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Chiral cyclopentadiene–cyclopentadienyl complexes of cobalt

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Abstract

Reactions of $(C_5H_4R)_2CoX$ (X = PF_6 or BPh_4; R = Et, ${}^tBu$ or $SiMe_3$) with R'Li (R' = Me, Et, Pr or Ph) and $NaBH_4$ and $(C_5H_4R)_2Co$ (R = Me, Et or Ph) with R'_2Cd (R' = Me, Et or Ph) resulting in isomeric complexes $(\eta^4$-exo-5-R'-1-R-$C_5H_4)(\eta^5$-$C_5H_4R)Co$ (I) and $(\eta^4$-exo-5-R'-2-R-$C_5H_4)(\eta^5$-$C_5H_4R)Co$ (II) have been studied. The composition and structure of complexes I and II have been confirmed by ^1H NMR spectroscopy. Complexes I and II are planar chiral systems. Electron and steric effects of substituents in the chiral complexes have been discussed. It has been established that the ratio of isomers I and II depends upon the method of synthesis of the complex, a substituent in a cyclopentadienyl ring and an attacking group. In a radical addition reaction, the isomer ratio is mainly determined by the steric factors of the substituents and the attacking group. In a nucleophilic addition reaction, orientation effects are determined by the competition of steric and electron factors

Introduction

The most widespread methods for the synthesis of cyclopentadiene–cyclopentadienyl complexes of cobalt are reactions of nucleophilic [1,2] or electrophilic addition [3,4] to a cation or an anion of cobaltocene, respectively, reactions of radical addition to a neutral cobaltocene [5–7] and reactions of cobaltocene with halogen alkyls [8].

In the reaction of substituted derivatives of cobaltocene, the formation of isomeric complexes in which a substituent in a cyclopentadiene ligand is in positiion 1 (I) or position 2 (II) is possible.

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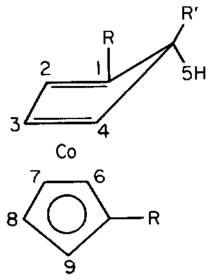
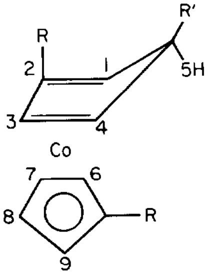


I



II

The first synthesis of such isomeric complexes **I** and **II** was carried out by the electrochemical reduction of dimethylcobalticinium in the presence of CO_2 [3].

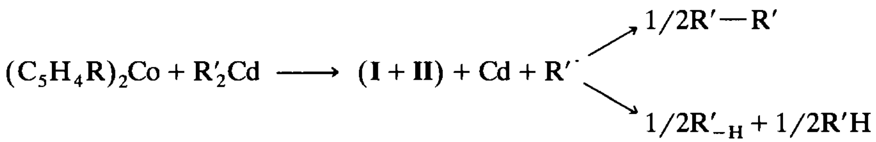
The reactions of bis-(alkylcyclopentadienyl) cobalt with organocadmium compounds [9] and of a substituted cobalticinium salt with nucleophilic agents [10] were used to prepare isomeric complexes.

Results and discussion

Reactions of complex formation

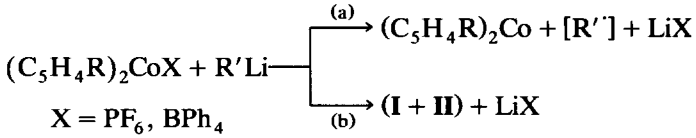
The reaction of radical addition to alkylcobaltocene and the reaction of nucleophilic addition to a cation of alkylcobalticinium were used to synthesize substituted cyclopentadiene–cyclopentadienyl complexes of cobalt.

The radical addition reaction took place on the interaction of alkylcobaltocene with organocadmium compounds. On adding 4–6-fold excess of R'_2Cd ($R' = Me$ or Ph) to $(C_5H_4R)_2Co$ ($R = Et$ or ^tBu), the reaction medium turned red-brown and the formation of metallic cadmium was observed. Analysis of the gaseous phase showed that, with $R' = Me$, it consists of methane and ethane (1:3) and of propane and propylene (1:1) for $R' = Pr$. Using Ph_2Cd, the synthesis reaction was conducted in toluene. Diphenyl and benzene were found in the reaction mixture. After chromatography on Al_2O_3, the cyclopentadiene–cyclopentadienyl complexes were isolated as a red liquid and for $R = {}^tBu$ and $R' = Ph$ in the form of red crystals in 60–80% yield. In almost all cases, the reaction leads to the formation of the mixture of position isomers **I** and **II**.



$$(C_5H_4R)_2Co + R'_2Cd \longrightarrow (\mathbf{I} + \mathbf{II}) + Cd + R'^{\cdot} \begin{cases} \nearrow 1/2R'\text{—}R' \\ \searrow 1/2R'_{-H} + 1/2R'H \end{cases}$$

The reaction of $(C_5H_4R)_2CoX$ ($X = PF_6$ or BPh_4; $R = Et$, ^tBu or $SiMe_3$) with R'Li ($R' = Me$, Et, Pr or Ph) in THF solution results in a mixture of isomers **I** and **II**. The reaction proceeds in two directions: a one-electron reduction of a cobalticinium cation to cobaltocene (reaction (a)) and a nucleophilic addition to cobalticinium (reaction (b)).



$$(C_5H_4R)_2CoX + R'Li \begin{cases} \xrightarrow{(a)} (C_5H_4R)_2Co + [R'^{\cdot}] + LiX \\ \xrightarrow[(b)]{} (\mathbf{I} + \mathbf{II}) + LiX \end{cases}$$

$$X = PF_6, BPh_4$$

The part of reaction (b) in the total process determines the yield of isomer I and II mixture. It was ascertained that the yield of complexes **I** and **II** depends on both the R substituent and the R′ attacking group (see Experimental section, Table 6). The largest yield of isomers **I** and **II** (95%) was obtained via the reaction of $(C_5H_4{}^tBu)_2CoPF_6$ with PrLi. A lower yield of the complexes was observed after reaction of a cobalticinium salt with MeLi and PhLi. The presence of the $SiMe_3$ substituent in the cyclopentadienyl ligand substantially decreased the yield of complex compared to alkyl substituted ligands. This is due to the increase of the one-electron reduction reaction in comparison with the addition reaction for $R = SiMe_3$ (Table 6).

On the reduction of $(C_5H_4R)CoX$ ($R = {}^tBu$ or $SiMe_3$; $X = PF_6$ or BPh_4) with $NaBH_4$, a mixture of isomers **I** and **II** ($R = {}^tBu$, $SiMe_3$; $R' = H$) was obtained in 71–80% yield.

In all three cases, the addition reaction proved to be non-regioselective leading to the isomer mixture. Separation of the mixture of isomers **I** and **II** was not performed. The quantitative composition of the mixture and the structure of isomers I and **II** were established by ^1H NMR investigations.

^1H NMR identification of complexes

The assignment of signals in the ^1H NMR spectra to each isomer was made on the basis of a comparative analysis of proton signals of the cyclopentadiene ring (Tables 1 and 2).

In isomer **I**, the signal from a H(3) proton was observed as a triplet while in isomer **II** the signal from a H(3) proton was seen as a doublet with an additional doublet splitting due to the spin–spin interaction with a H(1) proton. The values of ^3J(H(3)–H(4)) and ^4J(H(1)–H(3)) were within 2.4–2.6 Hz and 1.3–1.5 Hz, respectively (Fig. 1, Tables 1 and 2).

From the integral intensities of the H(3) protons of complexes **I** and II, the quantitative data on the ratio of the isomers in the mixture were obtained; they were used for the subsequent assignment of the signals of other protons to each isomer.

