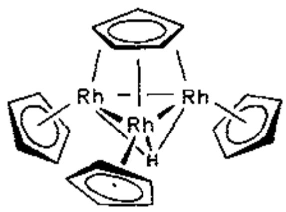


Fig. 33. Molecular structure of [(CpRh)$_3$(Cp)] **126**.



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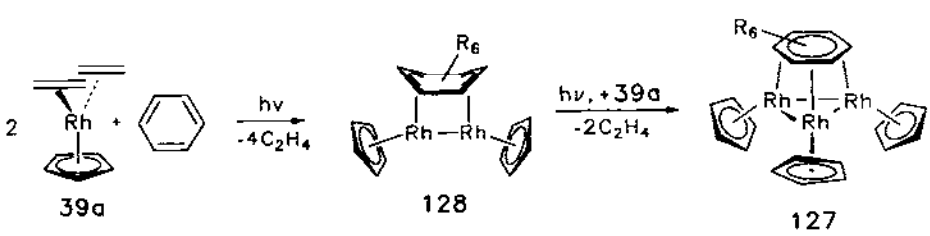
plexes [(CpRh)$_2$(μ-η^3:η^3-C$_6$R$_6$)] **128** are intermediates in the formation of **127** and can be isolated (Scheme 3) [133].

There is a large number of cluster complexes with the general composition [(CpCo)$_3$(μ$_3$-substituted arene)]. Since we have already discussed these and other systems with bridging arene ligands in a recent review [134] only a short summary is given here.

The complexes **98** are formed in sometimes excellent yields when sources of



Scheme 3

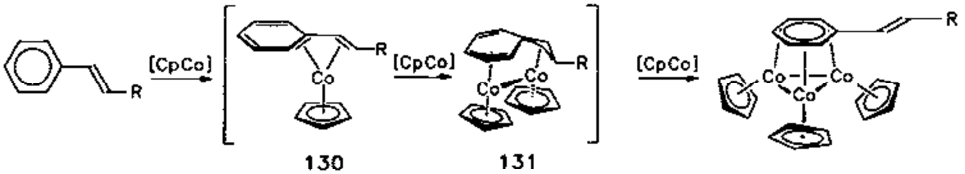
the CpCo fragment (e.g. [CpCo(C_2H_4)$_2$] **29a** and [CpCo(C_6Me_6)] **129**, but not [CpCo(CO)$_2$] **6a**) are treated with alkenylbenzenes [5,134,135]. Allylarenes and even 4-phenyl-1-butene could also be used to obtain **98**. In the presence of **29a** and **129** these ligands are catalytically rearranged to the corresponding alkenylarenes with the carbon–carbon double bond in the α-position to the arene ring [127].

A mechanism for the formation of the tricobalt cluster on the site of the alkenylbenzene template was proposed (Scheme 4) [135b,c]. Although the mononuclear and dinuclear intermediates **130**, **131** could be neither isolated nor spectroscopically observed, a number of model systems are available [5,134,135b,c]. Consistent with the key role of the olefinic side chain, alkylbenzenes do not give the cluster complexes **132** with **29a** or **129**. Some derivatives are, however, available from the catalytic hydrogenation of the alkenyl group in **98** [127,134].

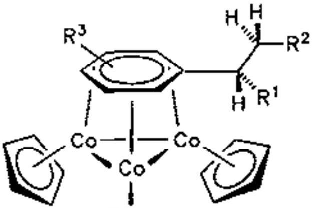
The novel M_3-face-capping coordination geometry of the arenes in **127**, **98** and **132** has been studied in detail [5,134]. In the solid state, the arene hexagons and trimetal triangles are parallel and staggered with respect to each other (Fig. 34). The μ_3-η^2:η^2:η^2-arenes are considerably expanded as compared with the free ligands. There is a small but noticeable trigonal distortion, with the shorter carbon–carbon bonds "on top" of the metal atoms (Table 11).

MO studies of the hypothetical [(CpCo)$_3$(η^2:η^2:η^2-benzene)] revealed a symmetry-allowed mixing of the HOMOs and LUMOs of benzene, in phase with the metal orbitals, as the electronic reason for the Kekule-type distortion of the μ_3-benzene [137].

