A Novel Type of Resonance-Stabilised Dicobalt Complex with a Cyclopentadienylidene Bridge—Synthesis, Structure and Electronic Properties of $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5R_5)']$ ($L = C_2H_4$, CO, CN*t*Bu, PR_3, $P(OMe)_3$; R = H, Me)

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Dedicated to Professor Gerhard E. Herberich on the occasion of his 60th birthday

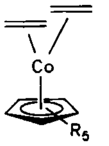
Abstract: The dinuclear μ-cyclopentadienylidene complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5R'_5)]$ (**5**) [**5aa** (R = R' = H), **5ab** (R = H, R' = Me), **5ac** (R = H, $R'_5 = H_4Me$), **5ba** (R = Me, R' = H), **5bb** (R = R' = Me) and **5da** ($R_5 = Me_4Et$, R' = H)] were synthesised from $[(C_5R_5)Co(\eta^4\text{-}C_5H_6)]$ (**4**) [**4a** (R = H), **4b** (R = Me), **4d** ($R_5 = Me_4Et$)] and $[(C_5R'_5)Co(C_2H_4)_2]$ (**1**) [**1a** (R' = H), **1b** (R' = Me) and **1c** ($R'_5 = H_4Me$)]. In these reactions, both CH bonds of the methylene group of coordinated cyclopentadiene are activated under mild conditions. Substitution of the ethylene ligand in **5** by L leads to the carbonyl, isocyanide, phosphine, and phosphite derivatives $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5R'_5)]$ [**6aa**, **6ab**, **6ba**, **6bb** (L = CO), **7aa** (L = *t*BuNC), **8aa**, **8ab** (L = PMe_3), **9aa** (L = PMe_2Ph), **10aa** (L = $PMePh_2$) and **11aa** (L = $P(OMe)_3$)]. The crystal structures of **5aa**, **5ab**, **5ba**, **6aa** and **8aa** have been determined. The experimental geometry is rationalised in terms of two limiting structures with $\mu\text{-}\eta^4{:}\eta^1$ and $\mu\text{-}\eta^5{:}\eta^1$ coordination of the bridging cyclopentadienylidene ligand. On the basis of the 18 valence electron rule, zwitterionic character is assigned to latter. This structure is preferred when L is an acceptor ligand, as in **6**. In solution, **5–11** are fluxional with rapid rotation about the very short cobalt–carbene C bond. In addition the hindered rotation of the ethylene ligand in **5ab** was studied by DNMR spectroscopy. In solution, a singlet–triplet equilibrium was established by variable-temperature NMR spectroscopy for **8aa**. The temperature-dependent ^1H NMR line shifts were analysed by means of an isotropic shift model to give $24 \leq \Delta H^\circ \leq 32\ \text{kJ mol}^{-1}$ and $45 \leq \Delta S^\circ \leq 74\ \text{J mol}^{-1}\,\text{K}^{-1}$ with the triplet state being preferred by entropy at higher temperatures.

Keywords
carbenes · CH activation · dinuclear complexes · sandwich complexes · spin equilibria

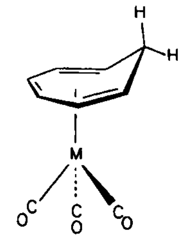
Introduction

The CH-activating properties of the complexes $[(C_5R_5)Co(C_2H_4)_2]$ (**1**) are now well documented.[1, 2] Though at a first glance it is somewhat surprising for a first-row transition metal complex, the Jonas reagent **1a** has been particularly useful in bringing about unusual transformations of hydrocarbon ligands. These reactions are often driven by the oligomerisation of CpCo fragments to give very stable tri- and tetranuclear cluster complexes. For example, μ-alkyne cluster complexes are formed from some vinylbenzenes[3] or even simple monoenes[4] and **1a** under mild conditions. CH activation by **1** is, however, not restricted to olefinic groups, nor is the formation of a metal cluster a necessary prerequisite.

We have reported on the abstraction of a hydrogen radical by **1** from the methylene group of complexed cycloheptatriene in



1a, R = H
1b, R = Me
1c, $R_5 = H_4Me$
1d, $R_5 = Me_4Et$



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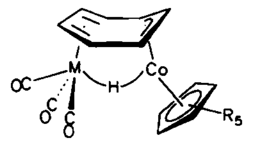

3, M = Cr, Mo; R = Me
M = W; R = H, Me

$[(CO)_3M(\eta^6\text{-}C_7H_8)]$ (**2**; M = Cr, Mo, W), to give the heterobimetallic complexes **3** with both a cycloheptatrienyl and a hydrido bridge.[5] The present work was sparked by our discovery of the contrasting behaviour of the methylene group of η^4-coordinated cyclopentadiene in $[(C_5H_5)Co(\eta^4\text{-}C_5H_6)]$ (**4a**).[6] On treatment with **1a**, *twofold* CH activation takes place to give the dinuclear cyclopentadienylidene-bridged complex $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5H_5)]$ (**5aa**) (Scheme 1). In this unprece-

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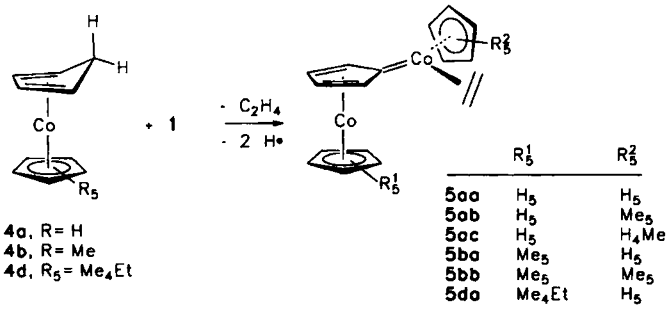


	R^1_5	R^2_5
5aa	H_5	H_5
5ab	H_5	Me_5
5ac	H_5	H_4Me
5ba	Me_5	H_5
5bb	Me_5	Me_5
5da	Me_4Et	H_5

Scheme 1. Twofold CH activation in **4** on treatment with **1a**.

dented reaction, a bridging carbene ligand is formed directly from a saturated hydrocarbon centre.

Cyclopentadienylidene is a member of the series of cyclic unsaturated carbenes [(CH)$_n$C], which have received considerable attention both by preparative and theoretical organic chemists.[7] The electronic structure and chemical properties of such carbenes are dominated by the interaction of the conjugated π-system (CH)$_n$ with the orbitals on the carbene carbon centre.[7, 8] With its diene and carbene functionalities, cyclopentadienylidene offers interesting possibilities as a "difunctional" bridging ligand. In an oversimplified bonding picture of **5**, these two functionalities are addressed independently by the two metal–ligand fragments, [$(C_5H_5)Co$] and Co(L)(C_5H_5)]. However, it appeared that intramolecular transfer of charge between the metals through the bridging ligand was important in these complexes.[6] Because of possible implications for nonlinear optical (NLO) organometallic materials,[9] we launched a comprehensive study of complexes like **5** with the intention of fine-tuning the transfer of charge by variation of the ligands on the two cobalt atoms. Here we present a detailed report of our synthetic and structural studies.

Results

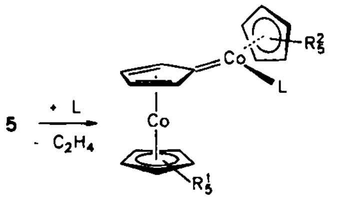
Syntheses:

a) CH activation of complexed cyclopentadiene: Reaction of the η^4-cyclopentadiene complexes **4** with the bis(ethylene) complexes **1** at room temperature gave the μ-cyclopentadienylidene dicobalt complexes **5aa**, **5ab**, **5ac**, **5ba**, **5bb** and **5da** (Scheme 1). When higher temperatures were employed less pure products were obtained in the case of **1a** and **1c** owing to partial decomposition of these reagents. Best results were obtained when the reactants were mixed in petroleum ether and the mixtures kept in large flasks under slightly reduced pressure at ambient temperature for a few days. However, conversion was slower for the reactions involving the pentamethylcyclopentadienyl complex **1b** (about 40% after 4 d at room temperature). Here, heating the reaction mixture to 40–60 °C proved favourable. Progress of the reaction was indicated by a colour change from orange-red to turquoise-green. Most of the products crystallised analytically pure directly from the reaction mixture (yield 20–70%). If necessary, the complexes **5** could be recrystallised from toluene or toluene–petroleum ether. Both the solutions and the pure solids are very air-sensitive.

During attempts to generate the pentamethylcyclopentadienyl complex **4b** from **1b** and excess cyclopentadiene in petroleum ether at 50–60 °C, nearly exclusive formation of **5bb** was observed. The expected primary product **4b** could only be obtained in 40% yield by heating **1b** in neat cyclopentadiene. Even then, the dinuclear **5bb** was formed in substantial amounts.

When [CpCo{η^4-(*exo*-CH_3)C_5H_5}] (**4a′**) was treated with **1a**, 90% of **4a′** was recovered even after heating the mixture to 50 °C for 2 h. Most of **1a** had been converted to the μ_3-ethylidyne cluster complexes [$(CpCo)_3(\mu_3\text{-}CCH_3)_2$][10b] and [H(CpCo)$_4$($\mu_3$-$CCH_3$)].[10] No heterodinuclear product was obtained by the reaction of [$(CO)_3Fe(\eta^4\text{-}C_5H_6)$] and **1a** (1 d at room temperature followed by 2 h at 50 °C).

b) The substituted derivatives [(C_5R_5)Co(μ-C_5H_4)Co(L)-(C_5R_5)′] (6–11): The complexes **5** underwent substitution of ethylene when treated with excess or stoichiometric amounts of donor ligands L (L = CO, *t*BuNC, P(OMe)$_3$, PR$_3$) (Scheme 2).



	L	R^1	R^2
6aa	CO	H	H
6ab	CO	H	Me
6ba	CO	Me	H
6bb	CO	Me	Me
7aa	^{t}BuNC	H	H
8aa	PMe_3	H	H
8ab	PMe_3	H	Me
9aa	PMe_2Ph	H	H
10aa	$PMePh_2$	H	H
11aa	$P(OMe)_3$	H	H

Scheme 2. Substitution of the ethylene ligand in complexes **5**.

The carbonyl derivatives **6aa**, **6ab**, **6ba** and **6bb** were prepared by warming toluene solutions of the corresponding ethylene complexes **5** from −60 °C to room temperature under an atmosphere of carbon monoxide. Pure **6** were obtained in 50–97% yield after recrystallisation from toluene–petroleum ether. The isocyanide, phosphine and phosphite derivatives **7aa** and **8–11** are also formed from **5** with an excess of ligand. Except in the case of **5aa** and PMe$_3$ or P(OMe)$_3$, pure products were only obtained when the reactants were mixed in stoichiometric amounts. This was partially due to the extreme sensitivity and low tendency towards crystallisation of the products, which made recrystallisation very tedious. Separation from an excess of the less volatile phosphine ligands (if present) was nearly impossible.

A triphenylphosphine complex did not form from the ethylene derivative **5aa** and PPh$_3$. Likewise, attempts to prepare the tricyclohexylphosphine-substituted dinuclear complex also failed. No reaction took place when the bis(pentamethylcyclopentadienyl)-substituted complex **5bb** was treated with PMe$_3$ at room temperature or at 60 °C.

The complexes **6–10** are deep green with a turquoise tint. The phosphite derivative **11aa** is blue. Solutions of all derivatives are very air-sensitive. However, the carbonyl derivatives are distinctly less so than the others and, as solids, can even be handled in air for a few seconds. On contact with air, **7–11** immediately decompose and have to be handled under rigorously anaerobic conditions throughout.

An attempt was made to prepare **8aa** directly from [$(C_5H_5)Co(\eta^4\text{-}C_5H_6)$] and [$(C_5H_5)Co(C_2H_4)(PMe_3)$]. However, no reaction occurred between these two complexes, even at 60 °C.

Crystal structure determinations: X-ray crystal structure determinations were carried out for **5aa**, **5ab**, **5ba**, **6aa** and **8aa**. Details are described in the Experimental Section. Three typical molecules are depicted in Figures 1–3. Important bond lengths and angles are compiled in Tables 1 and 2.

