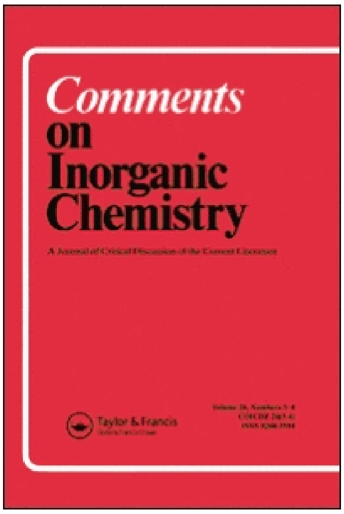

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Construction of Novel Oligonuclear Complexes from Metal Coordinated Hydrocarbons and Cyclopentadienylcobalt Fragments

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Construction of Novel Oligonuclear Complexes from Metal Coordinated Hydrocarbons and Cyclopentadienylcobalt Fragments

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Cyclopentadienylcobalt fragments [CpCo] are used as the building blocks of oligonuclear complexes with hydrocarbons as bridging ligands. The main reaction routes are addition of several [CpCo] to an unsaturated hydrocarbon ligand, often resulting in an unusual coordination mode of the latter, and CH-activation. The range of addition products includes dinuclear complexes of hexatriene, cycloheptatriene and alkenylbenzenes as well as cluster complexes with face capping arene ligands. The more important products from CH-activation are CpCo-complexes of cobaltafulvenes, dinuclear cycloheptatrienyl bridged heterobimetallic hydrido complexes and cluster complexes with face capping alkylidyne or alkyne ligands.

Key Words: *cyclopentadienyl, cobalt, hydrocarbon, CH-activation, cluster*

INTRODUCTION

The structures and reactions of organometallic molecules are much more diverse and more difficult to classify than their organic coun-

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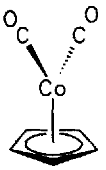
terparts. In the theoretical description of organometallic chemistry a particular qualitative tool, the fragment molecular orbital method, has proved to be very powerful and instructive. The idea behind it was that the valence orbitals of a molecule can be constructed from the valence orbitals of a relatively small number of "standard" fragments.[1] For example, a large number of organometallic molecules can be constructed on paper from hydrocarbons and conical metal containing fragments $[M(CO)_3]$ and $[M\{\eta\text{-}(CH)_n\}]$ (n = 3–8), where $(CH)_n$ is a cyclic polyene or polyenyl system.[2] When we try and transfer this concept into benchtop synthetic chemistry, preparatively useful organometallic fragments must meet a number of important criteria:

—The metal-to-ligand bonds within the fragment must be very stable and inert to substitution. This should enable the fragment to keep its integrity throughout a reaction.
—Stable organometallic molecules quite often adhere to the 18 valence electron (VE) rule. If they are to be built from fragments, the VE count of the latter should neither be too far from nor too close to 18.
—Preferentially the fragment should have an even number of VE. Thus diamagnetic products are expected when it adds to common organic substrates.
—A stable yet reactive source must be available from which the fragment can be generated.

A fragment which meets all these requirements especially well is cyclopentadienylcobalt $[(\eta^5\text{-}C_5H_5)Co]$ or [CpCo]. In particular, compared to the dissociation of a CO ligand from a metal carbonyl fragment much more energy is needed to remove the Cp ligand from the metal since five carbon–cobalt bonds have to be cleaved. With 14 VE the fragment is flexible enough to contribute to the right electron count for a large number of mono-, di- and oligonuclear complexes. Moreover, the electronic and steric properties of [CpCo] can be modified to some extent by the introduction of substituents on the Cp ligand.

The protecting and activating properties of [CpCo] towards organic substrates have been used extensively by a number of research groups.[3] Since the *organic* chemistry of CpCo complexes



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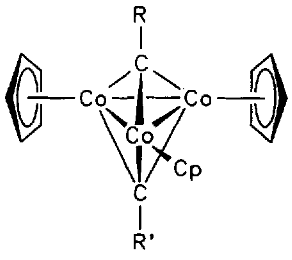

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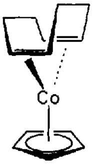
will not be discussed any further in this Comment, only three important but somewhat arbitrary examples must suffice here. These are the work of the groups of Yamazaki and Wakatzuki[4] on the formation of Cobaltoles (Cobaltacyclopentadienes) and their stoichiometric and catalytic organic reactions, of Vollhardt[5] and more recently Gleiter[6] on various cobalt mediated cycloadditions, and of Bönnemann[7] on the catalytic co-cyclotrimerisation of alkynes and nitriles.

A remarkable *organometallic* reaction of $[CpCo(CO)_2]$ **1** was observed by Vollhardt *et al.*[8] in 1979. Under certain conditions alkynes RC_2R' are cleaved by **1** into alkylidyne fragments which are incorporated into tricobalt cluster complexes **2**. The carbon–carbon bond is most likely cleaved on a $(CpCo)_3$ cluster which is formed by stepwise aggregation of CpCo fragments around the alkyne.[9] This example shows that not only carbon–carbon, but also metal–metal bond formation can be an important pattern in CpCo chemistry. However, the commercially available "classical" source of [CpCo], $[CpCo(CO)_2]$ **1**, requires rather high temperatures or photochemical activation to split off its CO ligands. High temperatures are also necessary for many other potential sources of [CpCo] like [CpCo(1,5-cyclooctadiene)] **3**. This severely limited the range of accessible products.

Our interest in CpCo chemistry was sparked by a report[10] of Jonas of the synthesis of $[CpCo(C_2H_4)_2]$ **4**. The Jonas reagent, as **4** soon became known, is an order of magnitude more reactive than **1** or **3**. With organic or organometallic substrates reaction usually takes place between −80 and +40°C. An even more reactive source of [CpCo] than the Jonas reagent, the 20 VE complex $[CpCo(\eta^6\text{-}C_6Me_6)]$ **7** can be obtained from **4**.[11] In contrast $[(\eta^5\text{-}$



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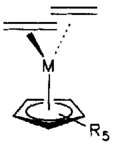
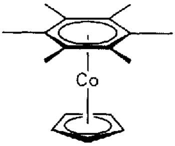


4, M= Co, R= H
5, M= Co, R_5= H_4Me
6, M= Co, R= Me
8, M= Rh, R= H



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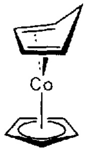

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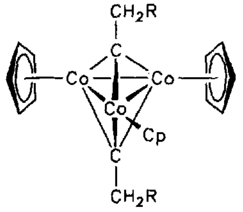
$C_5Me_5)Co(C_2H_4)_2]$ ($[Cp^*Co(C_2H_4)_2]$) **6** and $[CpRh(C_2H_4)_2]$ **8** are much less reactive than the CpCo analogs. Reaction temperatures as high as 140°C are required.

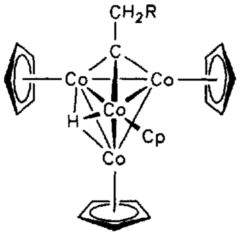
All the reactions described in the following sections were carried out with **4** or its Cp ring alkylated derivatives (e.g. **5**, **6**) and (in certain cases) **7**. During our work we screened a large number of other complexes like **1**, **3**, [CpCo(cyclopentadiene)] **9**, [CpCo-(anthracene)] and complexes of various α,β-unsaturated ketones with respect to their potential as sources of [CpCo]. Although some of these had been used before to generate [CpCo], they all proved to be useless in our chemistry. This is a striking example that the arrival of a new, more reactive reagent can open up new prospects in an area much studied before.

μ_3-ALKYLIDYNE, μ_3-ALKYNE AND μ_3-ARENE CLUSTER COMPLEXES

Because of the similarity of the energies and shapes of their frontier orbitals, CpCo and the BH fragment are isolobal.[12] Therefore a series of *closo*-cobaltaboranes $[(CpCo)_k(BH)_{n-k}H_2]$ ($k < n$) can be envisaged. Although a number of intermediate members of this series have been synthesised (e.g., $[(CpCo)_4(BH)_2H_2]$,[13] $[(CpCo)_3(BH)_3H_2]$ [14]), the all boron and all cobalt clusters $[(BH)_nH_2]$ and $[(CpCo)_kH_2]$ are still unknown. We thought that the reaction of **4**



2a, R= H
2b, R= Ph



10a, R= H
10b, R= Ph

with dihydrogen might provide a general route into the series $[(CpCo)_kH_2]$. Indeed reaction of **4** with 1 bar of H_2 proceeds. To our surprise the products were not the expected hydrido cluster complexes $[(CpCo)_kH_2]$ or the known[15] $[(CpCo)_4H_4]$ but a number of $(CpCo)_n(\mu_3$-ethylidyne) cluster complexes.[16] The main products, red $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ **2a** and brown $[(\mu_3\text{-}H)(CpCo)_4(\mu_3\text{-}CCH_3)]$ **10a** could be isolated by low temperature chromatography. $[(CpCo)_4(CCH_3)_2]$ and $[H(CpCo)_5(CCH_3)]$ were detected in the reaction mixture by field desorption mass spectroscopy but could not be completely separated from **10a**. When our work was in progress, Floriani *et al.*[17] reported **10a** as the product of the *thermal* decomposition of **4**. We were able to prove that the range of products is essentially the same in the low temperature hydrogenation and the thermal decomposition reactions. Quite significantly the same reaction also takes place when solid **4** is heated above 60°C.