In solution there is hindered mutual rotation of the M_3 and C_6 rings. This dynamic process was studied in some detail with various derivatives of **98** and **132** [134,136] using one- and two-dimensional NMR spectroscopy. Depending on the symmetry



Scheme 4



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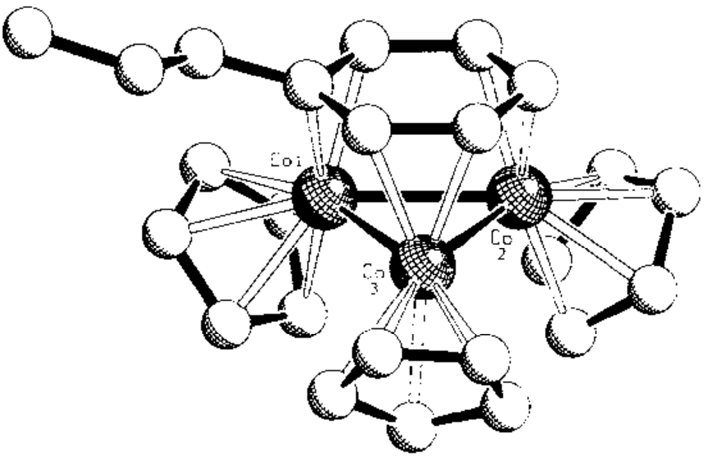


Fig. 34. Molecular structure of [(CpCo)$_3$(β-methylstyrene)] **98a**.

Table 11
Carbon–carbon bond lengths d(C–C)[a] in several μ_3-η^2:η^2:η^2-arene ligands

	d_{mean}(C–C) (Å)[b]		$\sigma(d)$ (Å)[c]
[(CpCo)$_3$(μ_3-β-methylstyrene)]	1.446(14)	1.420(9)	0.005
[(CpCo)$_3$(μ_3-2-phenyl-2-butene)]	1.46(2)	1.41(2)	0.01
[(CpCo)$_3$(μ_3-1,1-diphenylethene)]	1.448(3)	1.416(6)	0.003
[(CpCo)$_3$(μ_3-1,1-diphenylethane)]	1.439(6)	1.414(8)	0.006
[(μ_3-H)(CpCo)$_3$(μ_3-1,1-diphenylethane)][c]	1.46(1)	1.41(1)	0.02
[(CpCo)$_3$(μ_3-1,2-diphenylethane)]	1.442(9)	1.417(7)	0.005
[(CpRh)$_3$(μ_3-benzene)][d]	1.453(10)	1.424(17)	0.013

[a] Data from Ref. [136]. [b] Standard deviation of the mean in parentheses. [c] Standard deviation of the individual values. [d] Ref. [133].

of the arene, dynamic equilibria between enantiomers or diastereomers are observed. A sequence of [1, 2] shifts of the metal atoms along the μ_3-arene (60° twists of the two rings with respect to each other) was identified as the elementary step. The potential barriers for this rotation ($\Delta G^{\ddagger}_{(250\,K)}$ between 50 and 60 kJ mol^{-1}) appear to be dominated by steric effects, which are caused by the substituents on the α-carbon atom of the side chain.

The dynamics and molecular aggregation in the crystalline solids of **127** as well as several derivatives of **98** and **132** have also been investigated by atom atom packing potential energy calculations and computer graphics [138].

7. Miscellaneous

A number of cluster complexes which do not fall exactly into one of the categories defined in this review have nevertheless already been discussed above in connection with related systems. Most of these have either two of the different classes of ligands in the same molecule (such as both a μ-carbyne and a μ-alkyne or heteroalkyne ligand), or else are hetero-analogues of a particular species (such as the few cobaltaboranes or -phosphoraboranes mentioned above). In this section we shall discuss the few remaining systems.