The H(5) protons can also be considered as an indicator of assigning the signals to isomers **I** and **II**. Although the signals of the H(5) protons for complexes **I** and **II** appear in the case of close values of a magnetic field, they differ in multiplicity. In isomer **I**, the signals of the H(5) protons are characterized by an additional doublet splitting due to the spin–spin interaction with the H(4) protons. The values of J(H(5)–H(4)) for complexes **I** are 2.3–2.6 Hz.

In isomer **II**, the triplet splitting is typical of the H(5) signals because of the spin–spin splitting on the proton nuclei in positions 1 and 4 (J(H(1)–H(5)) $=J$(H(4)–H(5)) 2.3–2.5 Hz).

For complexes **I** and **II** ($R = {}^tBu$ or $SiMe_3$; $R' = H$) exo- and endo-hydrogen atoms were observed as AB quadruples (Fig. 1). The signals of the H(5) exo-protons of these complexes were observed with lower values of the magnetic field compared to endo-protons. For the signals of the H(5) exo- and endo-protons of complexes **I** and **II**, splitting similar to that for the rest of the complexes was seen. The values of the spin–spin interaction constants for the $H_{exo}(5)$ protons were much smaller than those of the $H_{endo}(5)$ protons for both types of complexes (1.9–2.0 Hz).

Table 1

Parameters of NMR spectra for complexes **I** (δ (ppm), J (Hz))

	Substituents		H(2)	H(3)	H(4)	H(5)	H(6)(9)	H(7)(8)	H(8)(7)	H(9)(6)
	R	R′								
1	Et 1.31 (t, CH_3) 2.49 (q, CH_2) $J(CH_3-CH_2)$ = 7.4	Me 0.52 (d) $J(5-CH_3)$ = 6.1	5.06 (d.d.) $J_{23} = 2.5$ $J_{24} = 1.5$	5.04 $J_{32} = 2.5$ $J_{34} = 2.5$	2.60 (t.d) $J_{43} = 2.5$ $J_{45} = 2.5$ $J_{42} = 1.5$	2.79 (q.d) $J(5-CH_3) = 6.1$ $J_{54} = 2.5$	4.32 (d.t) $J_{6(9)-7(8)} = 2.4$ $J_{6(9)-8(7)} = 1.7$ $J_{6(9)-9(6)} = 1.7$	4.48 (t.d) $J_{7(8)-6(9)} = 2.4$ $J_{7(8)-8(7)} = 2.4$ $J_{7(8)-9(6)} = 1.7$	4.62 (t.d) $J_{8(7)-7(8)} = 2.4$ $J_{8(7)-9(6)} = 2.4$ $J_{8(7)-6(9)} = 1.7$	4.69 (d.t) $J_{9(6)-8(7)} = 2.4$ $J_{9(6)-6(9)} = 1.7$ $J_{9(6)-7(8)} = 1.7$
2	Et 0.80–1.60	Pr 0.80–1.60	4.88 (m)	5.04 (t) $J_{32} = 2.5$ $J_{34} = 2.5$	2.36–2.71	2.36–2.71	4.33 (d.t) $J_{6(9)-7(8)} = 2.5$ $J_{6(9)-8(7)} = 1.5$ $J_{6(9)-9(6)} = 1.5$	4.51 (t.d) $J_{7(8)-6(9)} = 2.5$ $J_{7(8)-8(7)} = 2.5$ $J_{7(8)-9(6)} = 1.5$	4.88 (t.d) $J_{8(7)-7(8)} = 2.5$ $J_{8(7)-9(6)} = 2.5$ $J_{8(7)-6(9)} = 1.5$	4.66 (d.t) $J_{9(6)-8(7)} = 2.5$ $J_{9(6)-6(9)} = 1.5$ $J_{9(6)-7(8)} = 1.5$
3[a]	Et 1.21 (CH_3) 2.17 and 2.32 (CH_2) $^2J(HH) = 8.0$ $^3J(CH_3CH_2)$ = 7.5	Ph 7.51–6.95	4.85 (d.d) $J_{23} = 2.5$ $J_{24} = 1.5$	5.07 (t) $J_{32} = 2.5$ $J_{34} = 2.5$	2.62 (t.d) $J_{43} = 2.5$ $J_{45} = 2.5$ $J_{42} = 1.5$	4.00	4.30 (d.t) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.5$ $J_{6(9)-9(6)} = 1.5$	4.46 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.5$	4.62 (t.d) $J_{8(7)-7(8)} = 2.6$ $J_{8(7)-9(6)} = 2.6$ $J_{8(7)-6(9)} = 1.5$	4.85 (d.t) $J_{9(6)-8(7)} = 2.6$ $J_{9(6)-6(9)} = 1.5$ $J_{9(6)-7(8)} = 1.5$
4	^{t}Bu 1.02 (s) 1.24 (s)	H 2.16 (d.d) J(exo-endo) = 13.1 J(exo-4) = 1.9	5.14 (d.d) $J_{23} = 2.2$ $J_{24} = 1.5$	5.25 (t) $J_{34} = 2.2$ $J_{32} = 2.2$	2.48 (t.d) $J_{34} = 2.3$ $J_{45} = 2.3$ $J_{42} = 1.5$	2.82 (d.d) J(endo-exo) = 13.1 J(endo-4) = 2.3 J(exo-4) = 1.9	3.91 (d.t) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.6$ $J_{6(9)-9(6)} = 1.6$	4.82 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.6$	5.17 (t.d) $J_{8(7)-7(8)} = 2.7$ $J_{8(7)-9(6)} = 2.7$ $J_{8(7)-6(9)} = 1.6$	4.82 (d.t) $J_{9(6)-8(7)} = 2.7$ $J_{9(6)-6(9)} = 1.6$ $J_{9(6)-7(8)} = 1.6$
5	^{t}Bu 1.26 (s) 1.10 (s)	Me 0.55 (d) $J(5-CH_3)$ = 6.1	4.98	5.08 (t) $J_{23} = 2.5$ $J_{34} = 2.5$	2.51 (t.d) $J_{45} = 2.5$ $J_{43} = 2.5$ $J_{42} = 1.5$	2.89 (q.d) $J(5-CH_3) = 6.1$ $J_{54} = 2.5$	4.62 (d.t) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.4$ $J_{6(9)-9(6)} = 1.4$	4.07 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.4$	4.41 (t.d) $J_{8(7)-7(8)} = 2.6$ $J_{8(7)-9(6)} = 2.6$ $J_{8(7)-6(9)} = 1.4$	5.10 (d.t) $J_{9(6)-8(7)} = 2.6$ $J_{9(6)-6(9)} = 1.4$ $J_{9(6)-7(8)} = 1.4$