The gross molecular structures of all five derivatives are similar. A sandwich-like (η-C_5R_5)Co(cyclopentadienylidene) unit is

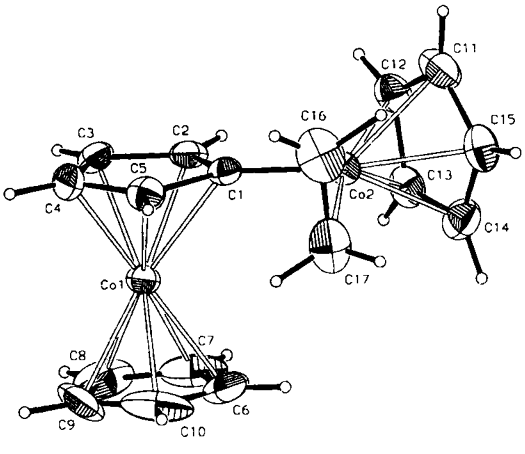


Fig. 1. Molecular structure of **5aa**.

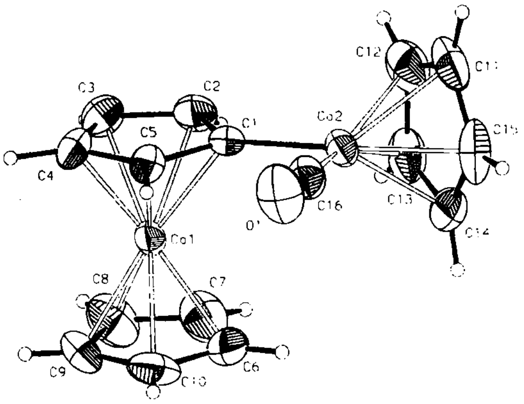


Fig. 2. Molecular structure of **6aa**.

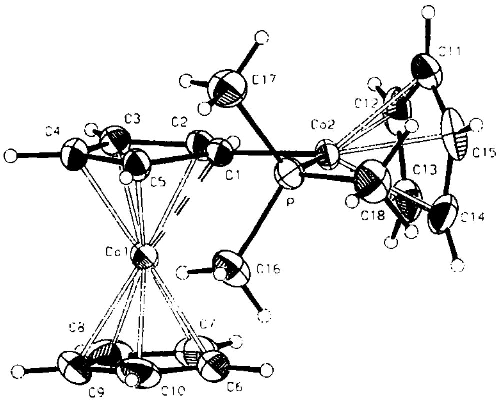


Fig. 3. Molecular structure of **8aa**.

Table 1. Important bond lengths [Å] and angles [°] for complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5R'_5)]$: **5aa** (R = R' = H), **5ab** (R = H, R' = Me) and **5ba** (R = Me, R' = H).

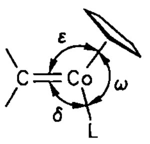
	5aa	**5ab**	**5ba**
Co(1)–C(1)	2.188(5)	2.228(2)	2.202(4)
Co(1)–C(2)	2.039(5)	2.048(2)	2.039(5)
Co(1)–C(3)	2.015(6)	2.011(2)	1.991(5)
Co(1)–C(4)	2.002(6)	2.015(2)	2.008(5)
Co(1)–C(5)	2.023(6)	2.041(2)	2.056(5)
Co(1)–C(Cp)	2.005(7) –2.036(5)	2.042(2) –2.078(3)	2.040(8) –2.076(4)
C(1)–C(2)	1.431(7)	1.448(3)	1.451(6)
C(1)–C(5)	1.445(7)	1.458(3)	1.451(6)
C(2)–C(3)	1.409(8)	1.426(3)	1.405(7)
C(3)–C(4)	1.390(9)	1.414(4)	1.392(7)
C(4)–C(5)	1.423(10)	1.422(3)	1.424(7)
Co(2)–C(1)	1.861(5)	1.865(2)	1.874(5
Co(2)–C(Cp)	2.086(6) –2.113(6)	2.105(2) –2.130(2)	2.079(5) –2.116(6)
Co(2)–C(16)	1.989(7)	1.991(2)	1.997(5)
Co(2)–C(17)	1.990(8)	1.990(2)	1.979(5
C(16)–C(17)	1.393(13)	1.399(4)	1.407(7)
C(2)–C(1)–C(5)	101.5(5)	101.3(2)	102.0(4)
C(2)–C(1)–Co(2)	127.2(4)	129.7(2)	127.5(3)
C(5)–C(1)–Co(2)	131.2(4)	128.9(2)	130.5(3)
C(3)–C(2)–C(1)	112.4(5)	111.9(2)	111.2(5)
C(4)–C(3)–C(2)	107.2(6)	107.3(2)	108.3(5)
C(3)–C(4)–C(5)	107.2(6)	106.7(2)	107.2(4)
C(4)–C(5)–C(1)	111.3(6)	112.1(2)	111.0(4)

Table 2. Important bond lengths [Å] and angles [°] for complexes $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5H_5)]$: **6aa** (L = CO) and **8aa** (L = PMe_3).

	6aa	**8aa**
Co(1)–C(1)	2.156(4)	2.240(5)
Co(1)–C(2)	2.030(5)	2.041(4)
Co(1)–C(3)	2.004(6)	2.035(5)
Co(1)–C(4)	2.032(6)	2.029(9)
Co(1)–C(5)	2.045(6)	2.056(9)
Co(1)–C(Cp)	2.027(6) –2.041(6)	2.042(11) –2.095(5)
C(1)–C(2)	1.422(7)	1.449(6)
C(1)–C(5)	1.446(7)	1.444(6)
C(2)–C(3)	1.441(8)	1.410(6)
C(3)–C(4)	1.382(10)	1.411(7)
C(4)–C(5)	1.393(8)	1.413(6)
Co(2)–C(1)	1.871(5)	1.880(4)
Co(2)–C(Cp)	2.070(6) –2.139(7)	2.078(10) –2.121(5)
Co(2)–C(16)	1.711(6)	
Co(2)–P		2.150(4)
C(16)–O(1)	1.162(6)	
Co(2)–C(16)–O(1)	176.6(5)	
C(2)–C(1)–C(5)	101.6(5)	100.5(4)
C(2)–C(1)–Co(2)	128.5(4)	125.2(3)
C(5)–C(1)–Co(2)	129.8(4)	134.0(3)
C(3)–C(2)–C(1)	110.4(5)	112.8(4)
C(4)–C(3)–C(2)	108.4(6)	106.5(4)
C(3)–C(4)–C(5)	106.0(5)	106.9(4)
C(4)–C(5)–C(1)	113.5(6)	112.6(4)

joined to a (η-C_5R_5)Co(ligand) moiety through a very short (1.86–1.88 Å) C(1)–Co(2) bond. The carbon atoms C(2) through C(5), which make up the formal diene system of the bridging cyclopentadienylidene ligand, are in a plane ($E1$). The "carbene" carbon atom C(1) is displaced from $E1$ away from Co(1), resulting in folding of the five membered ring along C(2)···C(5) (Table 3). Carbon–carbon bonds within the C_5H_4 ligands are not equal in length. In all the complexes studied there is the general pattern C(1)–C(2)/C(5) long, C(2)/C(5)–C(3)/C(4) intermediate and C(3)–C(4) short. However, the differences between "long" (around 1.45 Å) and "intermediate" (around 1.41 Å) bonds are larger than those between the latter and the "short" (around 1.40 Å) bonds. Because of the small effects and the experimental inaccuracies, the latter difference is not significant in some cases.

In all five complexes, a similar molecular conformation is attained with respect to torsion around the Co(2)–C(1) bond. The plane $E2$, defined by Co(2), L (i.e. the donor atom of CO



Scheme 3.

or PMe_3, or the centroid of the ethylene ligand) and the centroid of the C_5R_5 ligand on Co(2), is approximately parallel to $E1$. In **5aa**, **5ab** and **5ba** the carbon–carbon axis of the ethylene ligand is nearly perpendicular to $E2$. The distribution of the ligands around Co(2) is best described by the "interligand angles" δ, ε and ω within the coordination plane $E2$ (Scheme 3). As can be seen from Table 3, the sum of δ, ε and ω is almost 360° and illustrates the approximate C_s local symmetry of the $(C_5R_5)Co(L)(carbene)$ fragment.

Table 3. Important geometrical parameters (angles in deg, distances in Å) for the molecular structures of complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5R'_5)]$: **5aa** (R = R' = H), **5ab** (R = H, R' = Me), **5ba** (R = Me, R' = H), **6aa** (R = R' = H) and **8aa** (R = R' = H).

	5aa	**5ab**	**5ba**	**6aa**	**8aa**
L	C_2H_4	C_2H_4	C_2H_4	CO	PMe_3
ϕ [a]	5.8	7.2	5.2	2.7	7.7
Co(1)···Co(2)	3.69	3.75	3.77	3.64	3.74
$E2$ [b]/C(16)C(17)	89.2	89.5	89.0		
$E2$ [b]/C(11) to C(15)	89.7	88.6	90.1	88.9	89.0
δ	96.1	94.7	95.1	90.5	97.0
ε	129.8	133.5	129.5	130.2	132.7
ω	134.1	131.7	135.4	139.3	130.4
$\sum(\delta+\varepsilon+\omega)$	360.0	359.9	360.0	360.0	360.1
$E2/E1$ [b]	3.1	8.6	7.4	5.6	2.3
Co(1)–C_5R_5 [c]	1.661	1.673	1.662	1.651	1.698
Co(2)–C_5R_5 [c]	1.726	1.735	1.734	1.734	1.730

[a] Fold angle along C(2)···C(5). [b] See text for the definition of the planes $E1$ and $E2$. [c] Distance from best plane of the C_5 ring.

Cobalt–carbon distances within the sandwich-type part of the molecules fall into two groups: the distances Co(1)–C(1) are about 6 to 11% larger than those between Co(1) and the diene carbons C(2) through C(5). This is caused by the above-mentioned folding of the ring and by a shift of Co(1) from the position below the centre of the ring towards the "diene" system. The latter distances are roughly comparable to the cobalt–carbon bonds to the other C_5R_5 ring on the same cobalt atom [Co(1)]. The C_5R_5 ligands on Co(2) are distinctly further away from the metal, regardless of the nature of R or L (Table 3).

The bonds from Co(1) to the "inner" carbons of the diene system of the bridging ligand [C(3), C(4)] are somewhat shorter than those to the "outer" carbon atoms [C(2), C(5)], but these differences are not always significant within the individual structures.

Spectroscopic Investigations:

a) The ethylene, carbonyl, and isocyanide derivatives 5–7: NMR data for **5**–**7** are summarised in Tables 4–7. The solution NMR spectra of these complexes are surprisingly simple. There are only two resonances in both the ^1H and ^{13}C NMR spectra for the four CH groups of the cyclopentadienylidene bridge. In no case could a ^{13}C resonance due to the "carbene" carbon atom C(1) be detected at ambient temperature. Likewise, no signals were observed for the carbonyl and terminal quaternary isocyanide carbons. There is only one carbon signal for the two CH_2 units of the ethylene ligand in the range $31 \leq \delta \leq 44$. The protons of this ligand give two multiplets with typical shapes for a $(AB)_2$ spin system.

Table 4. ^1H NMR data [δ(multiplicity)] for the complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5R'_5)]$: **5aa** (R = R' = H), **5ab** (R = H, R' = Me), **5ac** (R = H, $R'_5 = H_4Me$), **5ba** (R = Me, R' = H), **5bb** (R = R' = Me), **5da** ($R_5 = H_4Et$, R' = H).

	C_5R_5	$C_5R'_5$	μ-C_5H_4	C_2H_4
5aa [b]	4.20 (s)	4.75 (s)	4.44 (m), 4.2 (m)	3.6, 2.1 [c]
5ab	4.34 (s)	1.82 (s)	4.63 (m), 4.34 (m)	2.8, 2.4 [c]
5ac	4.20 (s)	5.20 (m), 4.45 (m), 1.61 (s)	4.45 (m), 4.20 (m)	3.3, 2.2 [c]
5ba [d]	1.40 (s)	4.67 (s)	3.85 (m), 3.5 (br)	3.0, 1.2 [c]
5bb	1.44 (s)	1.87 (s)	4.00 (m), 3.75 (m)	2.2, 1.7 [c]
5da	1.48 (s), 1.53 (s), 1.39 (q), 2.68 (t)	4.68 (s)	3.85 (m), 3.43 (m)	3.0, 1.2 [c]

[a] 200 MHz, ambient temperature, in C_6D_6. [b] 300 MHz. [c] $(AB)_2$ spin system. [d] In $[D_8]$toluene.

Table 5. ^1H NMR data for complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5R'_5)]$: **6aa**–**11aa** ($\delta$ at ambient temperature, in C_6D_6 unless otherwise indicated).