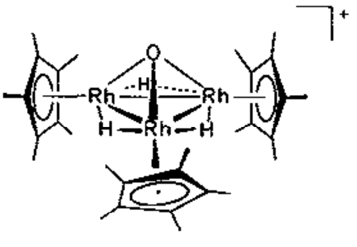
During the reaction of yellow–orange $[(Cp^*Rh)_2(\mu_2\text{-}OH)_3]^+$ **4** with dihydrogen to give the green tetranuclear $[(Cp^*Rh)_4H_4]^{2+}$ **3** (Section 2) a transient colour change to red was observed. The same colour change occurs when **4** is warmed in isopropanol. After 24 h at 45 °C the red–brown $[H_3(Cp^*Rh)_3(\mu_3\text{-}O)]^+$ **133** can be precipitated with hexafluorophosphate. As a byproduct, the dinuclear $[(Cp^*Rh)_2(\mu\text{-}OH)(\mu\text{-}H)_2]^+$ is also formed [13,139]. Interestingly, **133** could not be converted into **3**, although the former can be trapped as an intermediate during the formation of the latter from **4** using either H_2 [12] or isopropanol [139].

[**133**](PF_6) crystallizes as a hydrate; a crystal structure analysis revealed an essentially isolateral triangle of rhodium atoms (mean Rh–Rh distance, 2.758 Å) which is capped on one side by an oxygen ligand (Fig. 35). There is hydrogen bonding between the water of crystallization and the μ_3-oxygen atom as well as the PF_6 anion. Three Rh–Rh edge-bridging hydrido ligands were assumed, although only one hydride was actually localized [139].

In solution, the complex appears very rigid; three static μ_2-hydrides were identified by their ^1H NMR lineshapes (an $[AX]_3$ spin system). An explanation for the lack of hydride fluxionality was suggested. This involved constraints to movement and rehybridization of the metal atoms caused by the capping oxygen and the intermeshed methyls of the Cp* ligands [139].

When Li_2S or elemental sulphur is treated with $[CpCo(PPh_3)_2]$ at 60 °C the tetranuclear disulphur complex $[(CpCo)_4S_2]$ **134** can be isolated. As judged from the ^1H NMR spectrum, **134** is paramagnetic in solution. An octahedral Co_4S_2 molecular cluster core was established in the solid state using X-ray crystallography (Fig. 36). The four cobalt atoms form a square, which is capped on both sides by the μ_4-S ligands [140]. The Co—Co bonds (2.483(9) Å) are shorter than those found in other sulphur-capped systems, e.g. $[\{(C_5R_5)Co\}_3S_2]$ **60** (Table 7). As expected for geometrical reasons, the Co—S bonds are longer in **134**.

Counting S as a four-electron ligand, 18 VEs can be assigned to every cobalt atom in **134** if four Co—Co bonds are assumed. The observed paramagnetism was rational-



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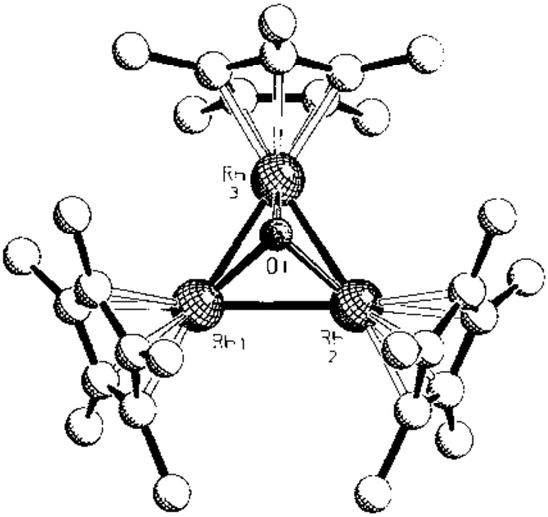


Fig. 35. Molecular structure of $[H_3(Cp^*Rh)_3O]^+$ **133**.

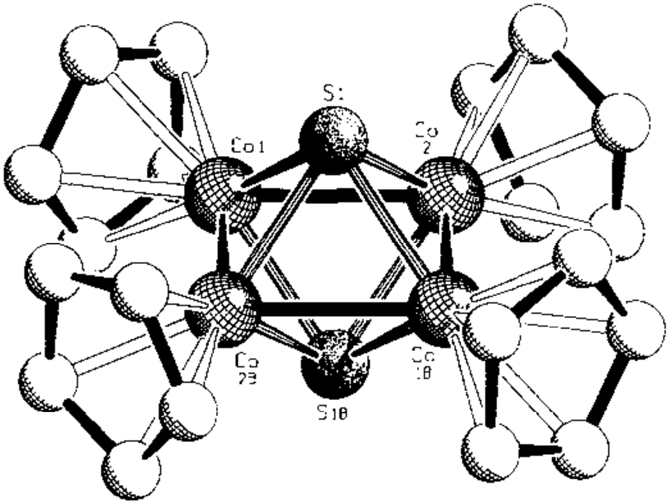
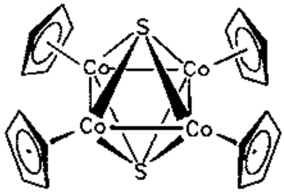