6	^{t}Bu 1.28 (s) 1.11 (s)	Pr 0.60–1.30	4.96 (d.d) $J_{23} = 2.5$ $J_{24} = 1.5$	5.08 (t) $J_{32} = 2.5$ $J_{34} = 2.5$	2.64–2.74 (m)	2.64–2.74 (m)	3.94 (d.t) $J_{6(9)-7(8)} = 2.5$ $J_{6(9)-8(7)} = 1.7$ $J_{6(9)-9(6)} = 1.7$	4.79 (t.d) $J_{7(8)-6(9)} = 2.5$ $J_{7(8)-8(7)} = 2.5$ $J_{7(8)-9(6)} = 1.7$	5.08 (t.d) $J_{8(7)-7(8)} = 2.5$ $J_{8(7)-9(6)} = 2.5$ $J_{8(7)-6(9)} = 1.7$	5.10 (d.t) $J_{9(6)-8(7)} = 2.5$ $J_{9(6)-6(9)} = 1.7$ $J_{9(6)-7(8)} = 1.7$
7	^{t}Bu 1.17 (s) 1.15 (s)	Ph 7.00–7.45	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
8	SiMe$_3$ 0.30 (s) 0.13 (s)	H 2.01 (d.d) J(exo-4) = 1.9	5.46 (d.d) $J_{23} = 2.1$ $J_{24} = 1.2$	5.49 (t) $J_{32} = 2.1$ $J_{34} = 2.1$	2.60 J(4-exo) = 1.9 J(4-endo) = 2.6	2.64 (d.d) J(exo-endo) = 13.8 J(endo-4) = 2.6	3.92 (d.t) $J_{6(9)-7(8)} = 2.4$ $J_{6(9)-8(7)} = 1.5$ $J_{6(9)-9(6)} = 1.5$	5.14 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)}$-2.6 $J_{7(8)-9(6)} = 1.5$	5.42 (t.d) $J_{8(7)-7(8)} = 2.4$ $J_{8(7)-9(6)} = 2.4$ $J_{8(7)-6(9)} = 1.5$	4.75 (d.t) $J_{9(6)-8(7)} = 2.3$ $J_{9(6)-6(9)} = 1.5$ $J_{9(6)-7(8)} = 1.5$
9	SiMe$_3$ 0.31 (s) 0.19 (s)	Me 0.39 (d) $J(5\text{-}CH_3)$ = 6.0	5.23 (d.d) $J_{23} = 2.4$ $J_{24} = 1.2$	5.27 (t) $J_{32} = 2.4$ $J_{34} = 2.4$	2.75 (t.d) $J_{43} = 2.4$ $J_{45} = 2.5$ $J_{42} = 1.2$	2.72 (q.d) $J(5\text{-}CH_3) = 6.0$ $J_{54} = 2.4$	3.97 (d.t) $J_{6(9)-7(8)} = 2.7$ $J_{6(9)-8(7)} = 1.4$ $J_{6(9)-9(6)} = 1.4$	5.04 (t.d) $J_{7(8)-6(9)} = 2.7$ $J_{7(8)-8(7)} = 2.7$ $J_{7(8)-9(6)} = 1.4$	5.36 (t.d) $J_{8(7)-7(8)} = 2.7$ $J_{8(7)-9(6)} = 2.7$ $J_{8(7)-6(9)} = 1.4$	4.77 (d.t) $J_{9(6)-8(7)} = 2.7$ $J_{9(6)-6(9)} = 1.4$ $J_{9(6)-7(8)} = 1.4$
10	SiMe$_3$ 0.31 (s) 0.19 (s)	Et 0.85–1.50	5.24 (d.d) $J_{23} = 2.4$ $J_{24} = 1.2$	5.27 (t) $J_{34} = 2.4$ $J_{32} = 2.4$	2.85 (d.d.d) $J_{43} = 2.4$ $J_{45} = 2.5$ $J_{42} = 1.2$	2.57–2.77 (m)	3.98 (d.t) $J_{6(9)-7(8)} = 2.4$ $J_{6(9)-8(7)} = 1.3$ $J_{6(9)-9(6)} = 1.3$	5.06 (t.d) $J_{7(8)-6(9)} = 2.4$ $J_{7(8)-8(7)} = 2.4$ $J_{7(8)-9(6)} = 1.3$	5.38 (t.d) $J_{8(7)-7(8)} = 2.4$ $J_{8(7)-9(6)} = 2.4$ $J_{8(7)-6(9)} = 1.3$	4.74 (d.t) $J_{9(6)-8(7)} = 2.4$ $J_{9(6)-6(9)} = 1.3$ $J_{9(6)-7(8)} = 1.3$
11	SiMe$_3$ 0.19 (s) 0.31 (s)	Pr 0.60–1.30	5.26 (d.d) $J_{23} = 2.3$ $J_{24} = 1.2$	5.28 (t) $J_{32} = 2.3$ $J_{34} = 2.3$	2.86 (t.d) $J_{43} = 2.3$ $J_{45} = 2.4$ $J_{42} = 1.2$	2.79 (t.d) $J(5\text{-}CH_3) = 6.5$ $J_{54} = 2.4$	3.98 (d.t) $J_{6(9)-7(8)} = 2.4$ $J_{6(9)-8(7)} = 1.5$ $J_{6(9)-9(6)} = 1.5$	5.04 (t.d) $J_{7(8)-6(9)} = 2.4$ $J_{7(8)-8(7)} = 2.4$ $J_{7(8)-9(6)} = 1.5$	5.34 (t.d) $J_{8(7)-7(8)} = 2.4$ $J_{8(7)-9(6)} = 2.4$ $J_{8(7)-6(9)} = 1.5$	4.79 (d.t) $J_{9(6)-8(7)} = 2.4$ $J_{9(6)-6(9)} = 1.5$ $J_{9(6)-7(8)} = 1.5$
12	SiMe$_3$ +0.26 (s) −0.02 (s)	Ph 6.86–7.52	5.26 (d.d) $J_{23} = 2.5$ $J_{24} = 1.2$	5.30 (t) $J_{32} = 2.5$ $J_{34} = 2.5$	2.86 (t.d) $J_{43} = 2.5$ $J_{45} = 2.5$ $J_{42} = 1.2$	3.92 (d) $J_{54} = 2.5$	3.98 (d.t) $J_{6(9)-7(8)} = 2.5$ $J_{6(9)-8(7)} = 2.4$ $J_{6(9)-9(6)} = 1.4$	5.04 (t.d) $J_{7(8)-6(9)} = 2.5$ $J_{7(8)-8(7)} = 2.5$ $J_{7(8)-9(6)} = 1.4$	5.34 (t.d) $J_{8(7)-7(8)} = 2.5$ $J_{8(7)-9(6)} = 2.5$ $J_{8(7)-6(9)} = 1.4$	4.79 (d.t) $J_{9(6)-8(7)} = 2.5$ $J_{9(6)-6(9)} = 1.4$ $J_{9(6)-7(8)} = 1.4$

[a] The assignment of the signals was done using selective double NMR.

Table 2

Parameters of NMR spectra for complexes **II** (δ (ppm), J (Hz))