	L	C_5R_5	$C_5R'_5$	μ-C_5H_4	L [a]
6aa	CO	4.20	4.85	8.86 ("t"), 4.48 ("t")	
6ab	CO	4.44	2.01	4.68 ("t"), 4.48 ("t")	
6ba	CO	1.42	4.94	4.01 ("t"), 4.23 ("t")	
6bb	CO	1.46	2.03	4.09 ("t"), 4.25 ("t")	
7aa	CN*t*Bu	4.82 [b]	4.39 [b]	4.80 ("t"), 4.83 ("t")	1.35
8aa	PMe_3	4.53 [b]	4.32 [b]	3.88 ("t"), 4.99 ("t")	1.34 (br)
8ab	PMe_3	4.57	1.42	3.64 ("t"), 4.48 ("t")	1.23 (7)
9aa	PMe_2Ph	4.55 [b]	4.53 [b]	3.89 ("t"), 4.83 ("t")	1.65 (br), 7.0–7.7 [c]
10aa	$PMePh_2$	4.56 [b]	4.43 [b]	3.99 ("t"), 4.79 ("t")	1.91 (5), 7.0–7.7 [c]
11aa [d]	$P(OMe)_3$	4.62 [b]	4.33 [b]	4.57 (br), 4.73 ("t")	3.46 (12)

[a] Numbers in parentheses indicate J_{HP} in Hz. [b] Arbitrary assignment to a particular C_5R_5 ring. [c] Overlap with solvent resonance. [d] In $[D_8]$toluene.

Table 6. ^{13}C NMR data (δ at ambient temperature, in C_6D_6) for the complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5R'_5)]$: **5aa** (R = R' = H), **5ab** (R = H, R' = Me), **5ba** (R = Me, R' = H), **5bb** (R = R' = Me).

	C_5R_5	$C_5R'_5$	μ-C_5H_4 [a]	C_2H_4
5aa	85.0 [b]	81.0 [b]	81.6, 78.7	35.0
5ab	79.3	91.7 [c], 9.9 [d]	79.2, 78.3	43.8
5ba [d]	90.7 [c], 9.8 [d]	84.0	85.4, 79.4	31.7
5bb	90.6, [b,c] 10.24 [b,d]	90.0 [b,c], 10.17 [b,d]	82.8, 78.8	39.4

[a] Resonances due to the quaternary carbon were not detected. [b] Arbitrary assignment to a particular C_5R_5 ring. [c] Ring-C. [d] Methyl-C. [e] In $[D_8]$toluene.

Table 7. $^{13}C\{^1H\}$ NMR data [a] for complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5R'_5)]$, **6**–**11** ($\delta$ at ambient temperature, in C_6D_6 unless otherwise indicated).

	L	C_5R_5	$C_5R'_5$	μ-C_5H_4 [a,b]	L [b]
6aa	CO	82.3 [c]	83.7 [c]	80.0, 87.3	[d]
6ab	CO	81.0	91.4 [e], 10.4 [f]	80.4, 86.2	[d]
6ba	CO	91.4,[c,e] 9.6 [c,f]	83.0	80.4, 90.8	[d]
6bb	CO	92.1,[c,e] 11.3[c,f]	91.0,[c,e] 9.7 [c,f]	79.7, 88.7	[d]
7aa	CN*t*Bu	50.5 [c]	81.9 [c]	78.9, 84.9	55.5, 31.7
8aa	PMe_3	92 (br) [c]	80.1 [c]	75.9, 78.6	21 (br)
8ab	PMe_3	76.6	86.9,e] 10.7 [f]	78.3, 87.4	10.2 (8)
9aa	PMe_2Ph	77.4 [c]	79.5 [c]	75.9, 86.1	20.2 (br)
10aa	$PMePh_2$	77.5 [c]	80.3 [c]	76.0, 86.0	25.7 (22)
11aa [g]	$P(OMe)_3$	78.0 [c]	79.4 [c]	85.0 (8), 81.1 (3)	50.0

[a] Resonances due to the quaternary carbon were not detected. [b] Numbers in parentheses indicate J_{HP} in Hz; phenyl resonances were partially obscured by solvent signals. [c] Arbitrary assignment to a particular C_5R_5 ring. [d] Carbonyl and isocyanide carbons were not detected. [e] Ring-C. [f] Methyl-C. [g] In $[D_8]$toluene.

For **6**, carbonyl stretches were detected in the infrared spectra at the rather low frequency of 1875–1903 cm^{-1} (Table 8). The CN stretch in **7aa** could not be unambigously assigned.

Table 8. IR [$\tilde{\nu}$(CO)] data for complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(CO)(C_5R_5)']$ (**6**).

	R	R'	$\tilde{\nu}$(CO) [cm^{-1}]	solvent
6aa	H	H	1903	THF
6ab	H	Me	1882	toluene
6ba	Me	H	1888	toluene
6bb	Me	Me	1875	toluene

0947-6539/96/0211-1456 $ 15.00+.25/0

b) The phosphine and phosphite derivatives ***8–11***: Proton and carbon spectra of **8**–**11** follow the same pattern as those of the other derivatives. However, in several cases, the ^{1}H and ^{13}C NMR resonances of the methyl groups of the phosphine ligands appeared as broad features without any resolved coupling to the ^{31}P nucleus. Under standard measuring conditions, no ^{31}P resonances were found for **8**–**10**. When ^{31}P spectra were accumulated for a prolonged period of time at ambient temperature, a weak, broad resonance was detected at $\delta = 29$ ($b_{1/2} = 30$ Hz) for **9aa**. Complex **8aa** gave a very broad signal at $\delta = -45$ ($b_{1/2} = 500$ Hz) which was markedly temperature dependent (see below). The phosphorus resonance for **11aa** [$\delta = 170$] was also broad, but did not shift significantly when the temperature was lowered [$\delta = 166$ at 200 K].

*c) Variable temperature NMR spectroscopic investigations of representative ethylene (**5ab**) and substituted (**6aa**, **6ab**, **8aa**, **8ab**, **9aa**, **10aa**, **11aa**) derivatives*: The temperature dependence of the proton spectrum of **5ab** was investigated between 295 and 360 K. On warming, the resonances of the ethylene ligand broaden and then coalesce to a singlet (Fig. 4). Due to noticeable decomposition of the complex above 350 K, a limiting high-temperature spectrum could not be obtained. Other than minor line shifts, all other proton resonances of **5ab** were temperature independent.

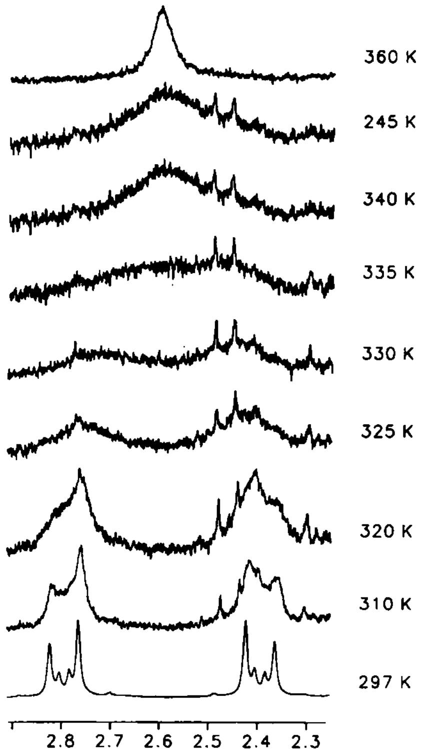


Fig. 4. Variable-temperature 200 MHz ^{1}H NMR spectra of **5ab** (region of the ethylene resonances). The sharp signals around $\delta = 2.48$, 2.44 and 2.3 are due to minor impurities, which result from slow decomposition of the sample.

Strong temperature-dependent line shifts were observed in the solution ^{1}H NMR spectra when a sample of **8aa** was heated. The largest shifts were found for one of the cyclopentadienylidene ring proton resonances although the other μ-C_5H_4 resonance and the Cp peaks also shifted (Fig. 5). The chemical shift of the PMe_3 resonance was only slightly affected by the increase in temperature, but this line progressively broadened. Unfortunately, spectra above 385 K as well as ^{13}C and ^{31}P NMR measurements were prohibited by slow decomposition of the sample above 340 K. A pseudo-triplet resonance at $\delta \approx 1.0$, which gradually grew in with time, could be assigned to $[CpCo(PMe_3)_2]$.[11] The spectral changes were completely reversible when the temperature was lowered again, except for the resonance at $\delta \approx 1.0$, which remained unaffected.

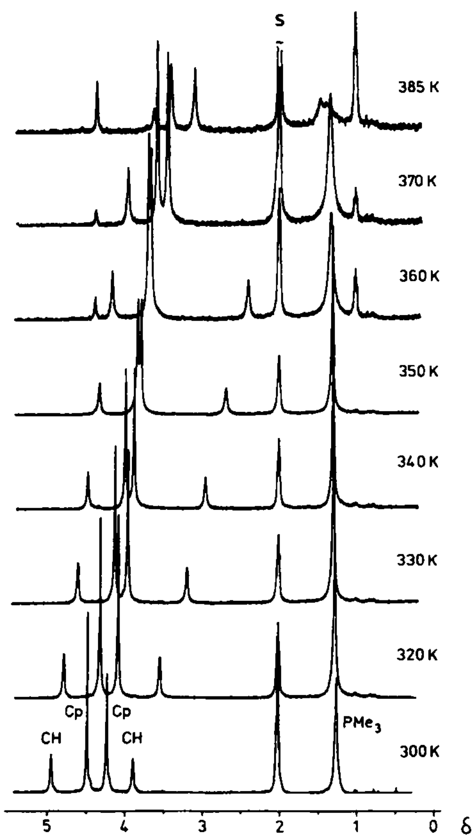


Fig. 5. Variable-temperature 200 MHz ^{1}H NMR spectra of **8aa** (high-temperature region). S = solvent resonance, X = $[CpCo(PMe_3)_2]$.

On cooling the sample below room temperature a number of changes were observed in the spectra. The ^{31}P NMR signal sharpened and shifted to lower field ($\delta = +12.4$ at 200 K, with a linewidth of 50 Hz). The proton resonance of the PMe_3 ligand also narrowed and showed a resolved doublet structure below 250 K ($J_{PH} = 8$ Hz). In addition, the resonance at $\delta = 3.9$, due to two of the hydrogens of the bridging cyclopentadienylidene ligand, broadenend below 230 K. At 160 K, the lowest temperature where spectra of reasonable quality could be measured, this resonance had disappeared into the baseline. One of the Cp resonances shifted somewhat to lower field without significant broadening, and, at 160 K, had nearly merged with the other Cp signal (Fig. 6).

Line shifts on heating were also observed with **9aa**, but to a much lesser extent. The proton resonances of **6aa**, **6ab**, **8ab**, **10aa** and **11aa** only showed insignificant changes in chemical shift in the temperature range 290–350 K. At 200 K, a weak signal at $\delta = 153.7$, due to quaternary carbon, was detected in the ^{13}C NMR spectrum of **11aa**, in addition to the resonances already visible at ambient temperature.

Electrochemical and ESR spectroscopic investigations: Cyclic voltammetry was carried out on solutions of **5aa**, **6aa** and **11aa**. In all three cases, the monocations and monoanions are generated reversibly (Table 9). The potential–current response for

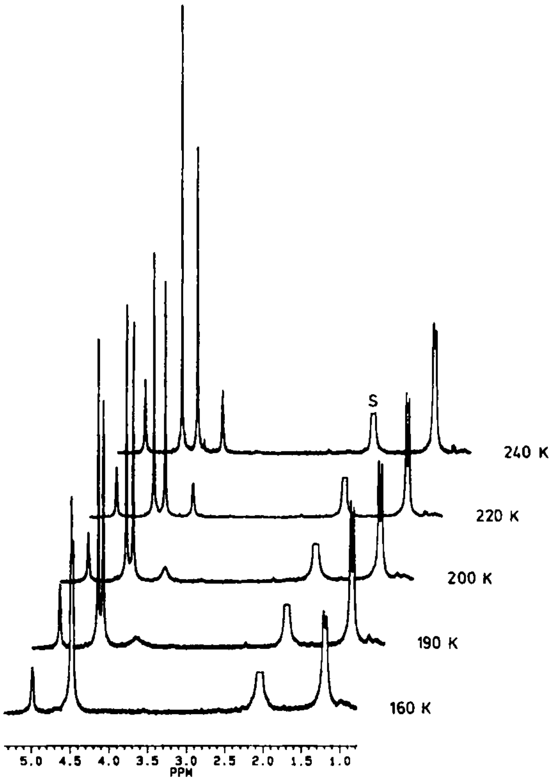


Fig. 6. Variable-temperature 200 MHz ^{1}H NMR spectra of **8aa** (low-temperature region). S = solvent resonance.