Fig. 36. Molecular structure of $[(CpCo)_4S_2]$ **134**.

ized by treating the metals as Co^{II} [140]. Application of the PSEP electron counting scheme predicts a nido Co_4S_2 polyhedron (eight electron pairs for intracluster bonding). Thus, like with many of the trinuclear $[\{(C_5R_5)(d^9\text{-}M)\}_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$, the structure of the tetranuclear **134** does not conform to PSEP theory.



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References

[1] D.M.P. Mingos and D. Wales, Introduction to Cluster Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1990, Chap. 1.
[2] S.M. Owen, Polyhedron, 7 (1988) 253, and references cited therein.
[3] (a) B.F.G. Johnson (ed.), Transition Metal Clusters, Wiley, New York, 1980.
(b) M. Moskovits (ed.), Metal Clusters, Wiley, New York, 1986.
(c) D.F. Shriver, H.D. Kaesz and R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH, Weinheim, 1990.
(d) G. Schmid, Clusters and Colloids, VCH, Weinheim, 1994.
[4] D.M.P. Mingos, Inorg. Chem., 21 (1982) 465.
[5] H. Wadepohl, Comments Inorg. Chem., 15 (1994) 369.
[6] T.P. Fehlner, New J. Chem., 12 (1988) 307; Adv. Inorg. Chem., 35 (190) 199.
[7] J.L. Kersten, A.L. Rheingold, K.H. Theopold, C.P. Casey, R.A. Widenhoefer and C.E.C.A. Hop, Angew. Chem., 104 (1992) 1364.
[8] J.J. Schneider, R. Goddard, S. Werner and C. Krüger, Angew. Chem., 103 (1991) 1145.
[9] J.J. Schneider, Angew. Chem., 104 (1992) 1422.
[10] J. Müller and H. Dorner, Angew. Chem., 85 (1973) 867.
[11] G. Huttner and H. Lorenz, Chem. Ber., 108 (1975) 973.
[12] P. Espinet, P.M. Bailey, P. Piraino and P.M. Maitlis, Inorg. Chem., 18 (1979) 2706.
[13] A. Nutton, P.M. Bailey and P.M. Maitlis, J. Organomet. Chem., 213 (1981) 313.
[14] J.S. Ricci, T.F. Koetzle, R.J. Goodfellow, P. Espinet and P.M. Maitlis, Inorg. Chem., 23 (1984) 1828.
[15] R. Hoffmann, B.E.R. Schilling, R. Bau, H.D. Kaesz and D.M.P. Mingos, J. Am. Chem. Soc., 100 (1978) 6088.
[16] A.R. Kudinov, D.V. Muratov, M.I. Rybinskaya, P.V. Petrovskii, A.V. Mironov, T.V. Timofeeva, Y.L. Slovokhotov and Y.T. Struchov, J. Organomet. Chem., 414 (1991) 97.
[17] R.B. King, Inorg. Chem., 5 (1966) 2227.
[18] (a) O.S. Mills and E.F. Paulus, J. Chem. Soc., Chem. Commun., (1966) 815. O.S. Mills and E.F. Paulus, J. Organomet. Chem., 10 (1967) 331.
(b) E.F. Paulus, E.O. Fischer, H.P. Fritz and H. Schuster-Woldan, J. Organomet. Chem., 10 (1967) P3. E.F. Paulus, Acta Crystallogr. B, 25 (1969) 2206.
[19] V.A. Uchtman and L.F. Dahl, J. Am. Chem. Soc., 91 (1969) 3763.