During the formation of the (CpCo)(μ-ethylidyne) cluster complexes most of the ethylene coordinated to the cobalt in **4** is lost. However CH-activation and rearrangement of some of the ethylene ligands takes place, resulting in μ_3-ethylidyne and (in some cases) μ_3-hydrido ligands coordinated to the newly formed CpCo-clusters. It is not clear at which stage of the cluster formation the transformation of ethylene takes place. Our experiments indicate that metal coordinated rather than free ethylene is involved. Interestingly, conversion of chemisorbed ethylene to μ_3-ethylidyne is rather common on metal surfaces.[18] Surface bound ethylidyne fragments are also formed during the catalytic hydrogenation of ethylene on certain metals.[19]

When the nuclearity of a metal cluster is increased, the amount of "surface" area available for the *exo*-cluster ligands decreases. Hence clusters of lower nuclearity are expected when the steric bulk of the ligands is increased. $[Cp'Co(C_2H_4)_2]$ **5** (Cp' = methylcyclopentadienyl) indeed gives a higher yield of the tricobalt cluster $[(Cp'Co)_3(\mu_3\text{-}CCH_3)_2]$ **11** compared to $[(\mu_3\text{-}H)(Cp'Co)_4(\mu_3\text{-}CCH_3)]$ **12** and no alkylidyne cluster complexes of higher nuclearity could be detected.[15] Only the trinuclear $[(Cp^*Co)_3(\mu_3\text{-}CCH_3)_2]$ **13** could be isolated as the thermal decomposition product of **6**.[20]

The steric shielding by the surrounding Cp ligands of the Co_4C cluster core in **10** is one of the reasons for its low reactivity. However, strong Brønstedt acids protonate the tetracobalt framework. Thus a series of hydrido ethylidyne tetracobalt cluster cations $[(\mu_3\text{-}H)_{1+n}(CpCo)_4(\mu_3\text{-}CCH_3)]^{n+}$ [**10a** + nH]$^{n+}$ (n = 1, 2) can be prepared by subsequent protonation of all the tricobalt faces (Scheme 1).[21] The protonations and deprotonations are fairly slow and show a strong kinetic isotope effect. The hydrido ligands in **10a** and [**10a** + H]$^+$ are mobile in solution. In the X-ray crystal structure[21] of $[X_2(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ [**10a** + X]$^+$ (X = H, D) (Fig. 1), only one of the two hydrido (or deuterido) ligands could be located unambiguously in a Co_3-face capping position on a crystallographic mirror plane. The apparent disorder of the other hydride (or deuteride) could well be an indication of the dynamic process going on in the solid state as well. The dideuteronated derivative $[(\mu_3\text{-}H)(\mu_3\text{-}D)_2(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}$ [**10a** + 2D]$^{2+}$ is rigid in solution on the NMR timescale. This behaviour can be explained by a merry-go-round movement of the hydrides around the metal clus-

$$\underset{\textbf{2a}}{[(CpCo)_3(CCH_3)_2]} \xrightleftharpoons[-H^+]{+H^+} \underset{[\textbf{2a}+H]^+}{[(\mu_2\text{-}H)(CpCo)_3(CCH_3)_2]^+}$$

$$\underset{\textbf{10a}}{[H(CpCo)_4CCH_3]} \xrightleftharpoons[-H^+]{+H^+} \underset{[\textbf{10a}+H]^+}{[(\mu_3\text{-}H)_2(CpCo)_4CCH_3]^+} \xrightleftharpoons[-H^+]{+H^+} \underset{[\textbf{10a}+2H]^{2+}}{[(\mu_3\text{-}H)_3(CpCo)_4(CCH_3)]^{2+}}$$

SCHEME 1

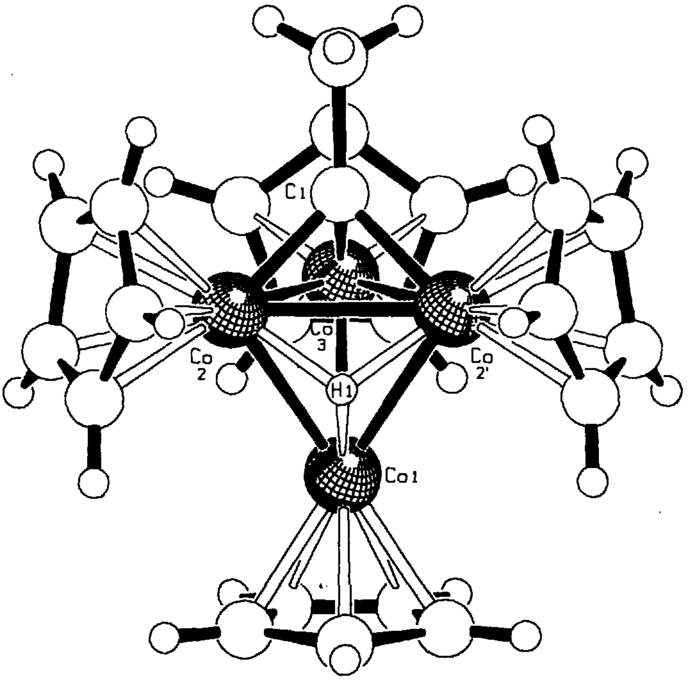


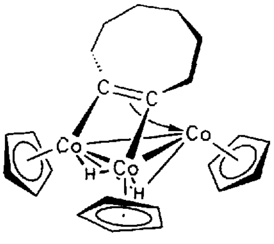
FIGURE 1 Molecular structure of $[X_2(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ [**10a** + X]$^+$ (X = H, D).

ter "surface," which requires at least one tricobalt face not permanently occupied by a hydrido ligand.

2a is also protonated by strong acids. The resulting cation [**2a** + H]$^+$ has a Co_2 edge bridging hydrido ligand which is highly dynamic in solution.[21] In contrast, $[(Cp^*Co)_3(\mu_3\text{-}CCH_3)_2]$ **13** does not react with strong Brønstedt acids.

The mechanism of the transformation of ethylene into ethylidyne and hydrogen radicals with concurrent formation of metal clusters, brought about somehow by [CpCo], is expected to be quite complicated. Hence it is not too surprising that it is only one of several reaction pathways which are open for an olefin.

The transformation of an alkene into an alkylidyne should be a lot more difficult when the carbon–carbon double bond is internal rather than terminal. Since the isomerisation *via* double bond shifts



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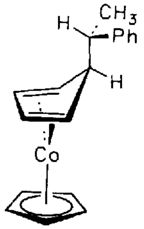
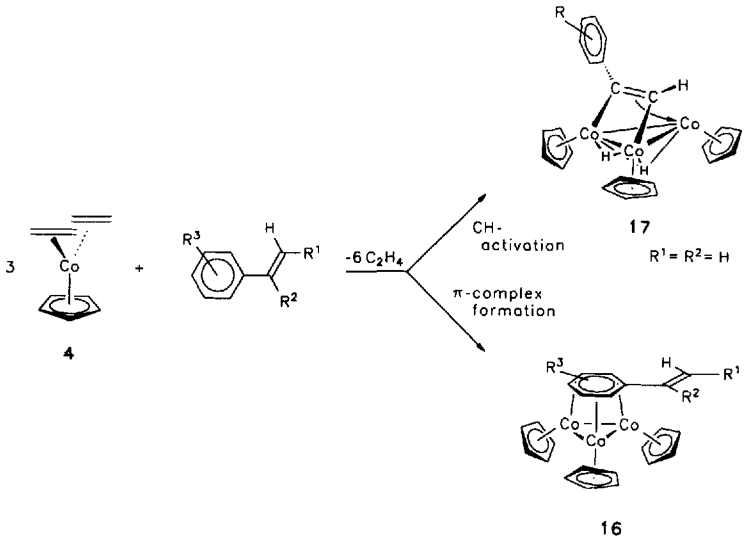


15

is catalysed by **4**, most internal olefins are unsuitable. *i*-Butene, which is innocent in this respect, does not even substitute ethylene in **4**, nor has it been possible to generate a CpCo complex with this olefin as a ligand. However, when **4** is heated with excess cyclooctene the trinuclear hydrido cluster complex **14** with a face capping alkyne ligand is formed.[22] The latter ligand is the product of CH-activation of the olefin which is dehydrogenated to form a cycloalkyne and two cluster bound hydrido ligands. Complex **14** is also formed when cobaltocene is treated with potassium and cyclooctene between −10°C and room temperature.

A very rewarding chemistry opened up when we investigated the reactions of phenyl substituted olefins with **4**. This, however, became obvious only on the second try. When styrene (either neat or in solution) is mixed with **4**, ethylene is evolved and a red solution is formed. Depending on the further treatment of these solutions and on the solvent, various products, mainly the mononuclear complexes $[CpCo(\eta^4\text{-}C_5H_6)]$ **9** and $[CpCo(\eta^4\text{-}\{Ph(H)Me\}\cdot CC_5H_5)]$ **15** can be isolated in low yields. The phenylethylidyne clusters **2b** and **10b** are only formed in very small amounts.[23] In general the reaction is quite messy, and although the formation of **15** can be explained by a stereospecific addition of the *exo*-CH bond of the methylene group of **9** across the olefinic double bond of styrene, there is no indication how and why **9** is formed in the first place.