Table 9. Cyclic voltammetry data for some complexes [$(C_5H_5)Co(\mu$-$C_5H_4)Co(L)(C_5H_5)$]. For each complex, E° [V] vs. SCE is given in the first line. The peak separation ΔE_p [mV] and the ratio of the cathodic and anodic currents i_c/i_a are given in the second line. Supporting electrolyte: nBu$_4$NPF$_6$.

	−1/0	0/+1	+1/+2	+2/+3
5aa [a]	−1.21	−0.41	+0.08	
	(80, 0.7)	(60, 1.0)	[b]	
6aa [c]	−1.62	−0.48	+0.38	1.46
	(90, 1.0)	(80, 1.0)	(100, 1.0)	[b]
11aa [a]	−1.87	−0.91	−0.11	
	(150, 1.1)	(110, 1.0)	[b]	

[a] In propylene carbonate. [b] Irreversible. [c] In propionitrile.

11aa is shown in Figure 7. The dication of **6aa** is also formed reversibly, whereas the second oxidations of **5aa** and **11aa** and the third oxidation of **6aa** are irreversible. Attempts to observe the ESR spectra of the radical cations or anions of the above derivatives were not successful except in the case of [**5aa**]$^-$, which was prepared in situ by reduction of a THF solution with a potassium mirror. In a glass matrix at 110 K a broad feature with poorly resolved hyperfine splitting was observed (Fig. 8). If we tentatively assign the first four lines on the low field edge of the resonance as part of an octet caused by hyperfine coupling to a ^{59}Co nucleus, $g_1 = 2.074$ and $A_1 \approx 15$ mT are obtained. Judging from the shape of the resonance a rather small g anisotropy can be assumed.

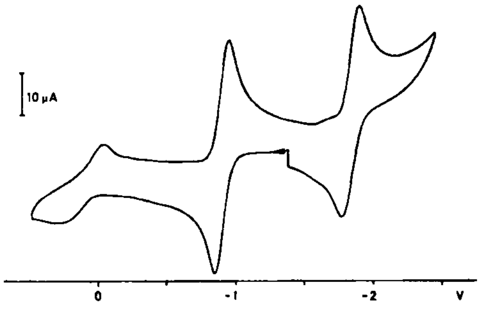


Fig. 7. Cyclic voltammogram of **11aa** (propionitrile/nBu$_4$PF$_6$, scan rate 200 mV s^{-1}, reference electrode: SCE).

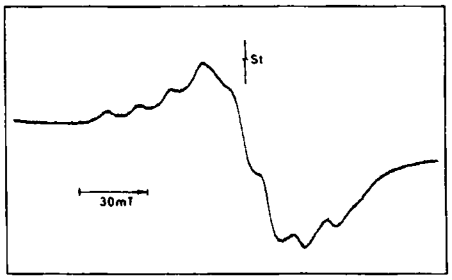


Fig. 8. X-band ESR spectrum of [**5aa**]$^-$ (frozen THF glass at 110 K).

Discussion

Formation of the μ-cyclopentadienylidene complexes: There are many methods for generating carbenes; most of them involve extrusion of a very stable molecule from a suitable precursor.[12] One of the most prominent examples is elimination of dinitrogen from diazo compounds.[13] Herrmann[14] has pioneered the "diazo route" to transition metal complexes with alkylidene (carbene) ligands. A large number of mainly dinuclear μ-alkylidene complexes has been prepared via this and related methods.[14, 15]

Elimination of dihydrogen from a hydrocarbon methylene group to give a carbene is very unfavourable. Such reactions do not play a role in solution chemistry, but are known to take place on certain metal surfaces.[16, 17] However, it has been long known that the methylene group of the cyclopentadiene ligand in **4a** exhibits enhanced reactivity towards a variety of reagents. For example, hydride ion is easily abstracted and some activated alkynes or even styrene insert into a CH bond.[18] These reactions are usually regiospecific and involve only the *exo*-CH bond.[19] The weakening of this bond in the complex has been attributed to a hyperconjugative interaction of the σ-bonding orbital with the adjacent diene π orbitals resulting in a drain of C–H bonding electron density.[20]

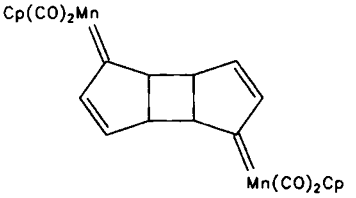
We presume that primary attack of **1**, or more likely an unsaturated species derived from **1**, also takes place in the *exo* position and leads to oxidative addition of this CH bond on the incoming cobalt atom. This is made likely by our observation that the *exo* substituted derivative **4a'** did not react with **1a**. However, we were unable to isolate or spectroscopically observe by NMR a primary, singly CH-activated product of **4a**. Apparently cleavage of the second (*endo*) CH bond of the former methylene group occurs rapidly, and the bridging carbene ligand is formed. No attempts were made to establish the fate of the two hydrogen atoms, which could combine and be released as dihydrogen or hydrogenate one of the ethylene ligands in **1**.

It is interesting to note that the ability of **1b** to CH-activate the complexed cyclopentadiene is much higher than its tendency to substitute both ethylene ligands. This is apparent from the nearly exclusive formation of the twofold CH activation product **5bb** from **1b** and cyclopentadiene in solution. In this reaction, the mononuclear intermediate, the cyclopentadiene complex **4b**, is consumed at least as fast as it is being formed.

We also note that the methylene group of the cycloheptatriene complexes $[(CO)_3M(\eta^6\text{-}C_7H_8)]$ (**2**, M = Cr, Mo, W) was only singly CH activated by **1**, which eventually led to the formation of the heterobimetallic cycloheptatrienyl bridged complexes **3**.[5] This contrasting behaviour was quite surprising considering the many similarities between the isolectronic η^4-cyclopentadiene (such as **4**) and η^6-cycloheptatriene complexes (such as **2**).[21] However, without any detailed knowledge of the mechanism of both types of reaction we do not venture to offer an explanation, which would be mostly speculative.

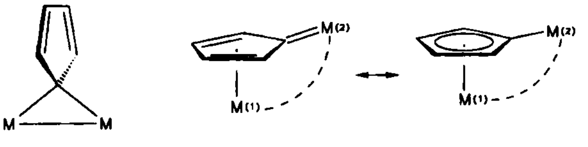
Substitution of the ethylene ligand in **5** is straightforward. Because of the problems in removing traces of excess phosphine and their reluctance to crystallise, the poor isolated yields of complexes **9aa** and **10aa** merely reflect product loss during repeated recrystallisation. As judged from the proton NMR spectra of the reaction mixtures, they are formed in much higher yields. Our inability to prepare the triphenylphosphine- and tricyclohexylphosphine-substituted derivatives can be attributed to the steric bulk of these ligands, which would lead to severe congestion on Co(2).

Structural chemistry of the cyclopentadienylidene bridge: As a ligand in transition metal complexes, cyclopentadienylidene C_5H_4 is almost invariably found in a bridging coordination. To our knowledge, mononuclear complexes with terminal cyclopentadienylidene ligands are unknown. The manganese complex **12**[23] comes closest to such a species. Here, the terminally (η^1) coordinated cyclopentadienylidene has been trapped by the formation of a [2+2] cycloaddition dimer.



12

Two main coordination modes of the cyclopentadienylidene bridge have been structurally characterised.[24] In a number of complexes with an η^1:η^1 C_5H_4 ligand (**A**),[25] the carbene centre spans a metal–metal bond. A metallacyclopropane is formed which is part of a [3.5] spirobicyclic ring system. The diene π system of the carbene ligand is not involved in bonding to the metals. A similar complex without a metal–metal bond, but with an oxo bridge between the metals, has also been reported.[26] Two limiting structures **B** and **C**[27] can be drawn for dinuclear complexes with a cyclopentadienylidene bridge where both the diene π-system and the carbene orbitals participate in bonding to the metals. In the μ-η^4:η^1 (diolefin/carbene) structure **B** the diene system of the bridging ligand coordinates to one metal, while the frontier orbitals of the carbene centre are involved in bonding to the other. The μ-η^5:η^1 structure **C** differs from **B** in that the carbene carbon bonds to both metal atoms through its π and σ orbitals. This type of cyclopentadienylidene bridge is more appropriately viewed as a centrally bound cyclopentadienyl ligand which has oxidatively added to a nearby second metal atom, thereby metallating one CH function. In both **B** and **C**, a metal–metal bond may be present.

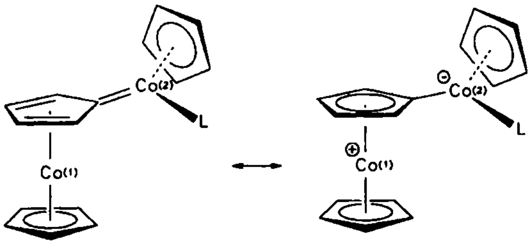


A **B** **C**

In 1981 it was stated[25g] that all examples structurally characterised at that time[28] belonged to the η^5:η^1 type (**C**). This view was based on geometric arguments, especially the bond lengths from the carbene centre to the metals [a short bond to M(1) and a rather long (σ-) bond to M(2)], and the tilt and folding of the five-membered ring towards M(2) in the metal–metal-bonded derivatives. Quite often, such bridges are indeed formed by CH activation of cyclopentadienyl ligands.

In most of the dinuclear complexes with a cyclopentadienylidene bridge there is no problem concerning the formal distribution of electrons in the molecule. Eighteen valence electrons (VE) can be assigned in the conventional way to each of the metal atoms when either of the coordination modes (η^4:η^1 or η^5:η^1) is assumed. However, a dative metal–metal bond M(1) → M(2) has to be assumed when the actual structures of $[Cp(CO)Mo(\mu\text{-}C_5H_4)Mo(CO)_2Cp]$,[25g, 28h] $[Cp_2(H)Mo(\mu\text{-}C_5H_4)MoCp]$[28h] and $[Cp(CO)Mo(\mu\text{-}C_5H_4)Mn(CO)_4]$[28c] are described with the η^5[M(1)]:η^1[M(2)] formalism.

A similar situation exists when the 18 VE rule is applied to **5**–**11**. There is no difficulty with the η^4:η^1 C_5H_4 bridge **D**. However, in the μ-η^5:η^1 structure no dative metal metal bond can be assigned to formally push electrons from Co(1) to Co(2) as direct interaction is clearly precluded by the large separation of the two metals (3.64–3.77 Å). Consequently charge separation has to be assumed, resulting in the zwitterion **E**.



D **E**

The bridging ligand in **D** may be viewed as a cyclopentadiene carbene which is bound to Co(1) through its diene system (contributes 4 VE) and to Co(2) through the carbene centre C(1) (contributes 2 VE). The zwitterion **E** can formally be derived from the cobaltocenium cation, where a hydrogen atom has been replaced by a $[CpCoL]^-$ unit (L = two-electron donor). Within this scheme, 5 VE are donated by the bridging five-membered ring to the positively charged $[CpCo]^+$ moiety, and a σ bond is formed between C(1) and Co(2). In any case 18 VE configurations are obtained for both metal atoms.

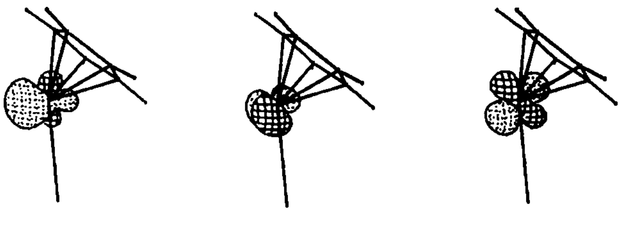
In addition to the differences concerning the connectivity to Co(1), the internal geometry of the C_5H_4 bridge should also be different for **D** and **E**. For the non-centrally bound μ-η^4:η^1-cyclopentadienylidene ligand in **D** we would expect some alternation of the carbon–carbon bond lengths [C(3)–C(4) short, C(2)/(4)–C(3)/(5) intermediate, C(1)–C(2)/(5) long] similar to that usually found in cyclopentadiene ligands, and a folding along C(2)···C(5) away from Co(1). The Cp(L)Co-substituted μ-η^5:η^1-cyclopentadienyl ligand in **E** should be less distorted from the regular pentagonal geometry. In addition, the central (η^5) coordination to Co(1) does not allow for substantial deviations from planarity.