[20] E.O. Fischer and K. Bittler Z. Naturforsch., Teil B, 16 (1961) 835.
[21] R.J. Lawson and J.R. Shapley, J. Am. Chem. Soc., 98 (1976) 7433.
[22] R.J. Lawson and J.R. Shapley, Inorg. Chem., 17 (1978) 772.
[23] J.R. Shapley, P.C. Adair and R.J. Lawson, Inorg. Chem., 21 (1982) 1701
[24] K.P.C. Vollhardt, J.E. Bercaw and R.G. Bergman, J. Organomet. Chem., 97 (1975) 283.
[25] P. Hofmann and M. Padmanabhan, Organometallics, 2 (1983) 1273.
[26] W.A. Herrmann, J. Plank and D. Riedel, J. Organomet. Chem., 190 (1980) C47.
[27] W.I. Bailey, Jr., F.A. Cotton, J.D. Jamerson and B.W.S. Kolthammer, Inorg. Chem., 21 (1982) 3131.
[28] C.E. Barnes and M.R. Dial, Organometallics, 7 (1988) 782.
[29] L.M. Cirjak, J.-S. Huang, Z.-H. Zhu and L.F. Dahl, J. Am. Chem. Soc., 102 (1980) 6623.
[30] F. Faraone, S.L. Schiavo, G. Bruno, P. Piraino and G. Bombieri, J. Chem. Soc., Dalton Trans., (1983) 1813.
[31] H. Brunner, N. Janietz, J. Wachter, H.-P. Neumann, B. Nuber and M.L. Ziegler, J. Organomet. Chem., 388 (1990) 203.
[32] P. Caddy, M. Green, E. O'Brien, L.E. Smart and P. Woodward, Angew. Chem., 89 (1977) 671.
[33] R. Hörlein, W.A. Herrmann, C.E. Barnes, C. Weber, C. Krüger, M.L. Ziegler and T. Zahn, J. Organomet. Chem., 321 (1987) 257.
[34] W.A. Herrmann, C.E. Barnes, T. Zahn and M.L. Ziegler, Organometallics, 4 (1985) 172.
[35] F.A. Cotton and J.D. Jamerson, J. Am. Chem. Soc., 98 (1976) 1273.
[36] W.A. Herrmann, J. Planck, C. Bauer, M.L. Ziegler and E. Guggolz, Z. Anorg. Allg. Chem., 487 (1982) 85.
[37] W.A. Herrmann, C.E. Barnes, R. Serrano and B. Koumbouris, J. Organomet. Chem., 256 (1983) C30.
[38] W.A. Herrmann, J. Planck, D. Riedel, M.L. Ziegler, K. Weidenhammer, E. Guggolz and B. Balbach, J. Am. Chem. Soc., 103 (1981) 63.
[39] Y.N. Al-Obaidi, M. Green, N.D. White and G.E. Taylor, J. Chem. Soc., Dalton Trans., (1982) 319.
[40] M.I. Rybinskaya, A.R. Kudinov, D.V. Muratov, N.P. Gambaryan, I.V. Stankevich and A.L. Christyakov, J. Organomet. Chem., 413 (1991) 419.
[41] W.L. Olson, A.M. Stacy and L.F. Dahl, J. Am. Chem. Soc., 108 (1986) 7646.
[42] A.C. Bray, M. Green, D.R. Hankey, J.A.K. Howard, O. Johnson and F.G.A. Stone, J. Organomet. Chem., 281 (1985) C12.
[43] C.E. Barnes, J.A. Orvis, D.L. Staley, A.L. Rheingold and D.C. Johnson, J. Am. Chem. Soc., 111 (1989) 4992.
[44] C.E. Barnes, M.R. Dial, J.A. Orvis, D.L. Staley and A.L. Rheingold, Organometallics, 9 (1990) 1021.
[45] M. Green, D.R. Hankey, J.A.K. Howard, P. Louca and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1983) 757.
[46] M. Green, J.A.K. Howard, A. Bray, O. Johnson and F.G.A. Stone, Acta Crystallogr. A, 40 (1984) C295.
[47] C.P. Casey, R.A. Widenhoefer, S.L. Hallenbeck and J.A. Gavney, Jr., J. Chem. Soc., Chem. Commun., (1993) 1692.
[48] C.E. Barnes and J.A. Orvis, Organometallics, 12 (1993) 1016.
[49] S. Gambarotta, S. Stella, C. Floriani, A. Chiesi-Villa and C. Guastini, Angew. Chem., 98 (1986) 283.
[50] S. Stella, C. Floriani, A. Chiesi-Villa and C. Guastini, New J. Chem., 12 (1988) 621.
[51] M. Elian, M.M.L. Chen, D.M.P. Mingos and R. Hoffmann, Inorg. Chem., 15 (1979) 1148.
[52] R. Hoffmann, Angew. Chem., 94 (1982) 725.
[53] A.R. Pinhas, T.A. Albright, P. Hofmann and R. Hoffmann, Helv. Chim. Acta, 63 (1980) 29.
[54] N.E. Schore, C.S. Ilenda, M.A. White, H.E. Bryndza, M.G. Matturro and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 7451.
[55] S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Organomet. Chem., 296 (1985) C6.
[56] B.E.R. Schilling and R. Hoffmann, J. Am. Chem. Soc., 101 (1979) 3456.
[57] A.B. Rives, Y. Xiao-Zeng and R.F. Fenske, Inorg. Chem., 21 (1982) 2286.
[58] (a) M. Sorai, A. Kosaki, H. Suga, S. Seki, T. Yoshida and S. Otsuka, Bull. Chem. Soc. Jpn., 44 (1971) 2364.
(b) N. Kamijo and H. Terauchi, J. Chem. Phys., 74 (1981) 1944.