	Substituents		H(1)	H(3)	H(4)	H(5)	H(6)(9)	H(7)(8)	H(8)(7)	H(9)(6)
	R	R′								
1	Et 1.04 (t, CH_3) 2.41 (q, CH_2) $J(CH_3CH_2)$ = 7.4	Me 0.46 (d) $J(5\text{-}CH_3) = 6.1$	2.56	5.06 (d.d) $J_{34} = 2.4$ $J_{31} = 1.3$	2.49 (m) [a]	2.74 (q.t) $J(5\text{-}CH_3) = 6.1$ $J_{51} = 2.4$ $J_{54} = 2.4$	4.67 (d.t) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.6$ $J_{6(9)-9(6)} = 1.6$	4.37 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.6$	4.53 (t.d) $J_{8(7)-7(8)} = 2.6$ $J_{8(7)-9(6)} = 2.6$ $J_{8(7)-6(9)} = 1.6$	4.85 (d.t) $J_{9(6)-8(7)} = 2.6$ $J_{9(6)-6(9)} = 1.6$ $J_{9(6)-7(8)} = 1.6$
2	Et 0.80–1.60	Pr 0.80–.60	2.36–2.71	5.06 (m)	2.36–2.71	2.36–2.71	4.70 (d.t) $J_{6(9)-7(8)} = 2.5$ $J_{6(9)-8(7)} = 1.5$ $J_{6(9)-9(6)} = 1.5$	4.39 (t.d) $J_{7(8)-6(9)} = 2.5$ $J_{7(8)-8(7)} = 2.5$ $J_{7(8)-9(6)} = 1.5$	4.56 (t.d) $J_{8(7)-7(8)} = 2.5$ $J_{8(7)-9(6)} = 2.5$ $J_{8(7)-6(9)} = 1.5$	4.70 $J_{9(6)-8(7)} = 2.5$ $J_{9(6)-6(9)} = 1.5$ $J_{9(6)-7(8)} = 1.5$
3 [b]	Et 1.13 (CH_3) 2.36 and 2.41 (CH_2) $^2J(HH) = 8.0$ $^3J(CH_3CH_2)$ = 7.8	Ph 7.51–6.95	2.78 (d.t) $J_{15} = 2.5$ $J_{14} = 1.5$ $J_{13} = 1.5$	5.04 (m) $J_{34} = 2.5$ $J_{31} = 1.5$	2.72 (d.t) $J_{43} = 2.5$ $J_{45} = 2.5$	3.99	4.66 (m) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.6$ $J_{6(9)-9(6)} = 1.6$	4.34 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.6$	4.51 (t.d) $J_{8(7)-7(8)} = 2.6$ $J_{8(7)-9(6)} = 2.6$ $J_{8(7)-6(9)} = 1.6$	4.66 (m) $J_{9(6)-8(7)} = 2.6$ $U_{9(6)-6(9)} = 1.6$ $J_{9(6)-7(8)} = 1.6$
4	^{t}Bu 1.32 (s) 1.39 (s)	H 2.21 (d.t) J(exo-endo) = 13.0 J(exo-4) = 1.9 J(exo-1) = 1.9	2.49 (d.d) J(1-exo) = 1.9 J(1-endo) = 2.3	5.21 (d.d) $J_{34} = 2.9$ $J_{31} = 1.5$	2.48 (d.d.d) J(4-exo) = 1.9 J(4-endo) = 2.3 $J_{43} = 2.9$	2.83 (d.t) $J_{(endo\text{-}exo)} = 13.0$ $J_{(endo\text{-}4)} = 2.3$ $J_{(endo\text{-}1)} = 2.3$	4.42 (d.t) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.7$ $J_{6(9)-9(6)} = 1.7$	3.80 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.7$	4.84 (t.d) $J_{8(7)-7(8)} = 2.6$ $J_{8(7)-9(6)} = 2.6$ $J_{8(7)-6(9)} = 1.7$	5.08 (d.t) $J_{9(6)-8(7)} = 2.6$ $J_{9(6)-6(9)} = 1.7$ $J_{9(6)-7(8)} = 1.7$
5	^{t}Bu 1.36 (s) 1.32 (s)	Me 0.42 (d) $J(5\text{-}CH_3) = 6.1$	2.62 (d.d) $J_{15} = 2.5$ $J_{14} = 2.5$	4.98 (d.d) $J_{34} = 2.8$ $J_{31} = 1.5$	2.65 q $J_{45} = 2.5$ $J_{43} = 2.5$	2.76 (q.t) $J(5\text{-}CH_3) = 6.1$ $J_{51} = 2.5$	4.48 (d.t) $J_{6(9)-7(8)} = 2.6$ $J_{6(9)-8(7)} = 1.7$ $J_{6(9)-9(6)} = 1.7$	3.88 (t.d) $J_{7(8)-6(9)} = 2.6$ $J_{7(8)-8(7)} = 2.6$ $J_{7(8)-9(6)} = 1.7$	4.82 (t.d) $J_{8(7)-7(8)} = 2.6$ $J_{8(7)-9(6)} = 2.6$ $J_{8(7)-6(9)} = 1.7$	5.03 (d.t) $J_{9(6)-8(7)} = 2.6$ $J_{9(6)-6(9)} = 1.7$ $J_{9(6)-7(8)} = 1.7$

6	^{t}Bu 1.36 (s) 1.32 (s)	Pr 0.60–1 30	2.62–2.74	5.10 (d.d) J_{34} = 2.5 J_{13} = 1.7	2.64–2.74 (m)	2.64–2 74 (m)	4.46 (d.t) $J_{6(9)-7(8)}$ = 2 6 $J_{6(9)-8(7)}$ = 1.6 $J_{6(9)-9(6)}$ = 1.6	3.89 (t.d) $J_{7(8)-6(9)}$ = 2.6 $J_{7(8)-8(7)}$ = 2.6 $J_{7(8)-9(6)}$ = 1.6	4.86 (t.d) $J_{8(7)-7(8)}$ = 2.6 $J_{8(7)-9(6)}$ = 2.6 $J_{8(7)-6(9)}$ = 1.6	5.04 (d.t) $J_{9(6)-8(7)}$ = 2.6 $J_{9(6)-6(9)}$ = 1.6 $J_{9(6)-7(8)}$ = 1.6
7	^{t}Bu 1.26 (s) 1.23 (s)	Ph 6.90–7.30	2.89 q J_{15} = 2.3 J_{14} = 2.3 J_{13} = 2.3	5.04 ^{c}	2.81 (d.t) J_{43} = 2.7 J_{41} = 2.3 J_{45} = 2.3	3.98 (t) J_{51} = 2.3 J_{54} = 2.3	4.42 (d.t) $J_{6(9)-7(8)}$ = 2.8 $J_{6(9)-8(7)}$ = 1.6 $J_{6(9)-9(6)}$ = 1.6	3.87 (t.d) $J_{7(8)-6(9)}$ = 2.8 $J_{7(8)-8(7)}$ = 2.8 $J_{7(8)-9(6)}$ = 1.6	4.87 (t.d) $J_{8(7)-7(8)}$ = 2.8 $J_{8(7)-9(6)}$ = 2.8 $J_{8(7)-6(9)}$ = 1.6	5.04 $J_{9(6)-8(7)}$ = 2 8 $J_{9(6)-6(9)}$ = 1.6 $J_{9(6)-7(8)}$ = 1.6
8	SiMe$_3$ 0.40 (s) 0.37 (s)	H 2.03 (d.t) J(exo-endo) = 13.9 J(exo-1) = 2.0 J(exo-4) = 2.0	2.52 (d.d) J(1-exo) = 2.0 J(1-endo) = 2.3 J_{13} = 1 3	5 25 (d.d) J_{31} = 1.3 J_{34} = 2.7	2 79 (d.d.d) J(4-endo) = 2.3 J(4-exo) = 2.0 J_{43} = 2.7	2.88 (d.t) J(endo-exo) = 13.9 J(endo-1) = 2.3 J(endo-4) = 2 3	4.51 (d.t) $J_{6(9)-7(8)}$ = 2.5 $J_{6(9)-8(7)}$ = 1 4 $J_{6(9)-9(6)}$ = 1.4	4.06 (t d) $J_{7(8)-6(9)}$ = 2.4 $J_{7(8)-8(7)}$ = 2.4 $J_{7(8)-6(9)}$ = 1.4	4.82 (t.d) $J_{8(7)-7(8)}$ = 2.6 $J_{8(7)-9(6)}$ = 2.6 $J_{8(7)-6(9)}$ = 1.4	5.02 (d.t) $J_{9(6)-8(7)}$ = 2.6 $J_{9(6)-6(9)}$ = 1.4 $J_{9(6)-7(8)}$ = 1.4
9	SiMe$_3$ 0.39 (s) 0 35 (s)	Me 0.39 (d) J(5-CH$_3$) = 6.0	2.70 (m)	5.02 (d.d) J_{34} = 2.5 J_{31} = 1.3	2.98 t.d J_{43} = 2.5 J_{45} = 2.5 J_{41} = 1.8	2.85 (q.t) J(5-CH$_3$) = 6.0 J_{51} = 2.5 J_{54} = 2.5	4.54 (d.t) $J_{6(9)-7(8)}$ = 2.5 $J_{6(9)-8(7)}$ = 1.4 $J_{6(9)-9(6)}$ = 1.4	4.15 (t.d) $J_{7(8)-6(9)}$ = 2.5 $J_{7(8)-8(7)}$ = 2.5 $J_{7(8)-9(6)}$ = 1.4	4.89 (t.d) $J_{8(7)-7(8)}$ = 2.5 $J_{8(7)-9(6)}$ = 2.5 $J_{8(7)-6(9)}$ = 1.4	5.00 (d.t) $J_{9(6)-8(7)}$ = 2.5 $J_{9(6)-6(9)}$ = 1.4 $J_{9(6)-7(8)}$ = 1.4
10	SiMe$_3$ 0.39 (s) 0.35 (s)	Et 0.85–1.50	2.57–2.77 (m)	5.01 ^{c}		2.57–2.77 (m)	4.54 (d.t) $J_{6(9)-7(8)}$ = 2 5 $J_{6(9)-8(7)}$ = 1.4 $J_{6(9)-9(6)}$ = 1.4	4.17 (t.d) $J_{7(8)-6(9)}$ = 2.5 $J_{7(8)-8(7)}$ = 2.5 $J_{7(8)-9(6)}$ = 1.4	4.91 (t.d) $J_{8(7)-7(8)}$ = 2.5 $J_{8(7)-9(6)}$ = 2.5 $J_{8(7)-6(9)}$ = 1.4	5.01 (d t) $J_{9(6)-8(7)}$ = 2.5 $J_{9(6)-6(9)}$ = 1.4 $J_{9(6)-7(8)}$ = 1 4
11	SiMe$_3$ 0 35 (s) 0.41 (s)	Pr 0 60–1.30	2 75 (d.d.d) J_{15} = 2.5 J_{14} = 1.9 J_{13} = 1.4	5.04 (t.d) J_{34} = 2.6 J_{34} = 2.5 J_{31} = 1.4	3.04 (t.d) J_{43} = 2.5 J_{45} = 2.5 J_{41} = 1.9	2.82 (t.t) J(5-CH$_3$) = 6.5 J_{51} = 2.5 J_{54} = 2.5	4.56 (d.t) $J_{6(9)-7(8)}$ = 2 5 $J_{6(9)-8(7)}$ = 1.4 $J_{6(9)-9(6)}$ = 1.4	4.17 (t d) $J_{7(8)-6(9)}$ = 2.5 $J_{7(8)-8(7)}$ = 2.5 $J_{7(8)-9(6)}$ = 1.4	4.88 (t.d) $J_{8(7)-7(8)}$ = 2.5 $J_{8(7)-9(6)}$ = 2.5 $J_{8(7)-6(9)}$ = 1.4	5.01 (d.t) $J_{9(6)-8(7)}$ = 2.5 $J_{9(6)-6(9)}$ = 1.4 $J_{9(6)-7(8)}$ = 1.4
12	SiMe$_3$ 0.35 (s) 0.28 (s)	Ph 6.86–7.52 (m)	3.14 (d.d.d) J_{13} = 1.3 J_{15} = 2.5 J_{14} = 1.9	4.99 (d.d) J_{34} = 2.5 J_{31} = 1.3	2.82 (t.d) J_{34} = 2.5 J_{45} = 2.5 J_{41} = 1.9	4.05 (t) J_{51} = 2 5 J_{54} = 2.5	4.56 (d.t) $J_{6(9)-7(8)}$ = 2.5 $J_{6(9)-8(7)}$ = 1.4 $J_{6(9)-9(6)}$ = 1 4	4.17 (t.d) $J_{7(8)-6(9)}$ = 2.5 $J_{7(8)-8(7)}$ = 2.5 $J_{7(8)-9(6)}$ = 1.4	4.88 (t.d) $J_{8(7)-7(8)}$ = 2.5 $J_{8(7)-9(6)}$ = 2.5 $J_{8(7)-6(9)}$ = 1.4	5.01 (d t) $J_{9(6)-8(7)}$ = 2.5 $J_{9(6)-6(9)}$ = 1.4 $J_{9(6)-7(8)}$ = 1.4