The structural parameters of **5aa**, **5ab**, **5ba**, **6aa** and **8aa** (Tables 1–3) show that neither of the limiting structures **D** or **E** is attained. In all cases the geometry of the C_5H_4 bridge may be described as mostly μ-η^5:η^1 with a distortion in the direction of the μ-η^4:η^1 structure.

Quite significantly, the distortion towards **D** is most pronounced for the phosphine derivative **8aa** and least so in the carbonyl complex **6aa** as indicated, for example, by the Co(1)–C(1) distances of 2.240(5) and 2.156(4) Å, respectively. The same trend is also found in the fold angle ϕ of the bridging ligand (Table 3), which is largest in **8aa** and smallest in **6aa**. This can be explained by our simple model. Zwitterionic character of the molecule (i.e., a structure more like **E**) is expected to be stabilised by the presence of an acceptor ligand (like CO) on Co(2) which will delocalise the negative charge. This delocalisation is reflected by the observed very low stretching frequency of the CO ligand in **6**. In contrast, a donor ligand (like PMe_3) will destabilise **E** and consequently the actual structure should be shifted in the direction of **D**. However, the effect is not very pronounced, and the different steric requirements of L (and the C_5Me_5 ligands, if **5aa**, **5ab** and **5ba** are also considered) will also have some influence.

In all cases the bonds between C(1) and Co(2) are exceptionally short. They are quite close to or even shorter than the Co=C bonds in the very few reported simple cobalt–carbene complexes: 1.902(3) Å in [CpCo(SPh)(1,3-Me$_2$-imidazolidin-2-ylidene)],[29a] 1.815(4) and 1.829(5) Å in [Cp$_2$Zr(μ-butadien-1-yliden-1-olato)Co(CO)(C$_5$H$_4$R)] (R = H,[29b,c] Cl[29b]), 1.989(4) Å in [(CO)$_2$(PPh$_3$)(SnPh$_3$)Co=C(NCy$_2$)OEt],[29d] 1.94(2) Å in [(1,3-oxazol-2-ylidene)(1,3-oxazol-2-thiolato)Co$_3$(CO)$_6$S],[29e] 1.913(11) Å in [(GePh$_3$)(CO)$_3$Co=C(OEt)Et],[29f] and 1.974(5) Å in [(PPh$_3$)(CO)(NO)Co(1,3,4-Me$_3$-imidazolidin-2-ylidene)][29g]). There is, however, no clear-cut correlation of this parameter with the Co(1)–C(1) bond length.

The particular conformation with respect to rotation around Co(2)–C(1) shown in the solid state in all our structures may be explained by a maximisation of π-orbital overlap between these two atoms. The frontier orbitals of the (C_5R_5)CoL fragment are well known.[30] For a bent geometry, the LUMO, an empty σ orbital, points towards the missing ligand, while the fragment HOMO, a π-type orbital, also extends into the empty coordination site (Scheme 4). The latter orbital has a node in the plane $E2$ (defined by Co, L and the centroid of the C_5R_5 ligand).



Scheme 4. The frontier orbitals of the (C_5R_5)CoL fragment.

In free cyclopentadienylidene, the π orbital on the carbene carbon centre interacts with the cyclic π system resulting in an at least partial delocalisation of the carbene free electron pair into the ring system.[7c,8] In the μ-cyclopentadienylidene complexes there is competition for the carbene electron pair between the ring system and the C(1)–Co(2) bond. Complexation of the endocyclic diene system is therefore expected to enhance the π interaction between C(1) and Co(2), which in turn will favour the observed relative orientation of the two fragments. On the other hand, participation of the π orbital on C(1) in bonding to Co(1) (as required in the μ-η^5:η^1 structure) will have the reverse effect.

The spatial disposition of the ligands on Co(2) is quite similar in all our five structures. Comparing **5ab** with **5aa** and **5ba** we note that the much larger space requirements of the Cp* ligand only have a small effect on the angles δ, ε and ω. Likewise, these angles do not depend very much on the nature of L (Table 3). Steric effects, however, seem to be the reason for the observed twist around Co(2)–C(1), which places the $E1$ planes (the diene part of the μ-C_5H_4 ligand) at an angle of 2–9° with respect to $E2$ [(C_5R_5)CoL]. Consequently, a larger twist was found in the paramagnetic complex [(C$_5$Me$_5$)Co(μ-C$_5$H$_4$)Co(Br)(C$_5$Me$_5$)],[31] which is the only bis(pentamethylcyclopentadienyl) derivative that has been structurally characterised so far.

Electrochemistry: The high air sensitivity of our μ-cyclopentadienylidene complexes is reflected in the redox potentials. Oxidation takes place at rather negative potentials (Table 9). Consistent with the better donor properties of the P(OMe)$_3$ ligand, **11aa** is much more easily oxidised and less easily reduced than the ethylene and carbonyl derivatives **5aa** and **6aa**, respectively. Oxidation of the latter two takes place at roughly comparable potentials (−0.41, −0.48 V). However, the carbonyl complex **6aa** is less easily reduced than the ethylene derivative **5aa**.

Although not too much information can be drawn from the poorly resolved ESR spectrum of $[\mathbf{5aa}]^-$, the general shape of the resonance and its g value points to participation of cobalt orbitals in the singly occupied MO. The low number of lines would be consistent with significant contribution of only one cobalt atom in the HOMO, and hence more or less localisation of the single electron in only one part of the molecule.

Dynamic behaviour in solution: In the NMR spectra of all derivatives **5**–**11** a smaller number of resonances is consistently observed for the bridging cyclopentadienylidene ligand than would be required for the asymmetric structures that were found in the crystalline state. This can be explained by a rapid rotation of the two parts of the molecules around the bond C(1)–Co(2). Such a process averages the four CH groups of the bridging ligand in pairs, giving only two resonances in the ^{1}H (two pseudo triplets) and ^{13}C NMR spectra (two doublets if not proton decoupled). The changes which occurred in the proton spectrum of **8aa** when the sample was cooled indicate that the dynamic process has a fairly low activation barrier and only begins to slow down on the NMR timescale at very low temperature. This does not, however, exclude a substantial π-type interaction between C(1) and Co(2), as discussed above. There is a second π orbital on Co(2), a little below the HOMO and orthogonal to it (Scheme 4). This effectively generates an energy profile that varies only little with rotation around the Co(2)–C(1) bond.

A second dynamic process in **5** involves the η^2-ethylene ligand. In all derivatives, an (AB)$_2$ spin system is observed at ambient temperature for the four protons of this ligand. This is indicative of rigid η^2-coordination of the ethylene molecule. However, only one ^{13}C NMR resonance is detected for the two inequivalent CH$_2$ groups of the static ethylene ligands. This could be due to a coincidental degeneracy or, more likely, near degeneracy of the two resonances. For a small difference in chemical shift, coalescence is expected at a much lower temperature than for the proton resonances, which are further apart on the frequency scale.

The temperature dependence of the ^{1}H NMR spectrum for **5ab** indicates the onset of rotation of this ligand around its bonding axis at higher temperature. Although our variable-tem-

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perature NMR investigations were restricted to **5ab** we assume similar behaviour for the other derivatives.

Spin equilibria: The temperature dependence of the ^{1}H NMR resonances of **8aa** is highly unusual. Such line shifts with temperature are indicative of an equilibrium in solution of a diamagnetic with a paramagnetic isomer, with total spin quantum numbers of $S = 0$ and 1, respectively. NMR resonances of paramagnetic molecules can be observed in solution when the electron spin relaxation times are short.[32] If interconversion between the two isomers is sufficiently rapid ($> 10^3 - 10^4\ s^{-1}$) the observed NMR spectrum is the weighted mean of the diamagnetic and the paramagnetic species. Since the chemical shifts of paramagnetic molecules can be rather large, even small percentages of such species may be detected indirectly by their influence on the averaged chemical shifts.

The ^{31}P NMR resonance of **8aa** is influenced most strongly, showing a upfield shift of nearly 50 ppm when the temperature is increased from 220 to 300 K. The observed chemical shift at 200 K ($\delta = 12.4$) is well within the range of metal-coordinated PMe_3 in diamagnetic complexes.[33] The increase in linewidth of this resonance on warming correlates with the broadening of the methyl signal in the proton spectrum. This is indicative of an increase of the ^{31}P relaxation rates, which can also enhance proton relaxation in the methyl groups by a number of possible mechanisms.[34]

A simple set of equations can be used to correlate the temperature dependence of the observed chemical shifts [$\nu = f(T)$] with the thermodynamics (ΔG°) of the spin equilibrium if the following conditions hold: 1) there is rapid interconversion between the two isomers, 2) the paramagnetic isomer obeys the Curie law and 3) the dipolar (pseudocontact) electron-nuclear interactions are negligible.

Under these conditions, the temperature dependence of the NMR resonance frequency shift $(\Delta\nu_i)_{dia/para}$ for a given nucleus i from its diamagnetic position $(\nu_i/\nu_0)_{dia}$ can be expressed by Equation (1).[35] Attempts were made to fit the above

$$(\Delta\nu_i)_{dia/para} = (C/T)\{\exp[(\Delta H^\circ - T\Delta S^\circ)/RT] + 1\}^{-1} \qquad (1)$$

equation to the observed line positions.[36] When a nonlinear least-squares routine was used to obtain sets of best values for the constant C, the molar free enthalpy and entropy changes (ΔH°, ΔS°) and $(\nu_i/\nu_0)_{dia}$, a strong correlation between ΔH° and ΔS° became obvious. Therefore, the error functions defined by the root mean square deviation between observed and calculated values of $(\Delta\nu_i)_{dia/para}$ were evaluated for a wide range of values for ΔH° and ΔS°. These functions had several rather flat minima of comparable depth. As a consequence, it is impossible to find unique values for ΔH° and ΔS° in our system. Within the large range of examined positive and negative values, several combinations with $24 \leq \Delta H^\circ \leq 32\ kJ\,mol^{-1}$ and $45 \leq \Delta S^\circ \leq 74\ J\,mol^{-1}\,K^{-1}$ gave fits of comparable quality. The results for two extreme combinations are shown in Figure 9. The calculated curves for $(\nu_i/\nu_0) = f(T)$ are in good agreement with the experimental data in the temperature range $385\ K \geq T \geq 220\ K$. Below 220 K deviations occur, due to the onset of changes in the spectra caused by the decrease in molecular fluxionality.

Taken at face value, our analysis indicates that, despite the ambiguities, the singlet-state species ($\Delta H^\circ > 0$) is the thermodynamically stable isomer in solution. The existence of the triplet-state isomer is entirely due to the rather large entropy change. However, the concentration of the paramagnetic species remains low, even at the highest measured temperature ($x_{para} \leq 0.3$ at 385 K).

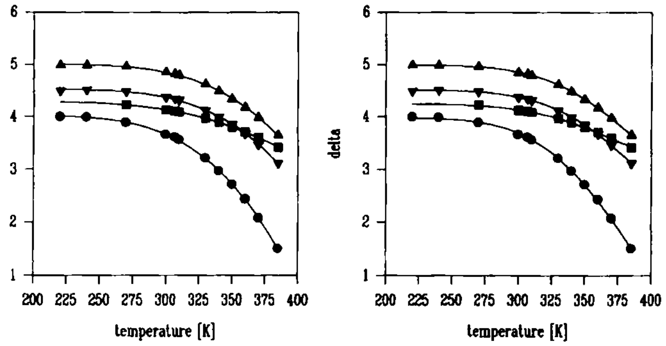


Fig. 9. Temperature dependence of the Cp and CH ^{1}H NMR resonances for **8aa**. The curves are calculated from Equation (1) with $\Delta H^\circ = 27\ kJ\,mol^{-1}$, $\Delta S^\circ = 45\ J\,mol^{-1}\,K^{-1}$ (left) and $\Delta H^\circ = 31\ kJ\,mol^{-1}$, $\Delta S^\circ = 72\ J\,mol^{-1}\,K^{-1}$ (right).

Apart from the problems with the strong correlation of ΔH° and ΔS°, our calculated thermodynamic parameters may be affected by non-neglegible, pseudo-contact (dipolar) interactions. These are determined by a geometric factor and the anisotropy of the g tensor. In the absence of ESR spectra for the triplet species, the latter is difficult to estimate. However, since the possible values for ΔH° and ΔS° span a considerable range in the first place, we do not expect even moderate pseudo-contact contributions to substantially affect the above conclusions.