[59] W.L. Olson and L.F. Dahl, J. Am. Chem. Soc., 108 (1986) 7657.

[60] M.S. Ziebarth and L.F. Dahl, J. Am. Chem. Soc., 112 (1990) 2411.

[61] S. Enoki, T. Kawamura and T. Yonezawa, Inorg. Chem., 22 (1983) 3821.

[62] S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 3 (1984) 1344.

[63] C.R. Pulliam, J.B. Thoden, A.M. Stacy, B. Spencer, M.H. Englert and L.F. Dahl, J. Am. Chem. Soc., 113 (1991) 7398.

[64] S. Otsuka, A. Nakamura and T. Yoshida, Inorg. Chem., 7 (1968) 261.

[65] S. Otsuka, A. Nakamura and T. Yoshida, Leibigs Ann. Chem., 719 (1968) 54.

[66] H. Werner and K. Leonhard, Angew. Chem., 91 (1979) 663.

[67] H. Werner, K. Leonhard, O. Kolb, E. Röttinger and H. Vahrenkamp, Chem. Ber., 113 (1980) 1654.

[68] J. Fortune and A.R. Manning, J. Organomet. Chem., 190 (1980) C95.

[69] J. Fortune and A.R. Manning, Organometallics, 2 (1983) 1719.

[70] E.P. Cullen, F. Fortune, A.R. Manning, P. McArdle, D. Cunningham and F.S. Stephens, Organometallics, 9 (1990) 1443.

[71] J. Fortune, A.R. Manning and F.S. Stephens, J. Chem. Soc., Chem. Commun., (1983) 1071.

[72] I.R. Beaumont, M.J. Begley, S.Harrison and A.H. Wright, J. Chem. Soc., Chem. Commun., (1990) 1713.

[73] R.L. Bedard, A.D. Rae and L.F. Dahl, J. Am. Chem. Soc., 108 (1986) 5924.

[74] E.W. Abel, T. Blackmore and R.J. Whitley, Inorg. Nucl. Chem. Lett., 10 (1974) 941.

[75] T. Madach and H. Vahrenkamp, Chem. Ber., 114 (1981) 505.

[76] R.L. Bedard and L.F. Dahl, J. Am. Chem. Soc., 108 (1986) 5933.

[77] P. Frisch and L.F. Dahl, J. Am. Chem. Soc., 94 (1972) 5082.

[78] K.A. Kubat-Martin, A.D. Rae and L.F. Dahl, Organometallics, 4 (1985) 2221.

[79] R.L. Bedard and L.F. Dahl, J. Am. Chem. Soc., 108 (1986) 5942.

[80] N. Kamijo and T. Watanabe, Acta Crystallogr. B, 35 (1979) 2537.

[81] Y. Wakatsuki, T. Okada, H. Yamazaki and G. Cheng, Inorg. Chem., 27 (1988) 2958.

[82] J. Müller and S. Schmitt, J. Organomet. Chem., 97 (1975) C54.

[83] R.S. Dickson, G.S. Evans, G.D. Fallon and G.N. Pain, J. Organomet. Chem., 295 (1985) 109.