Fortunately we did not stop at this point and turned to substituted styrenes. A very different reaction is observed when side chain substituted styrenes are treated with **4** or **7**. CH-activation



is not a preferred reaction pathway here. In many cases trinuclear cluster complexes **16** with Co_3-face capping arene ligands are formed in high yields.[24] We have studied these interesting complexes in some detail; the results are summarised elsewhere.[25]

Ring substituted styrenes take an intermediate position between styrene itself and the side-chain substituted derivatives. $(CpCo)_3$ clusters are always formed with **4**. However, usually two isomeric products are isolated: the μ_3-arene cluster complexes **16** and the μ_3-alkyne hydrido cluster complexes **17**.[26] The presence of a Co_3-face capping *p*-tolylacetylene ligand [rather than the alternative isomer (*p*-tolyl)vinylidene)] in **17a** (R^3 = *p*-CH_3) was proven by an X-ray crystal structure analysis (Fig. 2). The hydrido ligands occupy μ_2- and μ_3-positions on the Co_3-cluster. In solution both the bridging alkynes and the hydrides are fluxional.[26]

The main products of the reactions of *m*- and *p*-distyrylbenzene with **4** are the dinuclear complexes $[(CpCo)_2(\eta^4{:}\eta^4\text{-distyrylbenzene})]$ **18a**, **b**.[27] Here the two CpCo groups are each bound to an exocyclic and an endocyclic C–C double bond of the dialkenylbenzene. Using **7** as a source of CpCo fragments in the reaction with *p*-distyrylbenzene the μ_3-arene complex **19** was also obtained

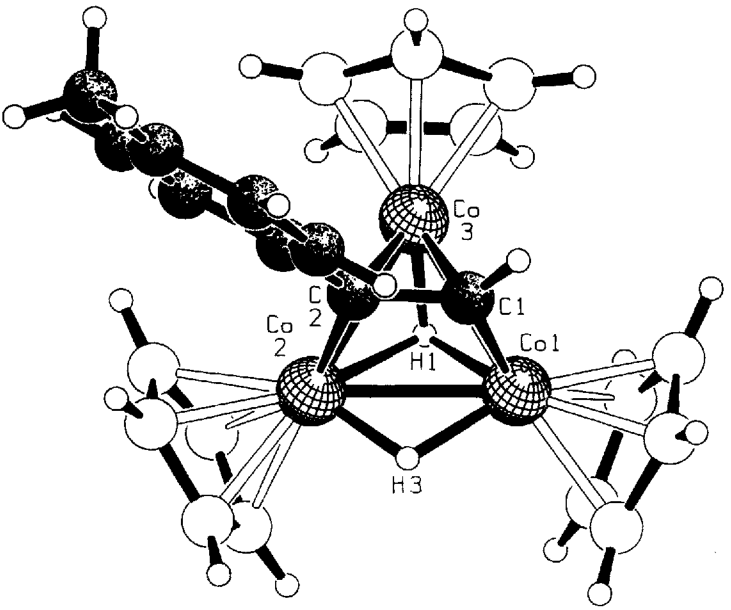
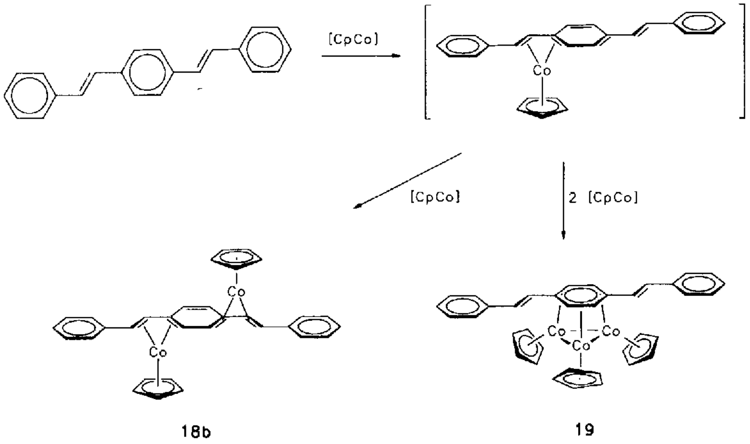
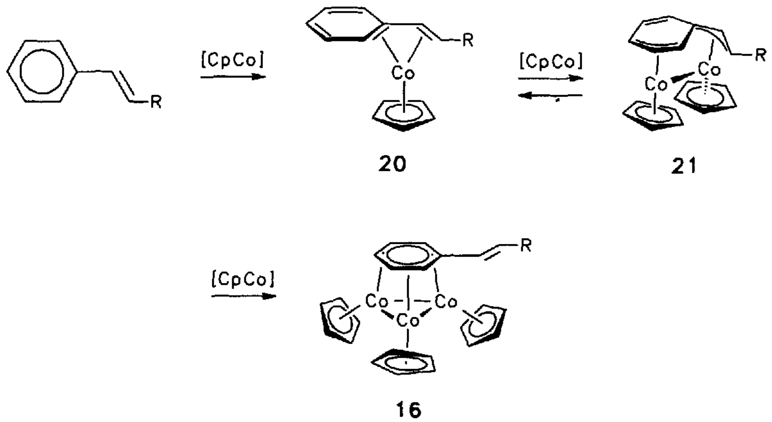


FIGURE 2 Molecular structure of $[(\mu_2\text{-H})(\mu_3\text{-H})(\text{CpCo})_3(1\text{-}\sigma\text{:}2\text{-}\sigma\text{:}1,2\text{-}\eta\text{-}p\text{-tolylacetylene})]$ **17a**.

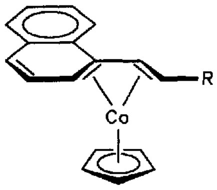




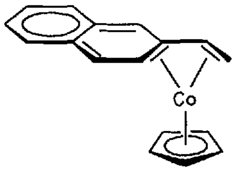
SCHEME 2

along with **18b**.[28] These results shed some light on the postulated mechanism of formation of the (CpCo)$_3$(μ_3-alkenylarene) cluster complexes (Scheme 2).[29] A (CpCo)$_3$ cluster can only be formed if additional CpCo fragments add to the mononuclear intermediate **20** in a *syn* position with respect to the first cobalt atom. Therefore the complex **21** with a bridging μ-(β,α,1-η^3:2-4-η^3-alkenylbenzene) ligand was postulated as a dinuclear intermediate. In **21** the cobalt atoms are held together on the same face of the arene by a metal–metal bond. A further [CpCo] could then add to the still uncomplexed C–C double bond in **21** and finally form the tricobalt cluster.

In the case of the distyrylbenzenes the mononuclear interme-



22a, R= H
23a, R= Me



22b

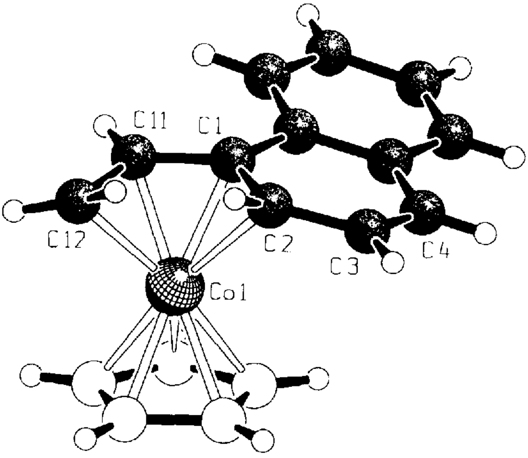


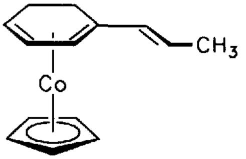
FIGURE 3 Molecular structure of [CpCo(β,α,1,2-η-α-vinylnaphthalene)] **22a**.

diates may be "trapped" by addition of a further CpCo fragment to the diene system which is formed by the second alkenyl group and one of the C–C bonds of the central arene ring. The products **18a**, **b** now have two CpCo groups *anti* to each other and do not react further.

With simple alkenylbenzenes neither of the intermediates **20** or **21** can be isolated or observed spectroscopically. Although the β,α,1,2-η^4-coordination of the alkenylbenzene in **20** does not seem to be too unusual there are only very few CpCo complexes with this type of coordination in the literature. We therefore attempted to model the coordination geometry postulated for **20** and **21**. Some of our models are the distyrylbenzene complexes **18a**, **b** and the alkenylnaphthalene complexes **22a**, **b** and **23a**.[29] The η^4-coordination of α-vinylnaphthalene was proven by an X-ray crystal structure analysis of **22a** (Fig. 3). Unfortunately **22** and **23** do not react further with [CpCo]. The *syn*-μ-(1-3-η^3:4-6-η^3)-coordination of a hexatriene unit, as postulated for the dinuclear intermediate **21**, is present in the complex **24b**[29] (see below), but the ligand is acyclic in this case.

1-Vinylcyclohexadiene-(1,3) would be the simplest cyclic ligand capable of a *syn*-μ-(α,β,1-η^3:2-4-η^3) coordination to a $(CpCo)_2$

24a, R= H
24b, R= Ph



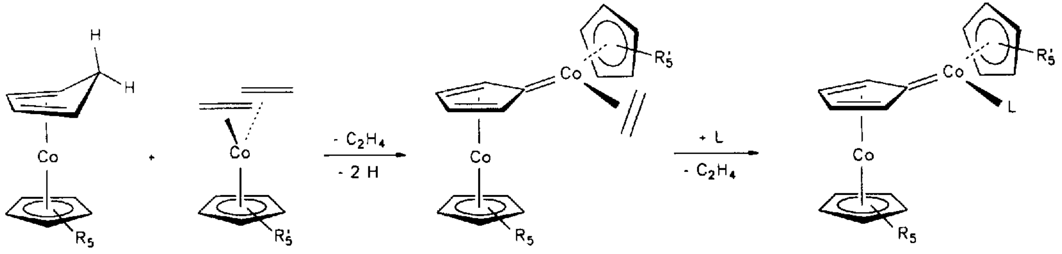
25

group. This ligand is, however, highly unstable. We were successful in preparing **25** from [CpCo{1-4-η-(1-formyl)cyclohexadiene-(1,3)}].[30] Unfortunately, when treated with **4**, **25** undergoes facile hydrogen shifts along the propenylcyclohexadiene ligand leading to a multitude of inseparable isomers.[31]