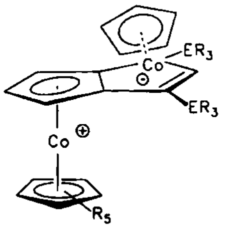
In the series of the complexes $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5H_5)]$ thermally accessible spin equilibria can be ruled out for the derivatives **5aa** ($L = C_2H_4$), **6aa** (L = CO), **10aa** ($L = PMePh_2$) and **11aa** ($L = P(OMe)_3$), because of their temperature-independent ^{1}H NMR spectra. This along with the diminution of the observed effect on going from the PMe_3 (**8aa**) to the PMe_2Ph-substituted complex **9aa** seem to indicate a correlation with the donor properties of the two-electron ligand L, and therefore with the actual structure of the complex within the $\mu\text{-}\eta^4{:}\eta^1/\mu\text{-}\eta^5{:}\eta^1$ continuum.

It is well known that substitution of the five hydrogens on the cyclopentadienyl ligand with methyl groups greatly increases its donor properties.[37] Therefore, in the complex $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(PMe_3)(C_5Me_5)]$ (**8ab**) the zwitterionic structure **E** is expected to be maximally destabilised by the combined effect of the C_5Me_5 and PMe_3 donors on Co(2). However, the proton spectrum of **8ab**, although similar to that of **8aa** at ambient temperature, did not change significantly when the sample was heated.

This result is in an apparent contradiction to our hypothesis. Unfortunately **8ab** obstinately refuses to crystallise, thus preventing its molecular geometry from being determined by a crystal structure analysis. Therefore we are presently unable to tell whether the thermally accessible triplet isomer really is characteristic of the more $\mu\text{-}\eta^4{:}\eta^1\text{-}(C_5H_4)$-type structure.

Conclusions

It appears that our μ-cyclopentadienylidene complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5R_5)']$ (**5**–**11**) owe their existence and (relative) stability to their ability to attain a cobaltocenium ion type substructure by an intramolecular charge separation. The high stability and tendency of formation shown by the cobaltocenium cation has been noted since the beginning of metallocene chemistry.[38] The isoelectronic sandwich cation $[(CO)_3Fe(C_5R_5)]^+$ is not nearly so favoured, and this may well be the reason why we failed to obtain a product analogous to **5** from $[(CO)_3Fe(C_5H_6)]$ and **1a**. In addition to **5**–**11**, there are several other neutral complexes that are highly polar or even zwitterionic because of the possible formation of a cobaltocenium substructure, for example, the dinuclear "cobaltapentalene" complexes **13**[39] and the mononuclear acenaphthylene complexes **14**.[40]



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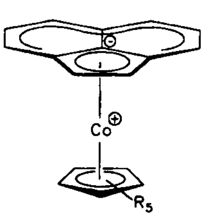
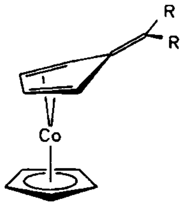


14, R = H, Me

An interesting analogy may be drawn between the dinuclear cyclopentadienylidene bridged complexes $[\{L'_nM(1)\}(\mu\text{-}\eta^n{:}\eta^1\text{-}C_5H_4)\{M(2)L_n\}]$ and some closely related mononuclear species. With the simple isolobal substitution of the $M(2)L_n$ metal fragment for CR_2, we can establish a relationship between the dinuclear μ-C_5H_4 species and mononuclear complexes **15** with a pentafulvene ligand. For example, the above-mentioned $[Cp(CO)Mo(\mu\text{-}C_5H_4)Mn(CO)_4]$ may be considered as an analogue of the ferrocenyl carbonium ions **16** (isolobal substitution of $[Mn(CO)_4]$ with $[CR_2]^+$). In this case, similar structures arise: the bent geometry of **16** with a strong interaction between Fe and the alpha carbon atom of the fulvene[41] is similar to that of $[Cp(CO)Mo(\mu\text{-}C_5H_4)Mn(CO)_4]$.[28c] On the other hand, all derivatives of **15** with known structures have η^4-coordinated fulvene ligands with the exocyclic carbon–carbon double bond bent away from the metal.[42] Structures that are intermediate between η^4 and η^5 (like those of **5**–**11**) have not been obtained with fulvene ligands. In the η^5 structure the negative charge would be located on a carbon atom (C-α), which is highly unfavourable.



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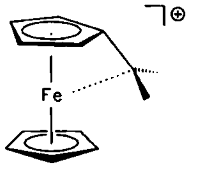

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Experimental Procedure

General Procedures: All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Petroleum ether refers to the fraction with b.p. 40–60 °C. The compounds $[(C_5R_5)Co(C_2H_4)_2]$ [**1a** (R = H) [43], **1b** (R = Me) [44]] and $[(C_5R_5)Co(C_5H_6)]$ [**4a** (R = H) [18b], **4b** (R = Me) [39], **4d** ($R_5 = Me_4Et$) [39]] were prepared by published methods. NMR spectra were obtained on Bruker AC 200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C and 81.0 MHz for ^{31}P NMR) or AC 300 (300.2 MHz for ^1H) instruments. ^1H and ^{13}C NMR chemical shifts are reported vs. $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. The multiplicities of the ^{13}C NMR resonances were determined using the DEPT or the *J*-modulated spin echo (JMOD) techniques. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4. Mass spectra were measured in the electron impact ionisation mode (EI) at 70 eV on Finnegan MAT 8230 and MAT CH 7 spectrometers. Infrared spectra were recorded in the $\nu(CO)$ region in CaF_2 cells on a Perkin-Elmer 983 grating IR spectrometer. Electrochemical experiments were carried out using a EG & G PARC Model 173 potentiostat and a Model 175 Universal Programmer; a platinum disk working electrode was employed. Redox potentials are referenced to the standard calomel electrode (SCE). Elemental analyses were performed locally by the microanalytical laboratory of the Organisch-chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen. Due to the extreme sensitivity of most of the new complexes, reproducible analyses could not be obtained from several derivative.

Synthesis of the complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5H_4R')]$ (5), General Procedure: Petroleum ether solutions of $[(C_5R_5)Co(C_5H_6)]$ (**4**) and $[(C_5H_4R')Co(C_2H_4)_2]$ (**1a**, R' = H; **1c**, R' = Me) were mixed in a large Schlenk tube fitted with a Teflon valve. Slight vacuum was applied to the reaction vessel, which was then sealed and allowed to stand without stirring at ambient temperature. The solution slowly changed colour from orange-red to dark turquoise-green. After several days the mother liquor was decanted from the first crop of product, which was then washed with petroleum ether and dried under vacuum. More product could be obtained from the mother liquor.

$[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5H_5)]$ (5aa): From 3.8 g (20 mmol) of **4a** and 3.6 g (20 mmol) of **1a** in 200 mL of petroleum ether, 4.6 g (67%) of **5aa** was obtained after 7 d as turquoise-green platelets. M.p. 146 °C (decomp.).

$[(C_5Me_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5H_5)]$ (5ba): After recrystallisation from toluene at −20 °C, deep green crystals of **5ba** (230 mg, 25%) were obtained from 0.58 g (2.23 mmol) of **4b** and 0.44 g (2.44 mmol) of **1a** in 40 mL of petroleum ether (reaction time 4 d). MS: *m/z* (relative intensity) = 382 (10, $[M - C_2H_4]^+$), 260 (16, $[Cp^*Co(C_5H_6)]^+$), 259 (100, $[Cp^*CoCp]^+$), 258 (23, $[Cp^*Co(C_5H_4)]^+$), 189 (18, $[Cp_2Co]^+$), 133 (8, $[Cp^* - 2H]^+$), 124 (18, $[CpCo]^+$), 59 (6, Co^+).

$[(C_5Me_4Et)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5H_5)]$ (5da): After recrystallisation from toluene at −20 °C, deep green microcrystals of **5da** (0.72 g, 55%) were obtained from 0.82 g (3.30 mmol) of **4b** and 0.60 g (3.35 mmol) of **1a** in 70 mL of petroleum ether (reaction time 4 d). M.p. 138–150 °C.

$[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5H_4Me)]$ (5ac): Dark green microcrystalline **5ac** (92 mg, 20%) was obtained from 0.25 g (1.30 mmol) of **4a** and 0.27 g (1.40 mmol) of **1c** in 150 mL of petroleum ether (reaction time 7 d). The product crystallised much less readily than the other derivatives of **5**.

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5Me_5)]$ (5ab): A solution of 0.28 g (1.47 mmol) of **4a** and 0.37 g (1.48 mmol) of **1b** in 50 mL of petroleum ether was slowly heated to 60 °C. The colour of the mixture gradually changed from orange-red to dark green. After 1 h the mixture was cooled to room temperature, and the volume of the solution then reduced in vacuo to about half. Most of the product **5ab** crystallised over a period of a few days at −20 °C. Further crops were obtained by repeatedly reducing the volume of the mother liquor and storing at −20 °C. The crude product was recrystallised from toluene at −20 °C. Yield, 0.24 g (40%) **5ab** as turquoise-green crystals. M.p. 151 °C (decomp.). MS: *m/z* (relative intensity) = 382 (3, $[M - C_2H_4]^+$), 259 (9, $[Cp^*CoCp]^+$), 189 (100, $[Cp_2Co]^+$), 124 (38, $[CpCo]^+$), 59 (26, Co^+), 28 (100, $[C_2H_4]^+$). Anal. calcd. for $C_{22}H_{28}Co_2$: C, 64.39; H, 6.88; found: C, 64.22; H, 7.04.

Synthesis of $[(C_5Me_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5Me_5)]$ (5bb): A 0.88 g (3.50 mmol) sample of **1b** was heated to reflux with 0.40 g (6 mmol) of pentamethylcyclopentadiene in 50 mL of petroleum ether for 3 h. The reaction mixture turned dark green and a dark solid precipitated. After cooling to room temperature solvent was removed in vacuo. The residue was recrystallised from ca. 10 mL of toluene at −20 °C to give 0.34 g (40%) of **5bb** as turquoise-green microcrystals. M.p. 154 °C. MS: *m/z* (relative intensity) = 452 (21, $[M - C_2H_4]^+$), 444 (22), 259 (100, $[Cp^*CoCp]^+$), 258 (38, $[Cp^*Co(C_5H_4)]^+$), 194 (4, $[Cp^*Co]^+$), 133 (12, $[Cp^* - 2H]^+$). Anal. calcd. for $C_{27}H_{38}Co_2$: C, 67.50; H, 7.91; found: C, 67.40; H, 7.70.

Synthesis of the complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(CO)(C_5R_5)']$ (6), General Procedure: A degassed toluene solution (ca. 20–30 mL) of **5** was cooled to −60 °C. The reaction flask was flushed with 1 bar of dry carbon monoxide, and the solution slowly warmed to room temperature. After stirring overnight the reaction mixtures were worked up as described below.

$[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(CO)(C_5H_5)]$ (6aa): The reaction mixture was filtered and the solvent removed in vacuo. From 300 mg (0.88 mmol) of **5aa**, 290 mg (97%) of deep green **6aa** was obtained. M.p. > 200 °C (decomp.). Anal. calcd. for $C_{16}H_{14}Co_2O$: C, 56.60; H, 4.16; Found: C, 56.69; H, 4.20.

$[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(CO)(C_5Me_5)]$ (6ab): The volume of the reaction mixture was reduced in vacuo to about 10 mL, and an equal volume of petroleum ether added. Deep green needles (50 mg, 50%) of **6ab** were isolated from 100 mg (0.24 mmol) of **5ab** after storage of the mixture at −20 °C. M.p. 186 °C. MS: *m/z* (relative intensity) = 410 (13, M^+), 382 (81, $[M - CO]^+$), 316 (100), 259 (55,

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$[Cp^*CoCp]^+$), 258 (62, $[Cp^*Co(C_5H_4)]^+$), 189 (45, $[Cp_2Co]^+$), 133 (10, $[Cp^* - 2H]^+$), 124 (28, $[CpCo]^+$). Anal. calcd. for $C_{21}H_{24}Co_2O$: C, 61.46; H, 5.85; found: C, 61.02; H, 6.12.

$[(C_5Me_5)Co(\mu\text{-}C_5H_4)Co(CO)(C_5H_5)]$ (6ba): Solvent was removed from the reaction mixture in vacuo, and the green crystalline residue washed with 5 mL of petroleum ether. A 100 mg (0.24 mmol) sample of **5ba** gave 90 mg (90%) of **6ba**. M.p. 183 °C. MS: m/z (relative intensity) = 410 (15, M^+), 382 (90, $[M - CO]^+$), 323 (48), 316 (100), 259 (16, $[Cp^*CoCp]^+$), 258 (33, $[Cp^*Co(C_5H_4)]^+$), 189 (22, $[Cp_2Co]^+$), 124 (11, $[CpCo]^+$), 59 (4, Co^+). Anal. calcd. for $C_{21}H_{24}Co_2O$: C, 61.46; H, 5.85; found: C, 61.56; H, 5.90.