[a] The signal is overlapped by impurity signals. [b] The assignment of the signals was done using selective double NMR. [c] The H(3) signal overlaps the H(9)(6) signal.

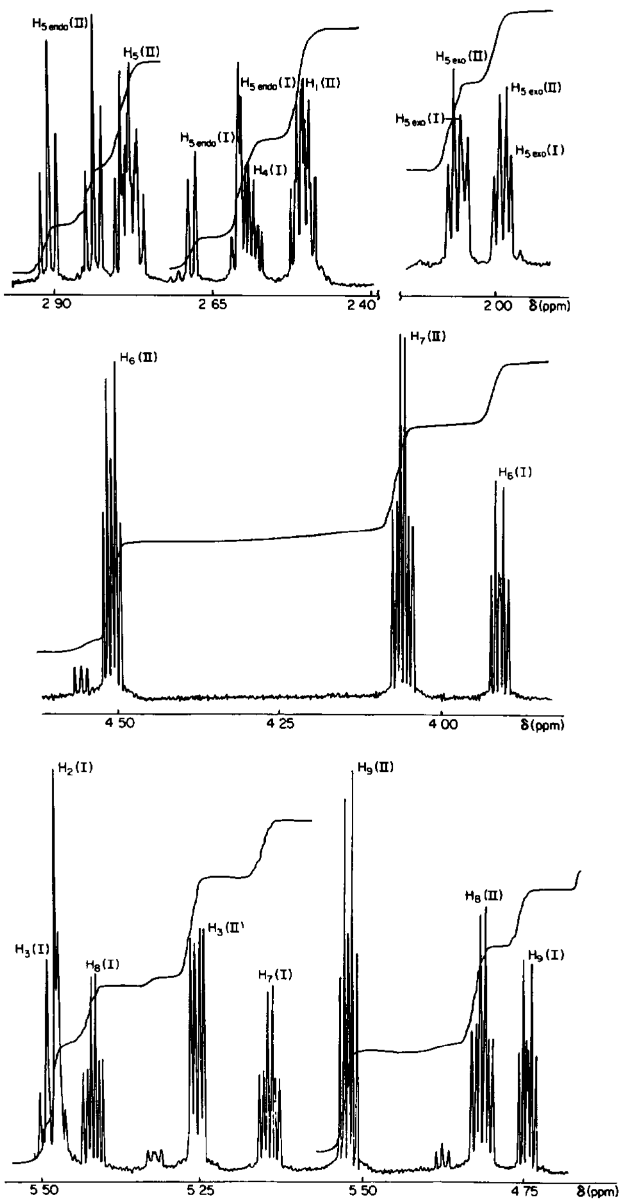


Fig. 1. ^{1}H NMR spectra of a mixture of the complexes (η^4-exo-5-H-1-SiMe$_3$-C$_5$H$_4$)(η^5-C$_5$H$_4$SiMe$_3$)Co and (η^4-exo-5-H-2-SiMe$_3$-C$_5$H$_4$)(η^5-C$_5$H$_4$SiMe$_3$)Co.

The signals were assigned to the H(1) protons of complexes **II** from the integral intensities of the signals of these protons and the multiplicity. The signal of the H(1) protons in most complexes **II** is characterized by an additional doublet-doublet splitting because of the spin–spin interaction with the H(5), H(3) and H(4) nuclei of the diene ring (Table 2). In most cases we succeeded in assigning the H(4) protons to each isomer by using the values of the proton integral intensities

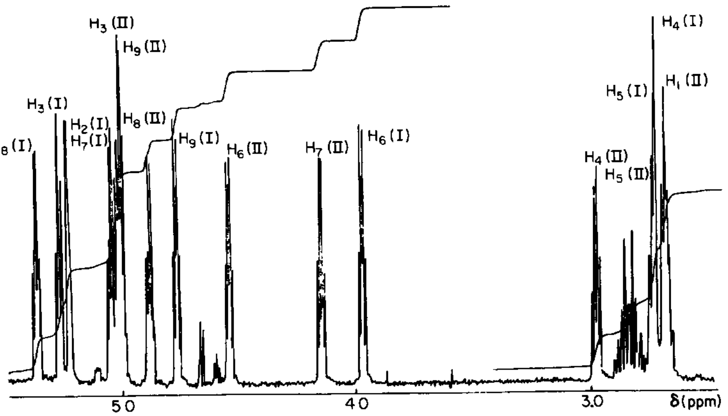


Fig. 2. ^{1}H NMR spectra of a mixture of the complexes (η^4-exo-5-Me-1-SiMe$_3$-C$_5$H$_4$)(η^5-C$_5$H$_4$SiMe$_3$)Co and (η^4-exo-5-Me-2-SiMe$_3$-C$_5$H$_4$)(η^5-C$_5$H$_4$SiMe$_3$)Co.

and the values of the constants of the spin–spin interaction with the neighbouring protons in the ring.