COBALTAFULVENE AND COBALTAPENTALENE COMPLEXES

As described in the preceding chapter, the reaction of certain olefins with [CpCo] can take one or several different routes and may lead to cluster complexes with a variety of organic ligands. We wished to utilise the CH-activating power of [CpCo] in a more controlled fashion for the generation of dinuclear complexes. Therefore a mononuclear complex with "built in" CH-activity was needed. [CpCo(Cyclopentadiene)] **9** is such a complex, since the $C-H_{exo}$ bond of the methylene group of its cyclopentadiene ligand shows enhanced reactivity.[32] **9** indeed reacts very readily with **4** already at room temperature. But again we were in for a surprise! During this reaction *both* C–H bonds of the methylene group in **9** are cleaved, and the dinuclear μ-cyclopentadienylidene complex **26a** precipitates analytically pure from the solution in high yield.[33] This is a very rare example where a carbene is generated directly from a saturated hydrocarbon center. Subsequently we prepared various substituted derivatives **27a–30a** from the appropriate starting materials in the same way.[34]

The tendency of formation of the dicobalt cyclopentadienylidene bridged complexes is very high indeed. When a hexane solution



9, R = H
31, R = Me

4, R' = H
5, R'_5 = H_4Me
6, R' = Me

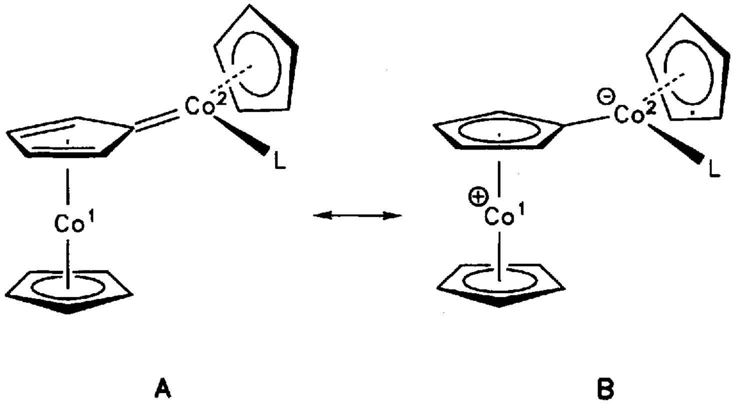
26a, R = R' = H
27a, R = H, R'_5 = H_4Me
28a, R = H, R' = Me
29a, R = Me, R' = H
30a, R = R' = Me

L = PR_3, $P(OR)_3$, CO, CNR

of **6** is heated with excess cyclopentadiene CpH, the intermediate [Cp*Co(C_5H_6)] **31** cannot be isolated but is immediately converted to **30a**. Even after heating of **6** in neat CpH, **32** can only be isolated in ca. 40% yield, and **30a** is still formed in considerable quantity.[35]

The complexes **26a**–**30a** still retain an ethylene ligand which can easily be substituted by two electron donors. It is interesting to note that the trimethylphosphine substituted complexes can only be made *via* this route and not directly, e.g., from **9** and [CpCo(C_2H_4)(PMe_3)]. This is probably due to the fact that the ethylene ligand is much more difficult to displace in the phosphine complex than in **4**.

The dicobalt(μ-cyclopentadienylidene) complexes have a number of remarkable properties. The molecule can be considered a CpCo-complex of a cobaltafulvene. Using the 18 VE rule, two "resonance structures" **A** and **B** can be drawn.[33] **A** has a bridging carbene ligand which is η^4-bound to Co1 *via* its diene system and η^1-bound to Co2 *via* its carbene carbon center. The zwitterion **B** is formally derived from the cobaltocenium cation, where one hydrogen atom has been replaced by a $[CpCo(L)]^-$ moiety. The bridging ligand should be η^5(Co1):η^1(Co2)-coordinated in this limiting structure. Within this simple picture an acceptor ligand L is expected to stabilise structure **B**, since negative charge can be delocalised more effectively. Conversely, a donor ligand L should destabilise **B** and hence the carbene structure **A** should be more



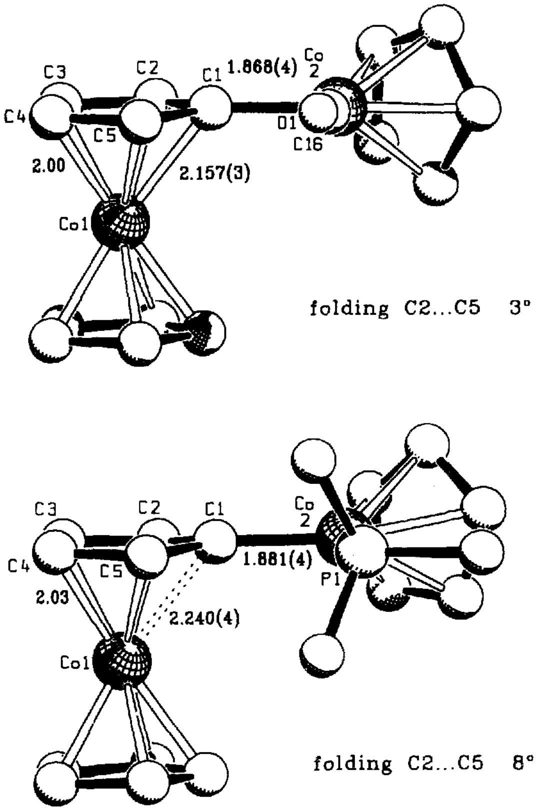


FIGURE 4 Molecular structures of [CpCo(μ-C_5H_4)Co(PMe_3)Cp] **26b** (bottom) and [CpCo(μ-C_5H_4)Co(CO)Cp] **26c** (top). Hydrogen atoms are omitted for clarity. Bond distances are given in Å.

favourable. This effect, although not very pronounced, is recognisable in the solid state structures. In Fig. 4 the molecular structures of crystalline [CpCo(μ-C_5H_4)Co(L)Cp] **26b** (L = PMe_3) and **26c** (L = CO) are shown. Neither molecule adopts one of the limiting structures **A** and **B**. Compared to **26c** there is a tendency of the cyclopentadienylidene ligand in **26b** towards the η^4:η^1-coordination, apparent from the increased folding of the C_5H_4 bridge along C2. . .C5 and the lengthening of the distance Co1. . .C1. In **26b** the latter distance is at the border of a bonding interaction (Fig. 4). A similar tendency is apparent in the series of structures of **26a**, **28a** and **29a**, this time caused by the varying electron donor properties of the Cp and Cp* ligands.[36]

The NMR spectra of **26b** show an unusual temperature dependence (Fig. 5). With increasing temperature there is a progressive shift of some of the ^{1}H resonances while others, e.g., the methyl protons of the PMe_3 ligand, show much less shift but a drastic increase in line width. The ^{31}P resonance, which at room temperature is a broad signal around $\delta = -45$, sharpens and moves to lower field on cooling ($\delta = 33.0$ at 190 K). The effects on the NMR spectra become much less pronounced along the series $L = PMe_3$–PMe_2Ph–$PMePh_2$ and are not noticeable with other derivatives.

The spectra can be explained by an equilibrium between two isomers, a diamagnetic molecule with the spin quantum number $S = 0$ and a paramagnetic species with $S = 1$. The latter is higher in energy and therefore its concentration increases from a very small value on raising the temperature. With a simple model (contact shifts only) the thermodynamics of this equilibrium can be calculated from the line shifts as a function of temperature. For **26b** $\Delta H^{0} = 27 \pm 3\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S^{0} = 50 \pm 8\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ were obtained in this way. The experimentally observed dependence of the effect on the ligand L can be corroborated with *Fenske–Hall* SCF MO calculations on various derivatives. If the energy difference between the HOMO and LUMO of the complexes is taken as an indication of the accessibility of a triplet isomer, an inverse correlation with the donor strength of L can be observed.

The complexes **26–30** are susceptible to oxidation and therefore very air sensitive. With mild oxidizing agents the blue paramagnetic chloro and bromo complexes **26d**, **e** and **30d**, **e** could be prepared from the appropriate ethylene derivatives.[37] In the crystal **30e** has a η^5:η^1-coordinated C_5H_4-bridge (Fig. 6).[37] In this complex the rotational orientation of the two parts of the molecule around the bond C1–Co2 is different from that observed in all of the derivatives of **26–29** which have been studied by X-ray crystallography (compare Fig. 4 and Fig. 6). The NMR spectra of all the diamagnetic derivatives, however, indicate that there is a rapid rotation around C1–Co2 in solution. The energy barriers for the rotation around C1–Co2, calculated with the extended Hückel MO method, are indeed very low.[37] In **30**, however, there would be considerable