$[(C_5Me_5)Co(\mu\text{-}C_5H_4)Co(CO)(C_5Me_5)]$ (6bb): The volume of the reaction mixture was reduced in vacuo to about 10 mL, and an equal volume of petroleum ether added. Deep green needles (60 mg, 60%) of **6bb** were isolated from 100 mg (0.21 mmol) of **5bb** after storage of the mixture at −20 °C. M.p. 186 °C. MS: m/z (relative intensity) = 480 (18, M^+), 452 (52, $[M - CO]^+$), 386 (57), 260 (16, $[Cp^*CoCpH]^+$), 259 (100, $[Cp^*CoCp]^+$), 258 (70, $[Cp^*Co(C_5H_4)]^+$), 194 (5, $[Cp^*Co]^+$), 193 (18, $[Cp^*Co - H]^+$), 135 (10, $[Cp^*]^+$), 133 (16, $[Cp^* - 2H]^+$), 59 (4, Co^+).

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(tBuNC)(C_5H_5)]$ (7aa): A 17 mg (0.2 mmol) sample of *t*BuNC, dissolved in ca. 20 mL of THF, was added dropwise to a THF solution (20 mL) of 70 mg (0.2 mmol) of **5aa** at room temperature. After 0.5 h solvent was removed in vacuo and the residue washed with a minimal amount of cold petroleum ether, to give 62 mg (79%) of green **7aa**.

Table 10. Details of the crystal structure determinations of complexes $[(C_5R_5)Co(\mu\text{-}C_5H_4)Co(C_2H_4)(C_5R'_5)]$: **5aa** (R = R′ = H), **5ab** (R = H, R′ = Me), **5ba** (R = Me, R′ = H).

	5aa	**5ab**	**5ba**
formula	$C_{17}H_{18}Co_2$	$C_{22}H_{28}Co_2$	$C_{22}H_{28}Co_2$
crystal size [mm]	0.4 × 0.4 × 0.8	0.3 × 0.3 × 0.6	0.1 × 0.6 × 0.8
crystal system	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a [Å]	9.486(11)	8.687(2)	8.901(10)
b [Å]	10.633(11)	10.446(2)	20.14(2)
c [Å]	14.01(2)	11.175(2)	10.665(13)
α [°]		77.22(2)	
β [°]		78.13(2)	102.55(5)
γ [°]		75.13(2)	
V [Å3]	1413(3)	943.8(3)	1866(4)
Z	4	2	4
M_r	340.17	410.30	410.30
d_c [gcm^{-1}]	1.599	1.444	1.460
F_{000}	696	428	856
$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.328	1.757	1.777
X-Radiation, λ [Å]		$Mo_{K\alpha}$, graphite monochromated, 0.71069	
T(data collect.)	ambient	ambient	ambient
$2\theta_{max}$ [°]	63	60	50
hkl range	0/13, 0/15, 0/20	0/12, −14/14, −15/15	−10/10, 0/23, 0/12
reflns measured	2655	4498	3284
reflns unique	2655	4218	3284
reflns observed [$I \geq 2\sigma(I)$]	1645	4218	2063
absorption correction	empirical	empirical	empirical
parameters refined	206	276	275
GooF	1.058	1.049	1.036
R (obs. reflections only)	0.041	0.030	0.039
wR2 (all reflns) [a]	0.098	0.077	0.097
A, B [a]	0.0364, 0.23	0.0492, 0.2	0.0428, 0

[a] $w = 1/[\sigma^2(F) + (AP)^2 + BP]$; $P = \max(F_o^2, 0) + 2F_c^2)/3$.

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(PMe_3)(C_5H_5)]$ (8aa): A 0.4 mL sample of PMe_3 was added dropwise to 430 mg (1.27 mmol) of **5aa** in 50 mL of toluene. After stirring overnight the solvent and excess phosphine was removed in vacuo. The green crystalline residue was redissolved in toluene and the solution filtered off from a small amount of purple, oily precipitate. After reduction of the volume in vacuo the filtrate was stored at −20 °C, to give 420 mg (68%) of deep green crystalline **8aa**.

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(PMe_3)(C_5Me_5)]$ (8ab): A mixture of 320 mg (0.78 mmol) of **5ab** and 59 mg (0.78 mmol) of PMe_3 in 30 mL of toluene was stirred at room temperature and slightly reduced pressure overnight. The volume of the mixture was reduced in vacuo by about half and the same volume of petroleum ether added. The product **8ab** (40 mg, 5%) precipitated as a green solid during storage at −20 °C.

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(PMe_2Ph)(C_5H_5)]$ (9aa): A 170 mg (1.23 mmol) sample of PMe_2Ph was slowly added to a toluene solution (40 mL) of 420 mg (1.23 mmol) of **5aa**. After stirring overnight all volatiles were removed from the mixture in vacuo and the oily residue treated with 100 mL of petroleum ether. The extract was concentrated and kept at −20 °C. The product **9aa** precipitated from this solution overnight as dark green microcrystals (130 mg, 24%).

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(PMePh_2)(C_5H_5)]$ (10aa): A 200 mg (1.0 mmol) sample of $PMePh_2$ was slowly added to a toluene solution (40 mL) of 330 mg (0.97 mmol) of **5aa**. After stirring overnight all volatiles were removed from the mixture in vacuo and the residue washed with petroleum ether. The product **10aa** separated as a waxy dark green solid (160 mg, 32%) when the volume of a toluene extract of the residue was reduced to a few mL.

Synthesis of $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co\{P(OMe)_3\}(C_5H_5)]$ (11aa): A 400 mg (3.3 mmol) sample of $P(OMe)_3$ was added to a solution of 100 mg (0.29 mmol) of **5aa** in 50 mL THF. After stirring overnight all volatiles were removed in vacuo. The blue oily residue partially crystallised on standing. The product was extracted with diethyl ether (ca. 20 mL). After filtration the blue extract was cooled to −30 °C. The product **11aa** crystallised as thin blue needles (100 mg, 79%).

Table 11. Details of the crystal structure determinations of complexes $[(C_5H_5)Co(\mu\text{-}C_5H_4)Co(L)(C_5H_5)]$: **6aa** (L = CO), **8aa** (L = PMe_3).

	6aa	**8aa**
formula	$C_{16}H_{14}Co_2O$	$C_{18}H_{23}Co_2P$
crystal size [mm]	0.2 × 0.3 × 0.7	0.4 × 0.5 × 0.2
crystal system	orthorhombic	monoclinic
space group	$Pcab$	$P2_1/a$
a [Å]	11.383(5)	12.40(1)
b [Å]	13.404(5)	8.105(4)
c [Å]	17.905(5)	16.81(1)
β [°]		93.61(5)
V [Å3]	2732(2)	1686(9)
Z	8	4
M_r	340.13	388.19
d_c [gcm^{-1}]	1.654	1.529
F_{000}	1376	800
$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.415	2.052
X-Radiation, λ [Å]	$Mo_{K\alpha}$, graphite monochromated, 0.71069	
T(data collect.)	ambient	ambient
$2\theta_{max}$ [°]	60	50
hkl range	0/12, 0/18, 0/24	0/14, 0/9, −19/19
reflns measured	2439	2941
reflns unique	2439	2941
reflns observed [$I \geq 2\sigma(I)$]	1871	2435
absorption correction	numerical	numerical
parameters refined	214	243
GooF	1.043	1.040
R (obs. reflections only)	0.047	0.048
wR2 (all reflections) [a]	0.131	0.129
A, B [a]	0.0878, 0.0	0.093, 0.0

[a] $w = 1/[\sigma^2(F) + (AP)^2 + BP]$; $P = \max(F_o^2, 0) + 2F_c^2)/3$.

Crystal structure determinations: Single crystals were grown from toluene or toluene/petroleum ether solutions and mounted in Lindemann capillary tubes. Intensity data were collected on STOE STADI2 two-circle (Weissenberg) (**6aa**, **8aa**) and Siemens STOE STADI4 four-circle diffractometers at ambient temperature and corrected for Lorentz, polarisation and absorption effects (Tables 10, 11). The structures were solved by the heavy-atom or direct methods and refined by full-matrix least-squares based on F^2 using all measured unique reflexions. All non-hydrogen atoms were given anisotropic displacement parameters. Some of the hydrogens (those of the μ-C_5H_4, ethylene and PMe_3 ligands, and of some Cp rings) were located in difference Fourier syntheses and refined with isotropic displacement parameters. All other hydrogen atoms were added in calculated positions. The calculations were performed using the programs SHELXS-86 and SHELXL-93 [45]. Graphical representations were drawn with the ORTEP-II program [46].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-31. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

Calculation of ΔH° and ΔS° from temperature-dependent NMR shifts: For each resonance, sets of values for ΔH°, ΔS° and C were obtained by fitting of the isotropic shift equation (1) to the experimental chemical shifts. An iterative least-sqares routine employing the Marquardt–Levenberg algorithm was used. Constraints had to be applied to ΔH° and ΔS° because of strong correlation. The calculated values for $(\nu_i/\nu_0)_{dia}$, the chemical shifts of the diamagnetic isomer, came out close to the experimental chemical shifts at and below ambient temperature. This is consistent with the diamagnetism of the solutions at room temperature. The error functions, defined by the root mean square deviation between observed and calculated values of $(\Delta\nu_i)_{dia/para}$, were evaluated with the program AUTOZYK [47].

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[1] H. Wadepohl, *Comments Inorg. Chem.*, **1994**, *15*, 369 and references therein.

[2] H. Wadepohl, S. Gebert, *Coord. Chem. Rev.* **1995**, *143*, 535 and references therein.

[3] H. Wadepohl, T. Borchert, K. Büchner, H. Pritzkow, *Chem. Ber.* **1993**, *126*, 1615.

[4] H. Wadepohl, T. Borchert, H. Pritzkow, *J. Chem. Soc. Chem. Commun.* **1995**, 1447.

[5] a) H. Wadepohl, W. Galm, H. Pritzkow, *Angew. Chem.* **1989**, *101*, 357; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 345. b) H. Wadepohl, W. Galm, H. Pritzkow, *Organometallics* **1996**, *15*, 570.

[6] H. Wadepohl, H. Pritzkow, *Angew. Chem.* **1987**, *99*, 132; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 127.

[7] a) T. L. Gilchrist, C. W. Rees, *Carbene, Nitrene und Dehydroaromaten*, A. Hüthig, Heidelberg **1972**, Chapt. 5. b) H. Dürr, *Top. Curr. Chem.* **1973**, *40*, 103; *ibid.* **1975**, *55*, 87 and references therein. c) H. Dürr, F. Werndorff, *Angew. Chem.* **1974**, *86*, 413; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 483. d) C. Wentrup, *Reaktive Zwischenstufen I*, Thieme, Stuttgart **1979**, Chapt. 4.

[8] a) R. Gleiter, R. Hoffmann, *J. Am. Chem. Soc.* **1968**, *90*, 5457. b) M. Z. Kassaee, M. R. Nimlos, K. E. Downie, E. E. Waali, *Tetrahedron* **1985**, *41*, 1579. c) J. M. Bofill, N. Bru, J. Farràs, S. Olivella, A. Solé, J. Vilarrasa, *J. Am. Chem. Soc.* **1988**, *110*, 3740.

[9] Systems where an electron donor is electronically coupled to an electron acceptor by a π bridge form the most important class of NLO compounds [N. J. Long, *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21. T. J. Marks, M. A. Ratner, *ibid.* **1995**, *107*, 167 and **1995**, *34*, 155]. Recently, high hyperpolarisabilities have been reported for bimetallic sandwich-type complexes: U. Behrens, H. Brussaard, U. Hagenau, J. Heck, E. Hendrickx, J. Körnich, J. G. M. v. d. Linden, A. Persoons, A. L. Spek, N. Veldman, B. Voss, H. Wong, *Chem. Eur. J.* **1996**, *2*, 98.

[10] a) S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Organomet. Chem.* **1985**, *296*, C6. b) H. Wadepohl, H. Pritzkow, *Polyhedron* **1989**, *8*, 1939.

[11] H. Werner, R. Feser, V. Harder, W. Hofmann, H. Neukomm, *Inorg. Synth.* **1989**, *25*, 158.

[12] For a comprehensive overview see H. Dürr in *Methoden der Organischen Chemie (Houben-Weyl)* (Ed.: M. Regitz), Thieme: Stuttgart **1989**, Vol. E19b.