The molecular geometry of the complexes of types **I** and **II** has its stereochemical peculiarities. The cyclopentadiene ligand in the complexes is η^4-coordinated, the CHR fragment does not participate in the coordination and is brought out of the plane of the diene system beside the metal. With $R = R' = H$, the complex is prochiral. The availability of the R substituents in position 1(4) or 2(4) of the η^4-coordinated ligand leads to the disappearance of the symmetry plane turning **I** and **II** ($R \neq H$, $R' = H$) into chiral complexes. The planar chirality of the complexes remains when a substituent other than H is in the exo-position of the η^4-ligand. The presence of the R substituent in the η^5-cyclopentadienyl ligand is not of major importance, however, it allows identification of a chiral complex by the NMR method in the case of spectrally distinguished diastereotopic hydrogen atoms.

The analysis of the NMR signals of isomers **I** and **II** in the range of the substituted cyclopentadienyl ring indicates that for each isomer, the cyclopentadienyl ligand protons are inequivalent and are shown by four multiplets (Figs. 1 and 2). Thus, these complexes contain diastereotopic hydrogen atoms and possess planar chirality.

An important problem is the assignment of the signals of α-H (H(6), H(9)) and β-H (H(7), H(8)) hydrogen atoms of the RC$_5$H$_4$ ligand. The assignment was made on the base of the comparison of ^3J(H–H) and ^4J(H–H) values of complexes **I** and **II** with ^{1}H NMR spectra of 1,2- and 1,3-disubstituted ferrocenes [11,12] and 1,1,3,3-tetra-tert-butylcobalticinium [13]. The doublet–triplet splitting is characteristic of α-protons and β-protons show triplet–doublet splitting. The values of the spin–spin interaction constants are: J^4(H(6)–H(8)) = J^4(H(7)–H(9)) = J^4(H(6)–H(9)) = 1.4–1.7 Hz; ^3J(H(6)–H(7)) = ^3J(H(7)–H(8)) = ^3J(H(8)–H(9)) = 2.4–2.8 Hz (Tables 1 and 2). These signals were assigned to each isomer taking into account the integral intensities and their correlation with the quantity of each isomer in the mixture, and when necessary, the assignment was made using selective double NMR analysis.

Table 3

Average chemical shifts (ppm) of diastereotopic hydrogen atoms in ^{1}H NMR spectra of chiral complexes **I** and **II**

Substituents		Complex I		Complex II	
R	R′	H_α	H_β	H_α	H_β
Et	Me	4.50	4.55	4.76	4.45
Et	Pr	4.50	4.69	4.70	4.47
Et	Ph	4.57	4.54	4.66	4.44
^{t}Bu	H	4.37	5.00	4.75	4.32
^{t}Bu	Me	4.86	4.24	4.65	3.96
^{t}Bu	Pr	4.52	4.93	4.75	4.37
^{t}Bu	Ph			4.73	4.37
$SiMe_3$	H	4.33	5.28	4.76	4.44
$SiMe_3$	Me	4.36	5.20	4.77	4.52
$SiMe_3$	Et	4.38	5.22	4.77	4.54
$SiMe_3$	Pr	4.41	5.19	4.73	4.52
$SiMe_3$	Ph	4.41	5.19	4.73	4.52

Electron and steric influence of substituents in chiral complexes

The position of the signals of α-H (H(6), H(9)) and β-H (H(7), H(8)) diastereotopic hydrogen atoms in the RC_5H_4 ligand for all chiral complexes depends upon the R group nature and its position in the cyclopentadiene ligand and is not essentially influenced by the R′ substituent in the non-coordinated fragment. On discussing the changes in the chemical shifts of the α- and β-protons of the diastereotopic hydrogen atoms, the data from Tables 1 and 2 as well as the averages of the chemical shifts for each pair of diastereotopic nuclei (Table 3) were used.

For complexes **I**, the chemical shifts of the α-protons in the RC_5H_4 ligand are strongly dependent on the R substituent and change in the sequence $\delta(H_\alpha)$: ^{t}Bu > Et > $SiMe_3$. The inverse relation of the chemical shifts is observed for β-protons of the RC_5H_4-ring $\delta(H_\beta)$: $SiMe_3$ > Et > ^{t}Bu.

For complexes **I** with R = $SiMe_3$ the α-protons are observed in a stronger field than the β-protons. For R = Et, the chemical shift values of the α- and β-protons are made equal and with R = ^{t}Bu, an inverse relation is seen. The α-protons are observed in a weaker field compared to the β-protons.

In the case of complexes **II**, the position of the α-protons of the RC_5H_4 ligand depends slightly upon the R substituent. The chemical shift of the β-protons $\gamma(H_\beta)$ in the RC_5H_4 ligand, changes in the substituent series as follows: $SiMe_3$ > Et > ^{t}Bu. For all complexes **II** H_β protons are in a stronger field in comparison with H_α.

^{13}C NMR investigation of substituted derivatives of ferrocene and zirconocene showed that the substituents (R = Et, ^{t}Bu, $SiMe_3$) bring about a different degree of shielding of the carbon nuclei of the ring that is also associated with the different electron effect of the substituents [14–16]. The inductive effect +I of ^{t}Bu is much higher than that of the ethyl group. With the $SiMe_3$ substituent, together with the +I effect, a mesomeric effect (−M) in the opposite direction is observed which is caused by the interaction of 3*d* orbitals of the silicon atom with the π-system of the ring, the −M effect predominating over the +I effect.

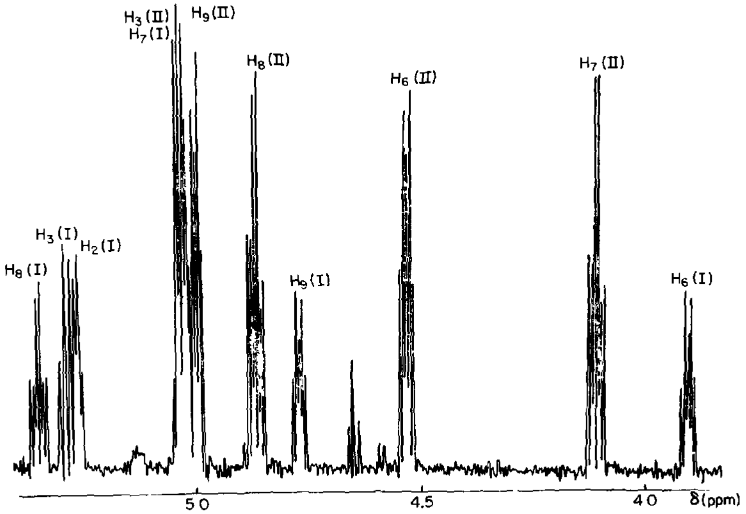


Fig. 3. Fragment of the ^1H NMR spectra of a mixture of the complexes $(\eta^4\text{-exo-5-Pr-1-SiMe}_3\text{-}C_5H_4)(\eta^5\text{-}C_5H_4SiMe_3)Co$ and $(\eta^4\text{-exo-5-Pr-2-SiMe}_3\text{-}C_5H_4)(\eta^5\text{-}C_5H_4SiMe_3)Co$.