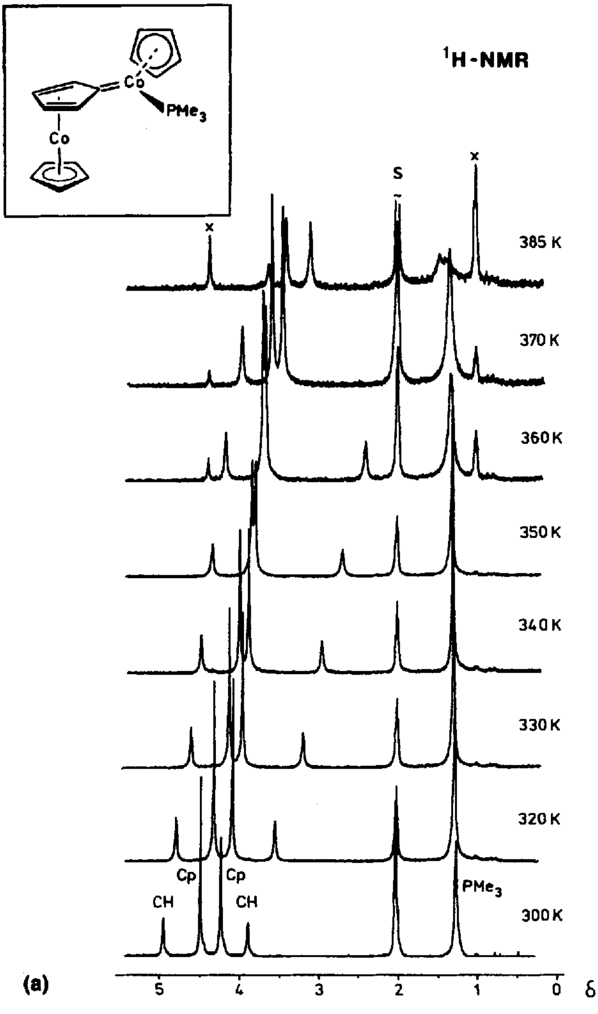


FIGURE 5 Variable temperature ^{1}H NMR spectra of [CpCo(μ-C_5H_4)Co(PMe_3)Cp] **26b** (in [D_8]-toluene, 200 MHz). (a) Measured spectra, S: solvent, x: [CpCo(PMe_3)$_2$] impurity due to partial decomposition above 90°C. (b) Chemical shifts versus inverse temperature. Solid lines are calculated (see text). Below 230 K further effects due to a slowdown of the rotation around the Co=C bond become noticeable.

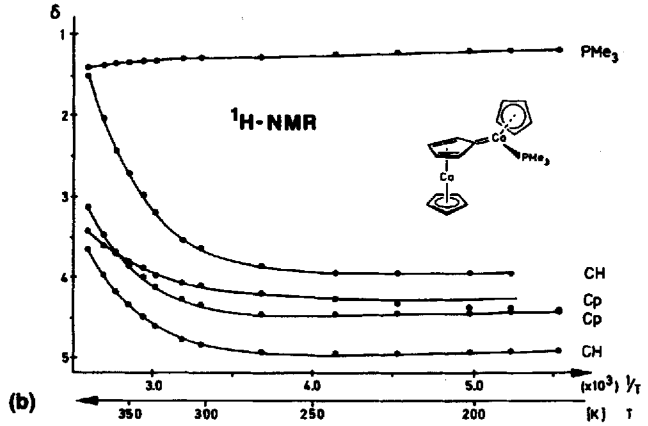
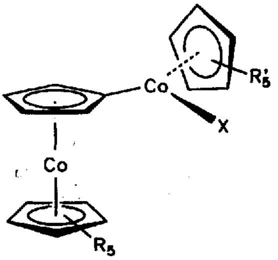


FIGURE 5 (*Continued*)

steric hindrance of the bulky Cp*-ligands in the "parallel" conformation. Therefore this conformation is not preferred, at least in the solid state.

Another dicobalt radical related to **26d**, the complex **26f**, was prepared from **26a** and diphenyldisulfide.

With some reagents **26a** is disrupted. Often this leads to uncontrolled decomposition, but in some cases aggregation of the frag-



26d, R= R'= H, X= Cl
26e, R= R'= H, X= Br
26f, R= R'= H, X= SPh
30d, R= R'= Me, X= Cl
30e, R= R'= Me, X= Br

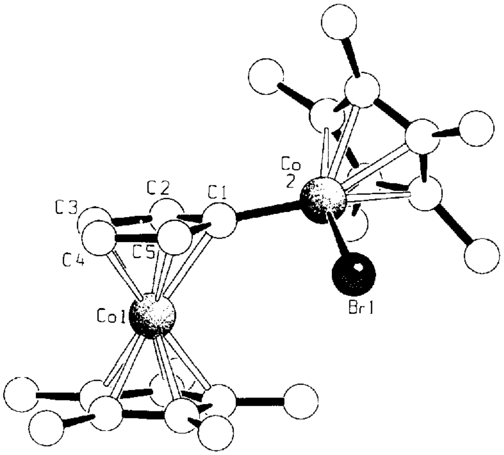


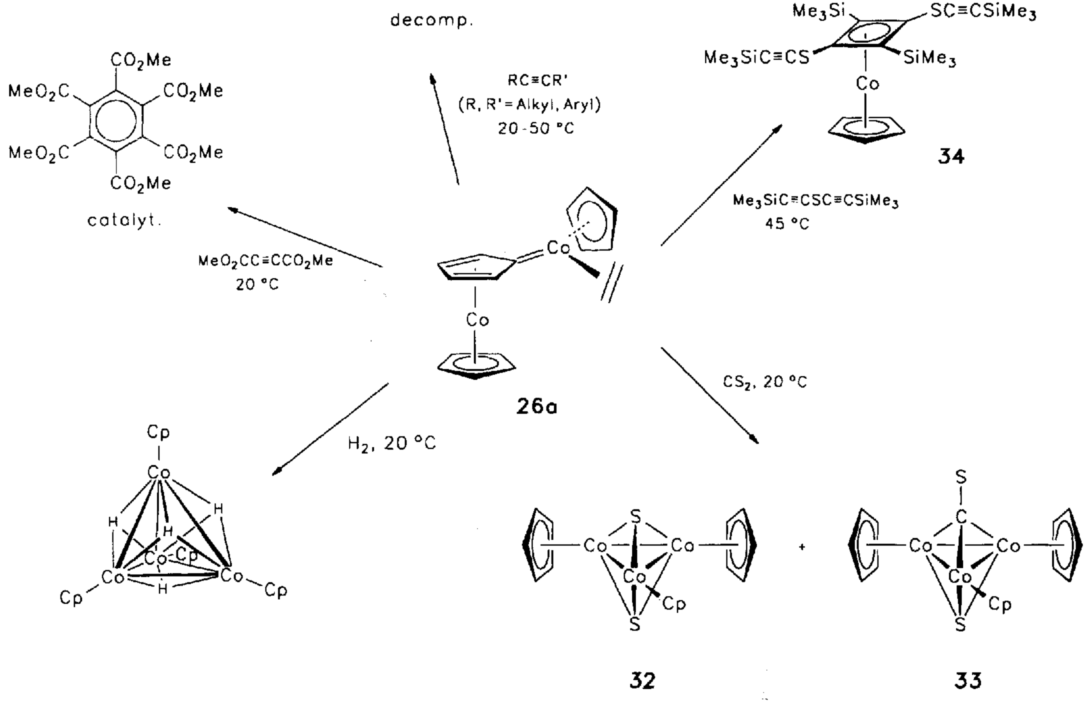
FIGURE 6 Molecular structure of [Cp*Co(μ-C_5H_4)Co(Br)Cp*] **30e**. Hydrogen atoms are omitted for clarity.

ments to clusters occurs (Scheme 3). **32** and **33** are formed in a total yield of as much as 80%.

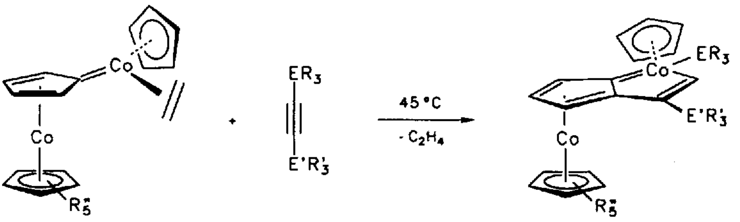
26a also reacts with many alkynes. In most cases decomposition of the dicobalt complexes occurs and no products can be isolated. Catalytic trimerisation of $(MeOOC)_2C_2$ was observed, but this could well be effected by mononuclear decomposition products. With $(Me_3SiC_2)_2S$ a cyclobutadiene complex **34** was obtained. These reactions again illustrate the high stability of the CpCo moiety which stays intact during disintegration of the dinuclear complex **26** and may be trapped by aggregation to cluster complexes and/or by newly formed ligands.

A very different reaction takes place when **26a** or **29a** is heated with certain silyl or germyl substituted alkynes. The products are the very unusual purple complexes **35–43** with metallabicyclic ring systems.[38] In marked contrast to **26–30**, the complexes **35–43** are thermally and chemically quite stable. They can be sublimed *in vacuo* without decomposition and even resist methanolic KOH at room temperature.

As with **26–30** two resonance structures can be drawn for **35–43**. Using the isolobal relationship CpCoR $\underset{0}{\longleftrightarrow}$ CH the metallabicycle in **C** can be related to the hydrocarbon pentalene and thus **35–43**, **C** can be termed CpCo complexes of η^4-(1-cobalta)pen-


decomp.
RC≡CR'
(R, R' = Alkyl, Aryl)
20-50 °C
Me$_3$SiC≡CSC≡CSiMe$_3$
45 °C
MeO$_2$CC≡CCO$_2$Me
20 °C
catalyt.
H$_2$, 20 °C
CS$_2$, 20 °C
26a
34
32
33
Me$_3$Si
SC≡CSiMe$_3$
Me$_3$SiC≡CS
SiMe$_3$
Co
Cp
S
C
H
CO$_2$Me
MeO$_2$C
+

SCHEME 3



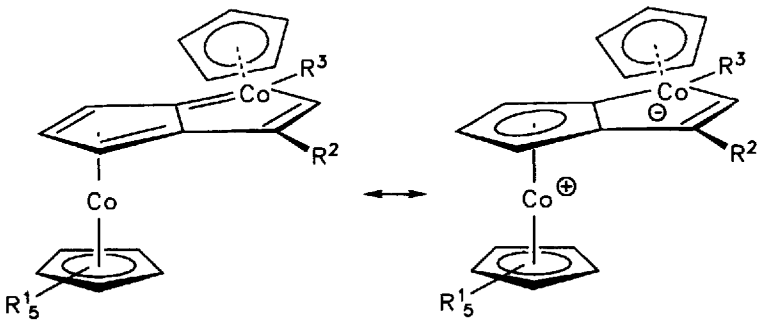
26a, R" = H
29a, R" = Me

35 - 43

talene. On the other hand, in the zwitterionic formulation **35–43**, **D** the η^5-coordinated metallabicycle is related to the 1-hydropentalenyl ligand *via* $[\mathrm{CpCoR}]^- \underset{0}{\longleftrightarrow} \mathrm{CH}_2$.