[84] M.G. Thomas, E.L. Muetterties, R.O. Day and V.W. Day, J. Am. Chem. Soc., 98 (1976) 4646.

[85] S.A. Gardner, P.S. Andrews and M.D. Rausch, Inorg. Chem., 12 (1973) 2396.

[86] R.S. Dickson, C. Mok and G. Pain, J. Organomet. Chem., 166 (1979) 385.

[87] S.A. Gardner, E.F. Tokas and M.D. Rausch, J. Organomet. Chem., 92 (1975) 69.

[88] R.S. Dickson, G.D. Fallon, R.J. Nesbit and G.N. Pain, Organometallics, 4 (1989) 355.

[89] A.D. Clauss, J.R. Shapley, C.N. Wilker and R. Hoffmann, Organometallics, 3 (1984) 619.

[90] M.F. Freeman, L.W. Hall and L.G. Sneddon, Inorg. Chem., 19 (1980) 1132.

[91] C.E. Barnes, J.A. Orvis and G.M. Finnis, Organometallics, 9 (1990) 1695.

[92] J.R. Fritch, K.P.C. Vollhardt, M.R. Thompson and V.W. Day, J. Am. Chem. Soc., 101 (1979) 2768.

[93] B. Eaton, J.M. O'Connor and K.P.C. Vollhardt, Organometallics, 5 (1986) 394.

[94] K.P.C. Vollhardt and M. Wolfgruber, Angew. Chem., 98 (1986) 919.

[95] Trinh-Toan, R.W. Broach, S.A. Gardner, M.D. Rausch and L.F. Dahl, Inorg. Chem., 16 (1977) 279.

[96] T. Yamamoto, A.R. Garber, G.M. Bodner, L.J. Todd, M.D. Rausch and S.A. Gardner, J. Organomet. Chem., 56 (1973) C23.

[97] L.J. Todd, J.R. Wilkinson, M.D. Rausch, S.A. Gardner and R.S. Dickson, J. Organomet. Chem., 101 (1975) 133.

[98] A. Goldhaber, K.P.C. Vollhardt, E.C.Walborsky and M. Wolfgruber, J. Am. Chem. Soc., 108 (1986) 516.

[99] H. Wadepohl, T. Borchert, K. Büchner and H. Pritzkow, Chem. Ber., 126 (1993) 1618.

[100] K. Jonas, E. Deffense and D. Habermann, Angew. Chem., 95 (1983) 729; Angew. Chem. Suppl., (1983) 1005.

[101] H. Wadepohl, T. Borchert and H. Pritzkow, J. Chem. Soc., Chem. Commun., (1995) in print.

[102] E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., 83 (1983) 203.

[103] H. Wadepohl, T. Borchert and H. Pritzkow, unpublished (1994).

[104] J. Feilong, T.P. Fehlner and A.L. Rheingold, J. Am. Chem. Soc., 109 (1987) 1860.