[13] W. Kirmse, *Angew. Chem.* **1959**.

[14] a) W. A. Herrmann, *Angew. Chem.* **1978**, *90*, 855; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 800. b) W. A. Herrmann, *Adv. Organomet. Chem.* **1982**, *20*, 159. c) W. A. Herrmann, *Pure Appl. Chem.* **1982**, *54*, 65. d) W. A. Herrmann, *J. Organomet. Chem.* **1983**, *250*, 319.

[15] H. Fischer in: *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, **1983**, pp. 1–68 and references therein.

[16] G. A. Somorjai, *Chem. Soc. Rev.* **1984**, *13*, 321 and references therein.

[17] On close-packed metal surfaces, cyclopentadiene is dehydrogenated to π-bonded cyclopentadienyl C_5H_5: a) E. L. Muetterties, personal communication, **1983**. b) N. Avery, *Surf. Sci.* **1984**, *137*, L109. c) N. Avery, *ibid.* **1984**, *146*, 363. d) F. P. Netzer, A. Goldmann, G. Rosina, E. Bertel, *ibid.* **1988**, *204*, 387.

[18] a) E. O. Fischer, G. Herberich, *Chem. Ber.* **1961** *94*, 1517. b) M. L. H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.* **1959**, 3753. c) P. L. Pauson, *J. Organomet. Chem.* **1980**, *200*, 207. d) G. R. Knox, M. Nutley, P. L. Pauson, S. Thoma, P. E. Watts, P. E. Elder, R. Griffiths, *J. Chem. Research (M)* **1981**, 1901.

[19] Abstraction of the *endo* hydrogen has been observed in some *exo*-substituted derivatives of **4**: N. El Murr, *J. Organomet. Chem.* **1981**, *208*, C9.

[20] I. U. Khand, P. L. Pauson, W. E. Watts, *J. Chem. Soc. (C)* **1969**, 2024.

[21] Both types of complexes have activated methylene groups [20], and hydride abstraction is a facile reaction. In addition, sigmatropic shifts of the *endo* hydrogens around the C_n rings have been observed [18d, 22].

[22] a) W. R. Roth, W. Grimme, *Tetrahedron Lett.* **1966**, *21*, 2347. b) M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, W. E. Watts, *J. Chem. Soc. Perkin Trans. II* **1972**, 1141. c) J. W. Faller, *Inorg. Chem.* **1980**, *19*, 2857. d) J. M. Brown, I. Midgley, W. J. Albery, *J. Chem. Soc. Perkin Trans. II* **1982**, 767. e) M. L. H. Green, P. A. Newman, J. A. Bandy, *J. Chem. Soc. Dalton Trans.* **1989**, 331.

[23] W. A. Herrmann, J. Plank, M. L. Ziegler, K. Weidenhammer, *Angew. Chem.* **1978**, *90*, 817; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 777.

[24] A number of complexes with μ_3 cyclopentadienylidene bridges is also known: a) N. D. Feasey, N. J. Forrow, G. Hogarth, S. A. R. Knox, K. A. Macpherson, M. J. Morris, A. G. Orpen, *J. Organomet. Chem.* **1984**, *267*, C41. b) A. J. Deeming, N. I. Powell, C. Whittacker, *J. Chem. Soc. Dalton Trans.* **1991**, 1875.

[25] a) W. A. Herrmann, C. Bauer, J. Plank, W. Kalcher, D. Speth, M. L. Ziegler, *Angew. Chem.* **1981**, *93*, 212; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 193. b) N. M. Boag, M. Green, M. R. Mills, G. N. Pain, F. G. A. Stone, *J. Chem. Soc. Chem. Commun.* **1980**, 1171. c) A. D. Clauss, P. A. Dimas, J. R. Shapley, *J. Organomet. Chem.* **1980**, *201*, C31 d) W. A. Herrmann, C. Bauer, G. Kriechbaum, H. Kunkeley, D. Speth, E. Guggolz, *Chem. Ber.* **1982**, *115*, 878. e) W. A. Herrmann, J. Plank, C. Bauer, M. L. Ziegler, E. Guggolz, R. Alt, *Z. Anorg. Allg. Chem.* **1982**, *487*, 85. f) W. A. Herrmann, C. Bauer, *Chem. Ber.* **1982**, *115*, 14. g) W. A. Herrmann, G. Kriechbaum, C. Bauer, E. Guggolz, M. L. Ziegler, *Angew. Chem.* **1981**, *93*, 838; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 815.

[26] A. A. Danopoulos, G. Wilkinson, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1991**, 181.

[27] Usually, the double-headed arrow stands between "resonance structures". The strict definition of resonance implies that the true electronic structure of a compound may be considered as a mixture of several nonexistant resonance structures with the same geometry, but a different arrangement of localised bonds (see for example J. March, *Advanced Organic Chemistry*, McGraw-Hill, New York, 2nd ed. **1977**, Chapt. 2). Lacking a pre-defined symbol, in the context of this paper we use the double-headed arrow to indicate a continuum between two limiting structures (which may indeed exist) with different geometry and bonding.

[28] a) G. P. Pez, J. *Am. Chem. Soc.* **1976**, *98*, 8072. b) C. Couldwell, K. Prout, *Acta Crystallogr. Sect. B*, **1979**, *35*, 335. c) R. J. Hoxmeier, C. B. Knobler, H. D. Kaesz, *Inorg. Chem.* **1979**, *18*, 3462. d) B. Meunier, K. Prout, *Acta Crystallogr. Sect. B*, **1979**, *35*, 2558. e) C. Couldwell, K. Prout, *ibid.* **1979**, *35*, 335. f) D. A. Lemenovskii, V. P. Fedin, A. V. Aleksandrov, Y. L. Solokotov, Y. T. Struchkov, *J. Organomet. Chem.* **1981**, *201*, 257. g) A. A. Pasynskii, Y. V. Skripkin, V. T. Kalinnikov, M. A. Porai-Koshits, A. S. Antsyshkina, G. G. Sadikov, V. N. Ostrikova, *ibid.* **1981**, *201*, 269. More recently, further examples have been reported: h) M. L. H. Green, M. L. Poveda, J. Bashkin, K. Prout, *J. Chem. Soc. Chem. Commun.* **1982**, 30. i) J. Bashkin, M. L. H. Green, M. L. Poveda, K. Prout, *J. Chem. Soc. Dalton Trans.* **1982**, 2485. j) J. Bashkin, M. L. H. Green, M. L. Poveda, K. Prout, *ibid.* **1982**, 2485. k) G. P. Pez, P. Apgar, R. K. Crissey, *J. Am. Chem. Soc.* **1982**, *104*, 482. l) K. P. C. Vollhardt, T. W. Weidman, *ibid.* **1983**, *105*, 1676. m) F. H. Köhler, W. A. Geike, P. Hofmann, U. Schubert, P. Stauffert, *Chem. Ber.* **1984**, *117*, 904. n) C. P. Casey, R. E. Palermo, R. F. Jordan, A. L. Rheingold, *J. Am. Chem. Soc.* **1985**, *107*, 4597. o) T. T. Wenzel, R. G. Bergman, *ibid.* **1986**, *108*, 4856. p) L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, U. Thewalt, B. Honold, *J. Organomet. Chem.* **1986**, *310*, 27. q) M. W. Droege, W. D. Harman, H. Taube, *Inorg. Chem.* **1987**, *26*, 1309. r) D. H. Berry, T. S. Koloski, P. J. Carroll, *Organometallics*, **1990**, *9*, 2952. s) J. Ho, D. W. Stephan, *ibid.* **1992**, *11*, 1014.

[29] a) D. W. Macomber, R. D. Rogers, *ibid.* **1985**, *4*, 1485. b) G. Erker, R. Lecht, C. Krüger, Y.-H. Tsay, H. Bönnemann, *J. Organomet. Chem.* **1987**, *326*, C75. c) G. Erker, R. Lecht, J. L. Petersen, H. Bönnemann, *Organometallics* **1987**, *6*, 1962. d) A. C. Filippou, E. Herdtweck, H. G. Alt, *J. Organomet. Chem.* **1988**, *355*, 437. e) L. Qiwing, H. Xiang, L. Shutang, Y. Hong, W. Binfang, J. Zhenxing, S. Jianqiu, *Polyhedron* **1993**, *12*, 1527. f) F. Carre, G. Cerveau, E. Colomer, R. J. P. Corriu, J. C. Young, L. Richard, R. Weiss, *J. Organomet. Chem.* **1979**, *179*, 215. g) A. W. Coleman, P. B. Hitchcock, M. F. Lappert, R. K. Maskell, J. H. Müller, *ibid.* **1983**, *250*, C9.

[30] P. Hofmann, M. Padmanabhan, *Organometallics* **1983**, *2*, 1273.

[31] H. Wadepohl, W. Galm, H. Pritzkow, A. Wolf, *J. Chem. Soc. Chem. Commun.* **1993**, 1459.

[32] An overview of the literature may be found in H. Wadepohl, Dissertation, Universität Marburg **1982**. Important review articles: a) D. R. Eaton, W. D. Phillips, *Adv. Magn. Resonance* **1965**, *103*, 1. b) E. de Boer, H. van Willigen, *Progr. NMR Spectrosc.* **1967**, *2*, 111. c) H. J. Keller in P. Diehl, E. Fluck, R. Koesfeld (eds.) *NMR, Basic Principles and Progress 2*, Springer Verlag, Berlin **1970**. d) G. N. LaMar, W. DeW. Horrocks, Jr., R. D. Holm (eds.) *NMR of Paramagnetic Molecules: Priciples and Applications*, Academic Press, London **1973**.

[33] P. S. Pregosin, R. W. Kunz in *NMR, Basic Principles and Progress 16* (Eds.: P. Diehl, E. Fluck, R. Koesfeld), Springer Verlag, Berlin **1979**.

[34] R. R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford **1987**, Ch.2.3.

[35] a) W. L. Olson, A. M. Stacy, L. F. Dahl, *J. Am. Chem. Soc.* **1986**, *108*, 7646. b) B. Bachmann, F. Hahn, J. Heck, M. Wünsch, *Organometallics* **1989**, *8*, 2523.

[36] Only the resonances of the CH and Cp protons were included in the fitting procedure.

[37] D. C. Calabro, J. L. Hubbard, C. H. Blevins II, A. C. Campbell, D. L. Lichtenberger, *J. Am. Chem. Soc.* **1981**, *103*, 6839.

[38] a) E. O. Fischer, W. Pfab, *Z. Naturforsch. Sect. B* **1952**, *7*, 377. b) G. Wilkinson, *J. Am. Chem. Soc.* **1952**, *74*, 6148. c) E. O. Fischer, R. Jira, *Z. Naturforsch. Sect. B* **1953**, *8*, 327.

[39] H. Wadepohl, W. Galm, H. Pritzkow, A. Wolf, *Angew. Chem.* **1992**, *104*, 1050: *Angew. Chem. Int. Ed. Engl.* **1992**, *104*, 1058.

[40] K. Jonas, *J. Organomet. Chem.* **1990**, *400*, 165.

[41] a) R. Gleiter, R. Seeger, *Helv. Chim. Acta* **1971**, *54*, 123. b) R. Gleiter, R. Seeger, H. Binder, E. Fluck, M. Cais, *Angew. Chem.* **1972**, *84*, 1107; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 1028. c) J. J. Dannenberg, M. K. Levenberg, J. H. Richards, *Tetrahedron* **1973**, *29*, 1575 d) U. Behrens, *J. Organomet. Chem.* **1979**, *182*, 89.

[42] a) H. Wadepohl, *Habilitationsschrift*, Universität Heidelberg, **1989** b) D. Rau, U. Behrens, *J. Organomet. Chem.* **1990**, *387*, 219. c) H. Wadepohl, H. Pritzkow, *Acta Crystallogr. Sect. C: Struct. Commun.* **1991**, *C47*, 2061.

[43] a) K. Jonas, E. Deffense, D. Habermann, *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 716. b) K. Jonas, E. Deffense, D. Habermann, *Angew. Chem. Suppl.* **1983**, 1005.

[44] S. A. Frith, J. L. Spencer, *Inorg. Synth.* **1985**, *23*, 15.

[45] a) *SHELXS-86*, G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467. b) *SHELXL-93*, G. M. Sheldrick, Universität Göttingen **1993**.

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

[47] F. Hahn, *AUTOZYK*, Universität Marburg **1987**.

0947-6539/96/0211-1465 $ 15.00+.25/0