The solid state structure of **37** was determined by X-ray crystallography.[38] As apparent from Fig. 7 the cobaltapentalene is η^5-coordinated to Co1. The bond lengths within the cobaltapentalene ligand are consistent with the formulation **C** ⟷ **D**.

During the formation of **35** the gross reaction includes: (1) loss of ethylene from **26a**, (2) oxidative addition of the alkyne to Co2 in **26** (resulting in the cleavage of a C–Si bond and the formation of a Co–Si bond), (3) formation of a C–C bond from the alkyne to the cyclopentadienylidene and (4) a hydrogen shift from one of the CH-groups of the cyclopentadienylidene ligand to a carbon



C **D**

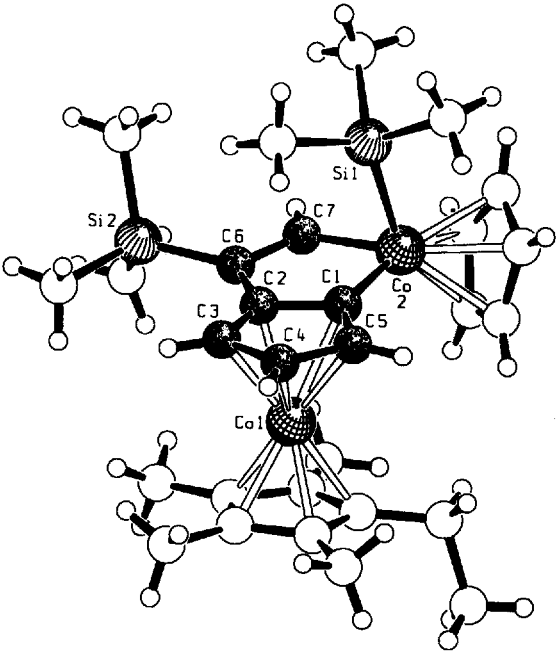


FIGURE 7 Molecular structure of the cobaltapentalene complex **37**.

atom of the former alkyne. At present the actual sequence of these key steps is not known. The reaction also proceeds (albeit at higher temperatures and with lower product yields) with **26b** and **26c**. As far as the alkyne is concerned the success of the reaction very critically depends on the substituents (Table I). The effect of steric hindrance is illustrated in the reaction of **26a** with the series of disilylalkynes $[Me_{3-n}Et_nSi]_2C_2$ (n = 0–3). With increasing n (increasing steric bulk of the silyl groups), the product yield gradually drops from 85% (n = 0) to 0% (n = 3), and higher reaction temperatures have to be used in every case (Table I).

With some unsymmetrical alkynes, regioisomers are obtained. For example, $Me_3SiC_2SiEt_3$ and **26a** give the cobaltapentalene complexes **39a**, **b** in 80% yield. When the reaction is carried out at 45°C, **39a** and **39b** are formed in a 2:1 ratio. At a reaction temperature of 65°C, a 1:1 mixture of the two isomers is formed.

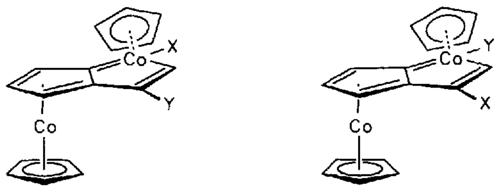
TABLE I

Complexes with the cobaltapentalene ligand

Complex	R''_5	ER_3	$E'R'_3$	Temp. [°C]	Yield [%]	$\delta(^{29}Si)$
35	H_5	$SiMe_3$	$SiMe_3$	45	80	30.2, −15.0
36	Me_5	$SiMe_3$	$SiMe_3$	50	70	29.9, −16.0
37	Me_4Et	$SiMe_3$	$SiMe_3$	55	80	29.9, −16.6
38a	H_5	$SiMe_2Et$	$SiMe_2Et$	50	65	
38b	H_5	$SiMeEt_2$	$SiMeEt_2$	65	35	
39a	H_5	$SiMe_3$	$SiEt_3$	a)	a)	30.6, −7.1
39b	H_5	$SiEt_3$	$SiMe_3$	a)	a)	38.5, −15.1
40a	H_5	$SiMe_3$	$SiMe_2^tBu$	45	b)	
40b	H_5	$SiMe_2^tBu$	$SiMe_3$	45	b)	
41a	H_5	$SiMe_3$	CMe_3	45	85	29.5
42a	H_5	$SiMe_3$	$GeMe_3$	a)	a)	30.0
42b	H_5	$GeMe_3$	$SiMe_3$	a)	a)	−15.4
43	H_5	$GeMe_3$	$GeMe_3$	45	60	–

a) See text.
b) Total yield 80%.

Even more convincingly, from $Me_3GeC_2SiMe_3$ and **26a**, only **42a** is obtained at 45°C in 80% yield. Again at 65°C **42a** and **42b** are formed in a 1:1 rato. Both **39a, b** and **42a, b** do not interconvert once they have been formed. This can be considered an example of kinetic control of the reaction where the two regioisomers are formed at different rates. The reaction of **26a** with $Me_3SiC_2^tBu$ is fully regiospecific: only the product **41a** with the silyl group on the cobalt atom is formed.



a b

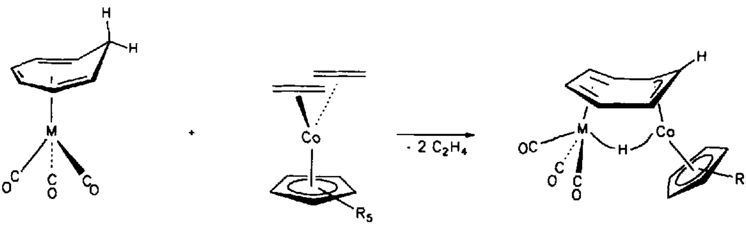
39, X= $SiMe_3$, Y= $SiEt_3$
42, X= $SiMe_3$, Y= $GeMe_3$

COMPLEXES WITH BRIDGING CYCLOHEPTATRIENYL AND CYCLOHEPTATRIENE LIGANDS

The η^4-cyclopentadiene complexes **9** and η^6-cycloheptatriene complexes **44–46** have many features in common. Along with structural similarities (planar metal coordinated diene resp. triene systems with the methylene groups folded away from the metal) they both have activated methylene groups. In **9** activation is commonly only observed for the C–H bond in the *exo*-position with respect to the metal. This is also the case for **44–46**, but in these complexes the *endo*-hydrogen also exhibits enhanced reactivity.[39]

When **44–46** are heated with **6** at 60–80°C CH-activation occurs at the methylene group of the coordinated cycloheptatriene. Unlike the reaction of the coordinated cyclopentadiene in **9**, only one of the two C–H bonds is cleaved, resulting in the formation of the brown (μ_2-cycloheptatrienyl)(μ_2-hydrido) complexes **47b–49b**.[34] Formally this reaction can be described as an insertion of [Cp*Co] into the C–H_{endo} bond of the methylene group. In the series **47b–48b–49b** the yields of the heterodinuclear complexes increase from 20 to 65%. Up until now, a heterodinuclear CpCo complex (**49a**) could only be prepared with M = W.

The hydrogen shift from the methylene group of the coordinated cycloheptatriene to the metal is reversible. Thus, upon treatment of **47b** with CO, **44** is regenerated along with [Cp*Co(CO)$_2$]. It is interesting to note that attempts to synthesise the (μ_2-cyclohep-



44, M = Cr
45, M = Mo
46, M = W

4, R = H
6, R = Me

47b, M = Cr, R = Me
48b, M = Mo, R = Me
49a, M = W, R = H
49b, M = W, R = Me

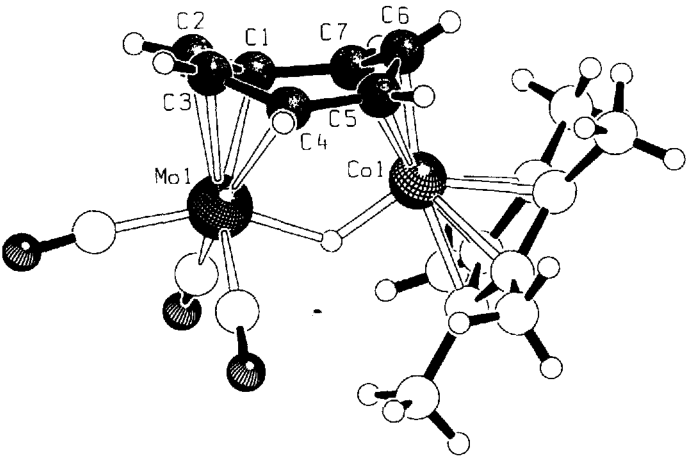


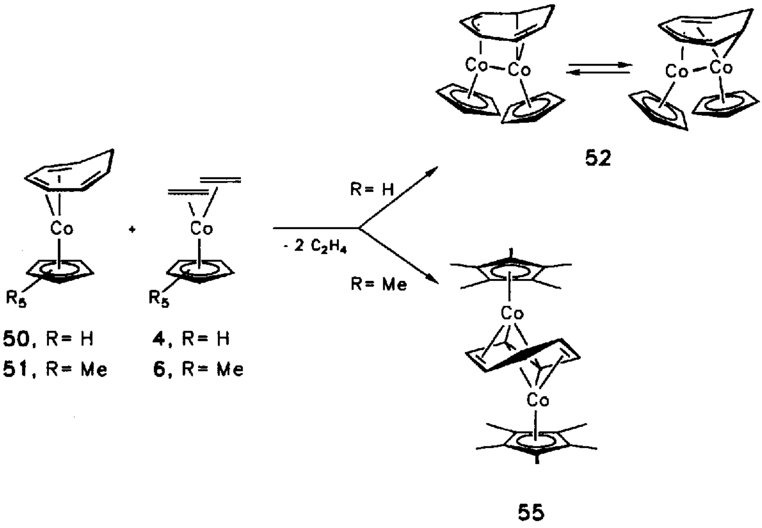
FIGURE 8 Molecular structure of $[(CO)_3Mo(\mu\text{-}1\text{-}4\text{-}\eta\text{:}5\text{-}7\text{-}\eta\text{-}C_7H_7)(\mu\text{-}H)CoCp^*]$ **48b**.