An attempt was made to correlate the values of the chemical shifts of the α- and β-protons of the RC_5H_4-ring with the electron effects of the substituents. The averages of the chemical shifts of the nuclei of a ^{13}C atom bound with the R substituent in an aromatic ring were used to characterize the substituent electron

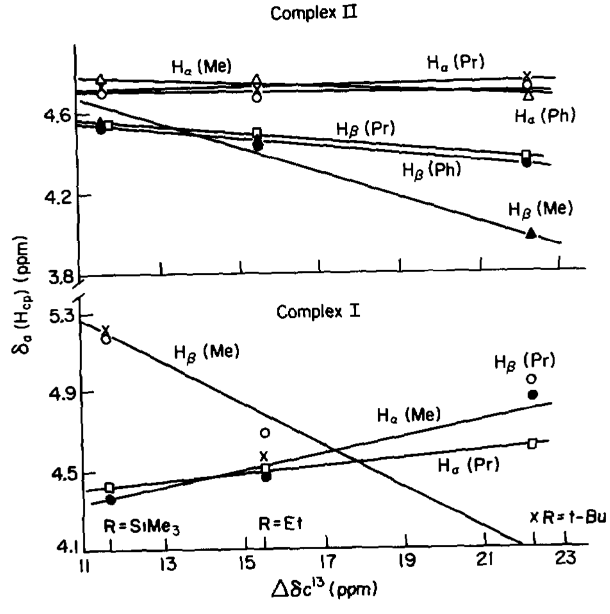


Fig. 4. Correlation of relationships between the values of average chemical shifts of α- and β-protons in the $C_5H_4R^-$ ligands ($\delta a(H_{Cp})$) and the values of the difference in chemical shifts of $^{13}C(I)$ atoms of C_6H_5R and the ^{13}C atom of C_6H_6 ($\Delta\delta^{13}C$).

Table 4

Values of difference in chemical shifts (ppm) of diastereotopic hydrogen atoms in ^1H NMR spectra of complexes **I** and **II**

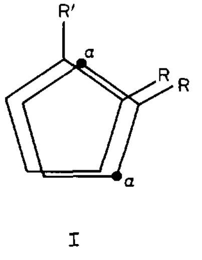
Substituents		Complex **I**		Complex **II**	
R	R′	H(9)(6)–H(6)(9)	H(8)(7)–H(7)(8)	H(9)(6)–H(6)(9)	H(8)(7)–H(7)(8)
Et	Me	0.37	0.14	0.18	0.16
Et	Pr	0.33	0.37	0	0.17
Et	Ph	0.55	0.16	0	0.17
^{t}Bu	H	4.37	5.00	4.75	4.32
^{t}Bu	Me	0.48	0.34	0.55	0.94
^{t}Bu	Pr	1.14	0.29	0.58	0.97
^{t}Bu	Ph			0.62	1.00
$SiMe_3$	H	4.33	5.28	4.76	4.44
$SiMe_3$	Me	0.80	0.32	0.46	0.74
$SiMe_3$	Et	0.76	0.32	0.47	0.74
$SiMe_3$	Pr	0.81	0.30	0.45	0.71
$SiMe_3$	Ph	0.81	0.30	0.45	0.71

effect. Correlation relationships are shown in Figs. 3 and 4. For many complexes **I** and **II**, the figures show the linear relationship between the averages of the chemical shifts of α- and β-protons in the RC_5H_4-ring and the chemical shift values of the nuclei of the ^{13}C atom bound with R in the aromatic ring. However, more complicated dependence of the chemical shifts for some complexes indicates that it is difficult to explain the change in the chemical shifts of α- and β-protons only in terms of the electron effects.

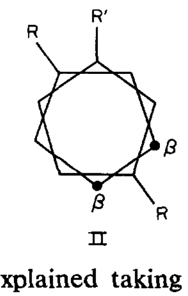
Table 4 presents the values of the difference in the chemical shifts ($\Delta\delta$) of the diastereotopic hydrogen atoms in the RC_5H_4 ligand of complexes **I** and **II**. The analysis showed that these values depend in a complicated manner upon the steric characteristics of the R substituent in the RC_5H_4 ligand and the R substituent position in a diene fragment of the η^4-coordinated ligand.

The influence of the R substituent in the diene ligand on the value of the difference in the chemical shifts of the diastereotopic hydrogen atoms of complexes **I** and **II** is of steric nature rather than electron.

In complexes **I**, the bulky ^{t}Bu and $SiMe_3$ substituents affect considerably the value of $\Delta\delta(H_\alpha)$, and in complexes **II**, the $\Delta\delta(H_\beta)$ value is affected by the Et substituent.



I



II

Such influence can be explained taking into consideration that each type of complex has its threshold of rotation of the cyclopentadienyl and cyclopentadiene

Table 5

Ratio of isomers **I** and **II** in reactions of nucleophilic (R'^-) and radical ($R'^{\cdot}$) addition

Reaction type	Substituents in complexes RR′											
	Et, Me	Et, Pr	Et, Ph	^{t}Bu, H	^{t}Bu, Me	^{t}Bu, Pr	^{t}Bu, Ph	$SiMe_3$, H	$SiMe_3$, Me	$SiMe_3$, Et	$SiMe_3$, Pr	$SiMe_3$, Ph
R'^-	0.82	0.75	1.0	2.1	5.6	3.0	Only **II**	1.5	0.9	1 3	2 1	5 0
$R'^{\cdot}$	1.3		1.5		5.2	10.0	Traces of **I**					

rings due to shielded (for complexes **I**) and hindered (for complexes **II**) conformation. The R′ substituent projects out of the plane of the diene ring in the opposite direction and, therefore, does not exercise a steric influence on the values of $\Delta\delta(H_\alpha)$ and (H_β).

Orientation effects in reactions of complex formation

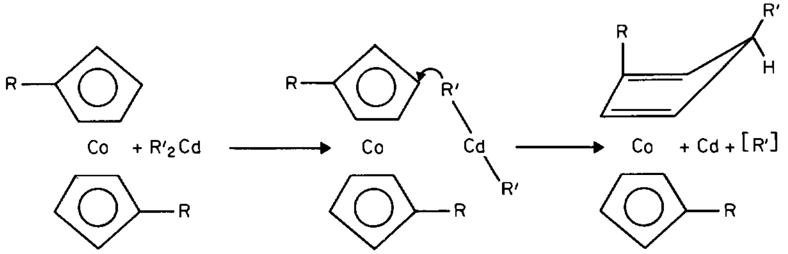
The quantitative data on the ratio of isomers **I** and **II** in the mixture were obtained from the results of NMR studies. The data in Table 5 point to the fact that the ratio of isomers **I** and **II** depends upon the R substituent in the cyclopentadienyl ligand, the R′ attacking group and the method of the substituent introduction.

In the radical substitution reaction proceeding on the interaction of $(C_5H_4R)_2Co$ with R'_2Cd, in the case of R groups of small volume (R = Et) isomer **II** prevails somewhat over isomer **I**. The increase in the steric volume of the substituent in the ring (R = ^{t}Bu) leads to the predominant formation of isomer **II**.

In the nucleophilic addition reaction, on interacting $(C_5H_4R)_2CoX$ (R = Et) with R′Li (R′ = Me, Pr) the main product is complex **I**. The amounts of isomers **I** and **II** become equal for R = Et, R′ = Pr. With R = ^{t}Bu, complex **II** is the main reaction product. The ratio of isomers **I** and **II** when R = $SiMe_3$ differs strongly from that with R = ^{t}Bu.

Comparison of the ratios of isomers **I** and **II** formed in the radical and nucleophilic addition reactions shows their substantial difference. To explain this fact, the mechanism of the introduction of the attacking group into the cyclopentadienyl ring should be considered.