[105] J.-F. Halet, J.-Y. Saillard, R. Lissillour, M.J. McGlinchey and G. Jaouen, Inorg. Chem., 24 (1985) 218.
[106] J.F. Blount, L.F. Dahl, C. Hoogzand and W. Hübel, J. Am. Chem. Soc., 88 (1966) 292.
[107] A.J. Deeming, J. Organomet. Chem., 150 (1978) 123.
[108] R.B. King and C.A. Harmon, Inorg. Chem., 15 (1976) 879.
[109] J.R. Fritch and P.C. Vollhardt, Angew. Chem., 92 (1980) 570.
[110] H. Yamazaki, Y. Wakatsuki and K. Aoki, Chem. Lett., (1979) 1041.
[111] S.M. Elder, B.H. Robinson and J. Simpson, J. Organomet. Chem., 398 (1990) 165.
[112] N.T. Allison, J.R. Fritch, K.P.C. Vollhardt and E.C. Walborsky, J. Am. Chem. Soc., 105 (1983) 1384.
[113] K.P.C. Vollhardt and E.C. Walborsky, Polyhedron, 7 (1988) 1023.
[114] H. Wadepohl and H. Pritzkow, Polyhedron, 8 (1989) 1939.
[115] S.B. Colbran, L.R. Hanton, B.H. Robinson, W.T. Robinson and J. Simpson, J. Organomet. Chem., 330 (1987) 415.
[116] C.P. Casey, R.A. Widenhoefer, S.L. Hallenbeck, R.K. Hayashi, D.R. Powell and G.W. Smith, Organometallics, 13 (1994) 1521.
[117] J. Feilong, T.P. Fehlner and A.L. Rheingold, Angew. Chem., 100 (1988) 400.
[118] K.J. Deck, T.P. Fehlner and A.L. Rheingold, Inorg. Chem., 32 (1993) 2794.
[119] M.B. Robin and P. Day, Adv. Inorg. Radiochem., 10 (1967) 247.
[120] D.W. van Horn and K.P.C. Vollhardt, J. Chem. Soc., Chem. Commun., (1982) 203.
[121] H. Wadepohl and H. Pritzkow, J. Organomet. Chem., 450 (1993) 9.
[122] T.P. Fehlner, Polyhedron, 9 (1990) 1955.
[123] A.V. de Miguel, K. Isobe, P.M. Bailey, N.J. Meanwell and P.M. Maitlis, Organometallics, 1 (1982) 1604.
[124] K.P.C. Vollhardt and E.C. Walborsky, J. Am. Chem. Soc., 105 (1983) 5507.
[125] R.B.A. Pardy, G.W. Smith and M.E. Vickers, J. Organomet. Chem., 252 (1983) 341.
[126] C.P. Casey, R.A. Widenhoefer and S.L. Hallenbeck, Organometallics, 12 (1993) 3788.
[127] H. Wadepohl, K. Büchner, M. Herrmann and H. Pritzkow, Organometallics, 10 (1991) 861.
[128] P.A. Dimas, E.N. Duesler, R.J. Lawson and J.R. Shapley, J. Am. Chem. Soc., 102 (1980) 7787.
[129] W.A. Herrmann, J. Plank, E. Guggolz and M.L. Ziegler, Angew. Chem., 92 (1980) 660.
[130] (a) K. Isobe, D.G. Andrews, B.E. Mann and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1981) 809.
(b) A.V. de Miguel, K. Isobe, B.F. Taylor, A. Nutton and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1982) 758.
[131] E.O. Fischer and H. Wawersik, J. Organomet. Chem., 5 (1966) 559.
[132] (a) E.O., Fischer, O.S. Mills, E.F. Paulus and H. Wawersik, J. Chem. Soc., Chem. Commun., (1967) 643.
(b) O.S. Mills and E.F. Paulus, J. Organomet. Chem., 11 (1968) 587.
[133] J. Müller, P. Escarpa Gaede and K. Qiao, Angew. Chem., 105 (1993) 1809.
[134] H. Wadepohl, Angew. Chem., 104 (1992) 253.
[135] (a) H. Wadepohl, K. Büchner and H. Pritzkow, Angew. Chem., 99 (1987) 1294.
(b) H. Wadepohl, K. Büchner and H. Pritzkow, Organometallics, 8 (1989) 2745.
(c) H. Wadepohl, T. Borchert, K. Büchner, M. Herrmann and H. Pritzkow, Organometallics (1995) in press.
[136] H. Wadepohl, in L. J. Farrugia and Y. T. Yates, Jr. (eds.), The Synergy Between Dynamics and Reactivity at Clusters and Surfaces, NATO ASI Series, to be published.
[137] (a) H. Wadepohl and L. Zhu, J. Organomet. Chem., 376 (1989) 115.
(b) L. Zhu, H. Wadepohl and N. Kostic, Wuji Huaxue Xuebao, 8 (1992) 1.
[138] D. Braga, F. Grepioni, H. Wadepohl and S. Gebert, J. Chem. Soc., Dalton Trans., (1995) 1089.
[139] A. Nutton, P.M. Bailey, N.C. Braund, R.J. Goodfellow, R.S. Thompson and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1980) 631.
[140] F. Jiang, X. Lei, Z. Huang, M. Hong, B. Kang, D. Wu and H. Liu, J. Chem. Soc., Chem. Commun., (1990) 1655.
[141] M.C. Comstock, S.R. Wilson and J.R. Shapley, Organometallics, 13 (1994) 3805.
[142] D. Braga, F. Grepioni, H. Wadepohl, S. Gebert, M.J. Calhorda and L.F. Veiros, Organometallics, 1995, in press.