tatrienyl)(μ_2-hydrido) complexes **47b–49b** the other way around by heating $[(CO)_3Cr(NCMe)_3]$ as a source of $(CO)_3Cr$-fragments with $[CpCo(\eta^4\text{-}C_7H_8)]$ **50** or $[Cp^*Co(\eta^4\text{-}C_7H_8)]$ **51** were not successful. Instead the mononuclear substitution products $[(CO)_3 \cdot Cr(C_7H_8)]$ **44** and $[CpCo(CO)_2]$ or $[Cp^*Co(CO)_2]$ are obtained.[35]

The solid state structures of **47b** and **48b** were investigated by X-ray crystallography (Fig. 8).[34,35] The two molecules are very similar. The cycloheptatrienyl ring has a boat conformation and is coordinated in a *syn*-η^4(M):η^3(Co)-fashion to the $(CO)_3MCoCp^*$ backbone (M = Cr, Mo). The bond lengths in the C_7 ring can be interpreted in terms of (η^4-diene)M and (η^3-enyl)Co units, joined to each other by longer C–C bonds. The d^6-metal M, Co and a bridging hydride make up a 3c–2e MHCo bond which allows the two metals to attain 18 VE configurations.

47–49 are fluxional in solution. Unlike in most other μ-C_7H_7 dinuclear complexes,[39] the ring-whizzing of the cycloheptatrienyl ligand on top of the dimetal backbone of **47–49** could be frozen on the NMR timescale at 200 K. According to the NMR data the ground state in solution corresponds to a μ-[η^4(M):η^3(Co)] coordinated C_7H_7-bridge as in the solid state.[34,35]

In the cyclopentadiene and cycloheptatriene complexes **9**, **31** and **44–46** all the olefinic carbon atoms of the ligand are coordi-



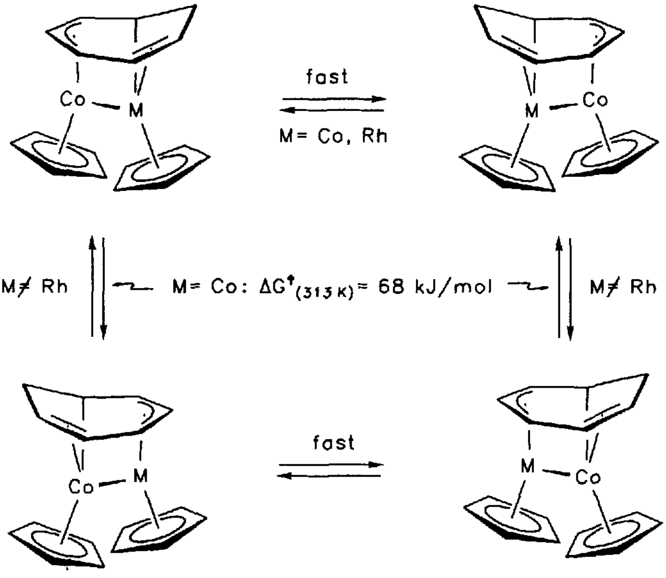
nated to the metal (Co and Cr, Mo, W, respectively). During the reactions with [CpCo], attack at the saturated carbon center (i.e., at the methylene group) takes place, resulting in CH-activation. In the complexes **50** and **51** only four of the olefinic carbon atoms of the cycloheptatriene ligand are metal coordinated. One of the C–C double bonds remains free and should be the preferred site of an attack by organometallic fragments.

50 and **51** react with **4** and **6**. However, the course of the reaction critically depends on the degree of substitution of all the Cp ligands, and may involve either addition of CpCo or Cp*Co fragments to the η^4-coordinated cycloheptatriene or exchange of this ligand.[40,41] CH-activation does not occur.

From the CpCo complexes **50** and **4**, the dicobalt complex **52** is obtained. In **52** the two CpCo groups are *syn* coordinated to the intact cycloheptatriene ligand. A similar heterobimetallic complex $[\mathrm{CpRh}(\mu\text{-}C_7H_8)\mathrm{CoCp}]$ **54** is formed when $[\mathrm{CpRh}(\eta^4\text{-}C_7H_8)]$ **53** is treated with **4**.[41] Addition of a Cp*Co fragment (generated from **6**) to **51** takes place in the *anti* position. The complex **55** which is formed in this reaction shows a novel coordination mode of cycloheptatriene which has so far been unique to this complex.

No "mixed" dinuclear complexes [CpM(μ-C_7H_8)M'Cp*] (M, M' = Co, Rh) could be prepared. Using **6** as a source of Cp*Co fragments, the main reaction pathway was exchange of cycloheptatriene. Thus **51** and **52** were generated from **50** and **6**. Likewise, **51** was one of the products of the reaction of **53** and **6**. No reaction took place between **51** and **4** or **7**.

The structures of **52** and **54** could only be determined in solution from NMR data. Both complexes are highly fluxional. Two distinct exchange processes were found for **52** (Scheme 4).[40] A low energy process interconverts the two enantiomers with a μ-(1-σ,5-6-η:2-4-η-cycloheptatriene) bridge. This valence tautomerisation is still fast at 190 K. A high energy process interconverts the two CpCo groups ($\Delta G^{\neq}$ (310 K) = 67.5 kJ/mol); this amounts to an almost free "rotation" of the cycloheptatriene on top of the dicobalt backbone. As apparent from the ^{103}Rh couplings in the ^{13}C NMR spectrum, the cycloheptatriene in **54** always has a *syn*-[η^3(Co):σ^1,η^2(Rh)] coordination. As in the dirhodium complex [$(CpRh)_2(\mu\text{-}C_7H_8)$] **56**,[42] the full rotation of the cycloheptatriene ring (i.e., exchange



SCHEME 4

of the metals involved in η^3- and σ^1,η^2-bonding) is no longer energetically accessible in **54**. With the reasonable assumption of similar chemical shift differences between the individual carbon atoms of the cycloheptatriene ligands, the activation barriers for the enantiomerisation of **52**, **54** and **56** can be compared. The relative order for $\Delta G^{\neq}$ **52** < **54** < **56** is in accord with the increased σ and π metal-to-carbon bond strength of Rh as compared to Co.[41]

In marked contrast to the *syn*-dimetal cycloheptatriene complexes, the *anti*-complex **55** is rigid in solution. According to the X-ray structure analysis (Fig. 9) the cycloheptatriene ligand in this "slipped triple decker" sandwich complex has an *anti*-μ-(1-4-η^4:3-6-η^4)-coordination.[40] One of the three C–C double bonds of the bridging polyolefin is coordinated to Cp*Co-groups from both sides. Consequently the distance C1–C1′ is enlarged to 1.516(6) Å.

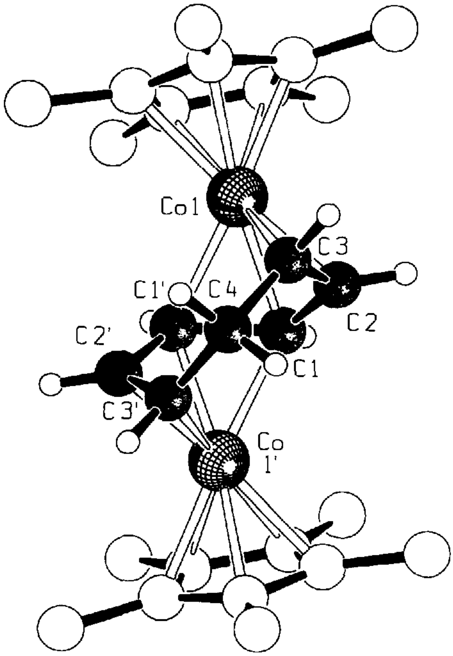


FIGURE 9 Molecular structure of *anti*-[(Cp*Co)$_2$(μ-1-4-η:3-6-η-cycloheptatriene)] **55**. Methyl hydrogens are omitted for clarity.