As was established earlier [7], the interaction of cobaltocene with organocadmium compounds proceeds by the scheme:

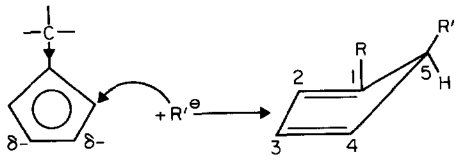


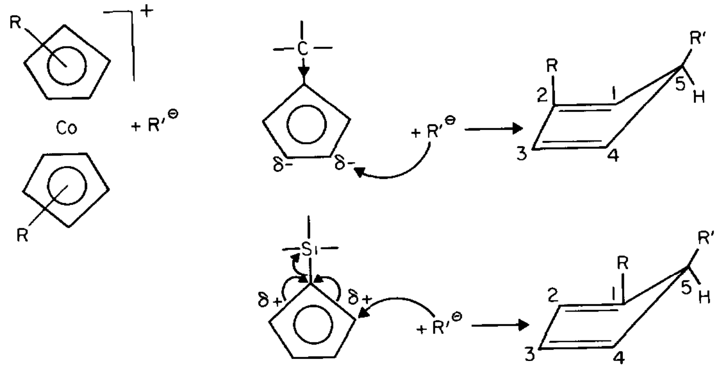
The process is accompanied by attack of the R′ radical into the cyclopentadienyl ring of cobaltocene, the orientation effects being determined by the steric effect of the substituent in the ring and the attacking group. Therefore, the formation of isomer **II** proves to be more preferential in all cases and the isomer ratio depends strongly upon the steric volume of the R and R′ groups.

On forming the cyclopentadiene complexes via the reaction of cobalticinium with R′Li a nucleophilic particle attacks the cyclopentadienyl ring with a lower electron density. When the substituent is available in the ring, the R′ group can be in position α or β. Position α proves to be sterically unfavourable compared with position β, particularly with bulky R and R′ groups. However, because of the introduction of an alkyl substituent with the positive inductive effect (+I) into the ring, position β becomes less preferable for the nucleophilic attack of R′.

For groups of small volume (R = Et, R′ = Me, Pr) isomer **I** is the main product of the nucleophilic addition. The increase of the steric volume of the R and R′ groups changes the isomer ratio in favour of isomer **II**.

In the case of the spatially bulky groups R and R′ (R = ${}^tBu$, R′ = Ph) the steric factor predominates over the electron one and the reaction results only in isomer **II**.





It is known that by the nature of the steric effect, the $SiMe_3$ and ${}^tBu$ groups are close. The steric hindrances, therefore, created by the $SiMe_3$ and ${}^tBu$ groups on the attack of the substituted cyclopentadienyl ring have to be approximately similar. But by the electron effect these groups are different. The inductive constant of the $SiMe_3$ group is known to be smaller than that of the ${}^tBu$ group. At the same time, the mesomeric effect (-M) of the group, due to the interaction of *d*-orbitals of the silicon atom with the π-system of the ring, gives rise to the gain in the orientation effect in the direction of isomer I formation due to the generation of a partly positive charge in positions 1 and 4.

Thus, in the nucleophilic addition reaction the orientation effect of the substituents is determined by the competition of the steric and electron factors.

Experimental details

All operations in the synthesis and purification of complexes **I** and **II** were performed under an argon atmosphere using oxygen-free solvents. Chromatography of complexes **I** and **II** was carried out on a column packed with Al_2O_3 of the first and second degree of activity according to Brockman. NMR spectra were recorded in a C_6D_6 solution on a Bruker WP-200 SY instrument with an operating frequency of 200.13 MHz.

Synthesis of complexes I and II by reaction of $(C_5H_4R)_2Co$ with R'_2Cd

An excess of R'_2Cd (R = Me, Pr) was added to $(C_5H_4R)_2Co$. The reaction mixture was kept at 20°C for 6 days. In the case of Ph_2Cd, the reaction was conducted in toluene (15 ml). After completing the reaction, an ampoule was evacuated at 30°C during 2 h; 15 ml of hexane was added to the reaction mixture. The metallic cadmium was separated by filtration and the filtrate was washed with water. An organic phase was evaporated to 2 ml and passed through the column packed with Al_2O_3, using hexane as eluent. After removing the solvent, the residue was chromatographed twice on the Al_2O_3 column. The eluent was pentane.

Synthesis of complexes I and II by reaction of $(C_5H_4R)_2CoX$ with R'Li

R'Li was added to $(C_5H_4R)_2CoX$ (X = BPh_4, PF_6) in 25 ml of THF at a temperature of −70 to −30°C. The reaction mixture was stirred for 30–60 min. The temperature of the reaction mixture was brought up to room temperature. At −20°C, 3 ml of H_2O was added. The organic phase was separated from the aqueous phase and the solvent was removed under a vacuum. The residue was twice passed through the chromatographic Al_2O_3 column. The eluent was pentane.

Synthesis of complexes I and II by reaction of $(C_5H_4R)_2CoX$ with $NaBH_4$

The compound $(C_5H_4R)_2CoX$ (X = BPh_4, PF_6) was added to $NaBH_4$ in 20 ml of THF. The reaction mixture was stirred for 40 min, then 30 ml of water was

Table 6

Experimental data for the synthesis complexes I and II

Initial reagents		Yield of complex I and II mixture	
		g	%
$(C_5H_4R)_2Co$ (g; mmol)	R_2Cd (g; mmol)		
$(C_5H_4Et)_2Co$ (0.72; 2.93)	Pr_2Cd (2.80; 13.7)	0.70	83
$(C_5H_4Et)_2Co$ (1.10; 4.49)	Ph_2Cd (2.30; 8.6)	0.87	60
$(C_5H_4{}^tBu)_2Co$ (0.35; 1.16)	Me_2Cd (1.60; 11.3)	0.29	79
$(C_5H_4{}^tBu)_2Co$ (0.28, 0.93)	Pr_2Cd (1.40, 7.1)	0.26	81
$(C_5H_4{}^tBu)_2Co$ (0.43; 1.43)	Ph_2Cd (2.51; 9.4)	0.38	70
$(C_5H_4R)_2CoX$ (g; mmol)	RLi (mmol)		
$(C_5H_4Et)_2CoBPh_4$ (0.33; 0.58)	MeLi (1.3)	0.05	33
$(C_5H_4Et)_2CoBPh_4$ (0.46; 0.82)	PrLi (2.0)	0.18	76
$(C_5H_4Et)_2CoBPh_4$ (0.30; 0.53)	PhLi (2.2)	0.10	58
$(C_5H_4{}^tBu)_2CoPF_6$ (0.37; 0.83)	MeLi (1.5)	0.16	61
$(C_5H_4{}^tBu)_2CoPF_6$ (0.37; 0.83)	PrLi (1.6)	0.27	95
$(C_5H_4{}^tBu)_2CoBPh_4$ (0.30; 0.48)	PhLi (2.2)	0.13	71
$(C_5H_4SiMe_3)_2CoBPh_4$ (0.40; 0.62)	MeLi (0.9)	0.12	56
$(C_5H_4SiMe_3)_2CoBPh_4$ (0.28; 0.43)	EtLi (3.9)	0.12	84
$(C_5H_4SiMe_3)_2CoBPh_4$ (0.44; 0.68)	PrLi (1.0)	0.16	67
$(C_5H_4SiMe_3)_2CoBPh_4$ (0.30; 0.46)	PhLi (1.8)	0.09	50
$(C_5H_4R)_2CoX$ (g; mmol)	$NaBH_4$ (g)		
$(C_5H_4{}^tBu)_2CoPF_6$ (0.48; 1.07)	$NaBH_4$ (0.70)	0.23	71
$(C_5H_3SiMe_3)_2CoBPh_4$ (0.37; 0.57)	$NaBH_4$ (0.60)	0.14	80

added at 0°C and stirred for another 30 min. The organic layer was separated from the aqueous phase, the solvent was removed *in vacuo* and the residue was twice passed through the chromatographic Al_2O_3 column. The eluent was pentane.

The experimental ratios of the reagents and the yields of the complex **I** and **II** mixture are shown in Table 6.

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