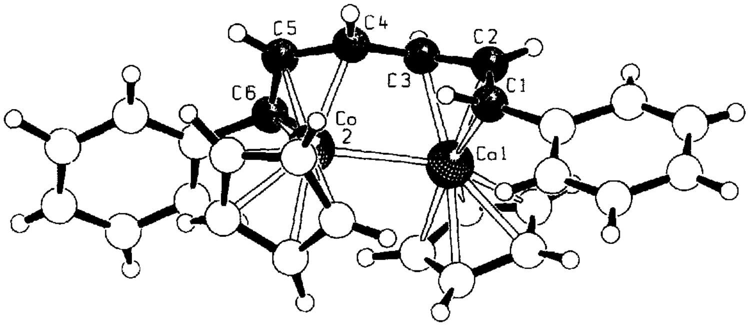
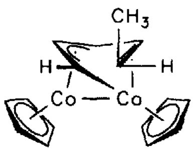


FIGURE 10 Molecular structure of *syn*-[(CpCo)$_2$(μ-1-3-η:4-6-η-1,6-diphenylhexatriene)] **24b**.

It may be noted here that dinuclear CpCo complexes of acyclic hexatrienes have structures which are quite different from **52** and **55**. [CpCo(1-4-η-1,6-diphenylhexatriene)] reacts with **4** to form the dicobalt complex **24b**.[29] In **24b** the hexatriene ligand adopts a bis(η^3-enyl) type coordination to the (CpCo)$_2$ backbone of the complex (Fig. 10). Although the bridging ligand is severely twisted around its "central" carbon–carbon bond the arrangement of the two metals is best described as a *syn*-configuration. The two cobalt atoms achieve an 18 VE configuration by means of a rather long (2.63(1) Å) metal–metal bond.

A similar complex **24a** with the unsubstituted 1,3,5-hexatriene as a ligand was postulated[43] as the unstable intermediate in the formation of [(CpCo)$_2$(1-σ,4-5-η:1-3-η-hexa-2,4-diene-1,1-diyl)] **57**. During this reaction, **24a** is thought to undergo a [1,6] hydrogen shift along the C$_6$ chain initiated by vinyl CH-activation. Such a reaction does not take place in **24b**. **24b** is, however, fairly labile



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and one of the CpCo-groups can easily be removed from the complex, e.g., by reaction with ethylene.

CONCLUDING REMARKS

Bridging hydrocarbon and hydrocarbyl ligands have been given "a pivotal position in the development of dinuclear and polynuclear organometallic chemistry."[44] Such complexes have been known for a long time and are of ever increasing interest.[45] When we set off in this chemistry our goal was to construct oligonuclear complexes from CpCo fragments using a hydrocarbon ligand as the molecular glue to keep them together. This approach was indeed rather fruitful; however, quite a few of the products were not what we initially expected and prompted further investigations. In the process we were able to gain some experience and a little insight into the various possible reaction pathways. We are, however, far from understanding all the factors which control the course of a particular reaction and decide which of the routes the system will choose. Even some of the very key steps, e.g., the mechanism of ligand substitution in [$CpCoL_2$], are still poorly understood. This reaction can be either associative or dissociative, and examples have been found experimentally for both possibilities.[46] A similar situation exists with the enylic CH activation at a metal center which can take place with or without prior π-coordination of the olefin.[47]

We are still at a stage where every new reaction—as trivial as it may seem—could be the entrance to a new and fascinating chapter of organometallic chemistry.

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References

1. R. Hoffmann, H. Fujimoto, J. R. Swenson and C.-C. Wan, J. Am. Chem. Soc. **95**, 7644 (1973); H. Fujimoto and R. Hoffmann, J. Phys. Chem. **78**, 1167 (1974).
2. M. Elian, M. M. L. Chen, D. M. P. Mingos and R. Hoffmann, Inorg. Chem. **15**, 1148 (1976).
3. See for example: S. G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis* (Pergamon Press, Oxford, 1982); R. D. W. Kemmitt and D. R. Russell, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel (Pergamon Press, Oxford, 1982), Vol. 5, Ch. 34; *Methoden der Organischen Chemie (Houben-Weyl)*, ed. J. Falbe, Vol. E18$_{\mathrm{I,II}}$ (Thieme Verlag, Stuttgart, 1986) and references therein.
4. Y. Wakatzuki and H. Yamazaki, J. Chem. Soc., Chem. Commun. **1973**, 280; Y. Wakatzuki, O. Nomura, K. Kitaura, K. Morokuma and H. Yamazaki, J. Am. Chem. Soc. **105**, 1907 (1983) and references therein.
5. K. P. C. Vollhardt, Acc. Chem. Res. **10**, 1 (1977); E. D. Sternberg and K. P. C. Vollhardt, J. Org. Chem. **49**, 1564 (1984); K. P. C. Vollhardt, Angew. Chem. **96**, 525 (1984) and references therein.
6. R. Gleiter and D. Kratz, Acc. Chem. Res. **26**, 311 (1993) and references therein.
7. H. Bönnemann, Angew. Chem. **97**, 264 (1985) and references therein.
8. J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson and V. W. Day, J. Am. Chem. Soc. **101**, 2768 (1979).
9. B. Eaton, J. M. O'Connor and K. P. C. Vollhardt, Organometallics **5**, 394 (1986).
10. K. Jonas and C. Krüger, Angew. Chem. **92**, 513 (1980).
11. K. Jonas, E. Deffense and D. Habermann, Angew. Chem. **95**, 729 (1983); Angew. Chem. Suppl. **1983**, 1005.
12. R. Hoffmann, Angew. Chem. **94**, 725 (1982) and references therein.
13. T. P. Fehlner, J. Feilong and A. L. Rheingold, J. Am. Chem. Soc. **109**, 1860 (1987).
14. J. R. Pipal and R. N. Grimes, Inorg. Chem. **16**, 3255 (1977).
15. J. Müller and H. Dorner, Angew. Chem. **85**, 867 (1973).
16. H. Wadepohl and H. Pritzkow, Polyhedron **8**, 1939 (1989).
17. S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Organomet. Chem. **296**, C6 (1985).
18. G. A. Somorjai, Struct. Bonding (Berlin) **38**, 1 (1979).
19. A. Wieckowski, S. D. Rosasco, G. N. Salaita, A. Hubbard, B. E. Bent, F. Zaera, D. Godbey and G. A. Somorjai, J. Am. Chem. Soc. **107**, 5910 (1985); but see also: T. P. Beebe, Jr. and J. T. Yates, Jr., J. Am. Chem. Soc. **108**, 663 (1986).
20. R. B. A. Pardy, G. W. Smith and M. E. Vickers, J. Organomet. Chem. **252**, 341 (1983).
21. H. Wadepohl and H. Pritzkow, J. Organomet. Chem. **450**, 9 (1993).
22. T. Borchert and H. Wadepohl, manuscript in preparation.
23. H. Wadepohl, K. Büchner, M. Herrmann and H. Pritzkow, Organometallics **10**, 861 (1991).
24. H. Wadepohl, K. Büchner and H. Pritzkow, Angew. Chem. **99**, 1294 (1987).
25. H. Wadepohl, Angew. Chem. **104**, 253 (1992).
26. H. Wadepohl, T. Borchert, K. Büchner and H. Pritzkow, Chem. Ber. **126**,

1615 (1993).
27. K. Büchner, Dissertation, Universität Heidelberg (1989).
28. M. Herrmann, Dissertation, Universität Heidelberg (1991).
29. H. Wadepohl, K. Büchner and H. Pritzkow, Organometallics **8**, 2745 (1989).
30. F.-J. Paffen, Diplomarbeit, Universität Heidelberg (1990).
31. H. Wadepohl and F.-J. Paffen, unpublished results.
32. E. O. Fischer and G. E. Herberich, Chem. Ber. **94**, 1517 (1961).
33. H. Wadepohl and H. Pritzkow, Angew. Chem. **99**, 132 (1987).
34. H. Wadepohl, W. Galm and H. Pritzkow, Angew. Chem. **101**, 357 (1989).
35. W. Galm, Dissertation, Universität Heidelberg (1990).
36. A. Wolf, Diplomarbeit, Universität Heidelberg (1991).
37. H. Wadepohl, W. Galm, H. Pritzkow and A. Wolf, J. Chem. Soc., Chem. Commun. **1993**, in press.
38. H. Wadepohl, W. Galm, H. Pritzkow and A. Wolf, Angew. Chem. **104**, 1050 (1992).
39. G. Deganello, *Transition Metal Complexes of Cyclic Polyolefins* (Academic Press, London, 1979), Ch. I and references therein.
40. H. Wadepohl, W. Galm and H. Pritzkow, Angew. Chem. **102**, 701 (1990).
41. H. Wadepohl, W. Galm and A. Wolf, J. Organomet. Chem. **452**, 193 (1993).
42. J. Evans, B. F. G. Johnson, J. Lewis and R. Watt, J. Chem. Soc., Dalton Trans. **1974**, 2368.
43. J. A. King, Jr. and K. P. C. Vollhardt, J. Am. Chem. Soc. **105**, 4846 (1983).
44. M. H. Chisholm, Polyhedron **7**, 757 (1988).
45. W. Beck, B. Niemer and M. Wieser, Angew. Chem. **105**, 969 (1993) and references therein.
46. (a) A. Wojcicki and F. Basolo, J. Inorg. Nucl. Chem. **17**, 77 (1961); H. G. Schuster-Woldan and F. Basolo, J. Am. Chem. Soc. **88**, 1657 (1966); M. E. Rerek and F. Basolo, Organometallics **2**, 372 (1983). (b) A. H. Janowicz, H. E. Bryndza and R. G. Bergman, J. Am. Chem. Soc. **103**, 1516 (1981).
47. (a) P. O. Stoutland and R. G. Bergman, J. Am. Chem. Soc. **107**, 4581 (1985); J. Silvestre, M. J. Calhorda, R. Hoffmann, P. O. Stoutland and R. G. Bergman, Organometallics **5**, 1841 (1986). (b) H. Werner, T. Dirnberger and M. Schulz, Angew. Chem. **100**, 993 (1988).