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A CORRELATION BETWEEN ^{13}C AND ^{59}Co NMR DATA AND THE CATALYTIC ACTIVITY OF ORGANOCOBALT COMPLEXES IN THE SYNTHESIS OF PYRIDINE DERIVATIVES *

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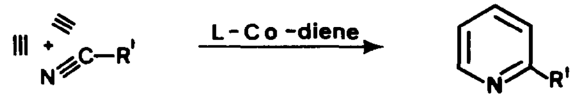
Summary

The correlation between the ^{13}C and ^{59}Co NMR spectra of substituted cyclopentadienylcobalt complexes and their catalytic properties in the synthesis of pyridine derivatives is examined. Since the correlations can be expressed as linear relationships, a direct screening of potential catalysts by NMR is possible.

1. Introduction

Following the discovery of the cobalt-catalysed synthesis of pyridines from alkynes and nitriles, further studies were undertaken in Mülheim aimed at developing highly efficient phosphine-free organocobalt(I) catalysts suitable for the preparative application of eq. 1 [1].



(1)

(L = η^3- allyl, η^5- cyclopentadienyl)

There are basically two types of catalyst for reaction 1 (see Fig. 1): (1) Allylcobalt compounds, in which a η^3-allyl group remains bonded to the metal during the

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* Dedicated to Prof. S. Otsuka on the occasion of his 65th birthday.

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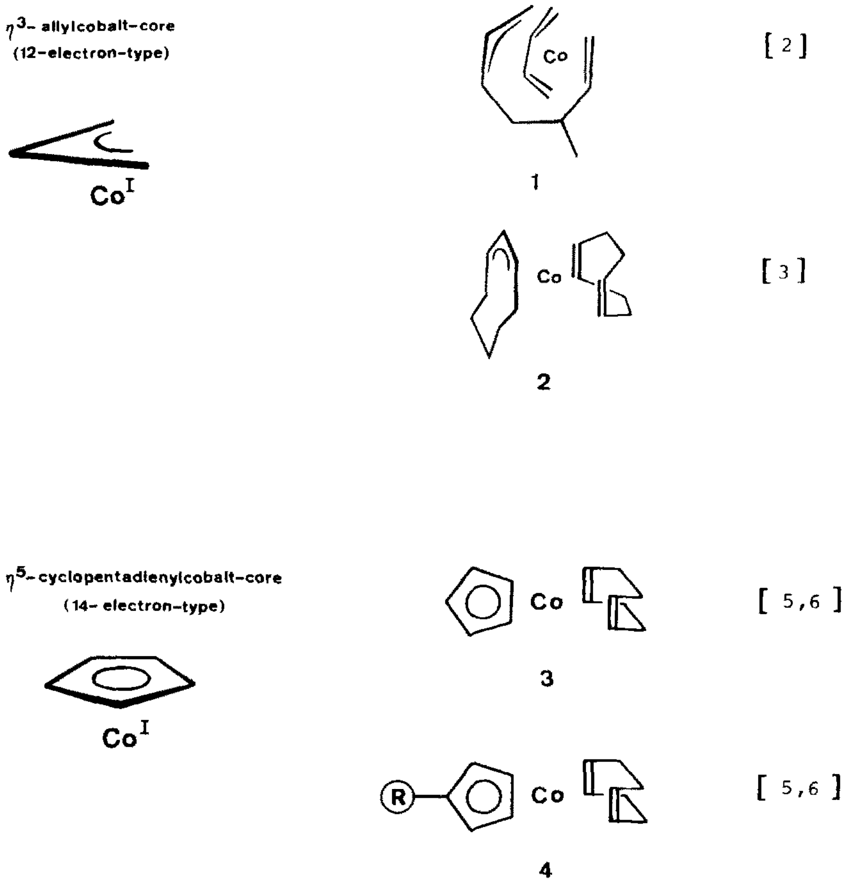


Fig. 1. Catalytically active organocobalt systems. ® = substituent.

catalytic cycle, and (2) η^5-cyclopentadienylcobalt half-sandwich compounds with different substituents R in the cyclopentadienyl ring.

5-Methylheptadienylbutadienecobalt (**1**) was first reported in 1965 by Natta, Pino and co-workers [2] and cyclooctenyl/cyclooctadienecobalt complexes were first prepared by Wilke and Grard in 1967 [3a]. Otsuka and co-workers described the preparation of the η^3-cyclooctenylcobalt complex **2** from $CoCl_2$, cyclooctadiene (COD) and sodium metal and determined its X-ray structure [3b,3c]. An electrochemical synthesis [3d] has also been published and we have developed a one-pot procedure for the production of pure **2** in 70% yield (see exp. part). In our laboratory **2** is now known as "Otsuka's complex". Since the Cp-Co-14-electron moiety is thermally and chemically relatively stable [4], we have developed several new syntheses for substituted R-Cp-Co(diolefin) complexes [5,6].

A particularly significant observation for the cobalt-catalyzed pyridine synthesis (eq. 1) was that the activity and selectivity of the LCo(diene) systems could be altered by changing the organic residue L (ligand control) [7].

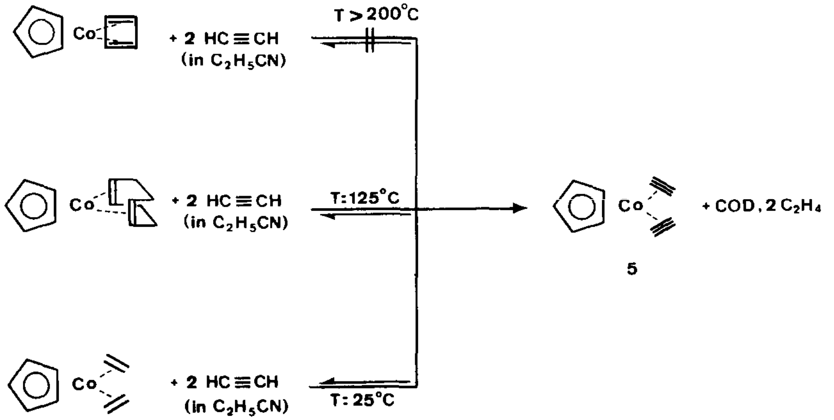
The availability of this series of closely related catalytically active complexes prompted us to seek correlations between their NMR data and their catalytic properties. Factors such as the strength of metal-substrate interaction and electron density on the metal may be expected to play a major role in both their spectroscopic and chemical properties.

2. Catalysis

Influence of the stabilizing diolefin ligand upon catalysis

The ease with which the initial dissociation of the diolefin (eq. 2) takes place, giving the propagating catalytic species **5**, depends strongly upon the nature of the stabilizing moiety [8]. In the Cp-Co series, the complexes of COD, cyclopentadiene or related diolefins all lead to the formation of catalysts active between 100 and 150 °C. Although the bis-ethylene compound [9] readily loses ethylene at 25 °C to give the propagating Cp-Co species **5**, this reaction is accompanied by some decomposition. We have therefore employed COD complexes because the diolefin dissociates at moderate temperatures without noticeable decomposition of the catalyst. Since the η^4-cyclobutadiene ligand does not dissociate from the cobalt even at 200 °C, this compound shows no catalytic activity.

Once initiated, the catalysis is independent of the olefin originally employed but is dependent upon the R-Cp ligand, which remains complexed to the cobalt. Temperatures of 100–250 °C are required to obtain reasonable turnover numbers. Typical examples are shown in eq. 2.



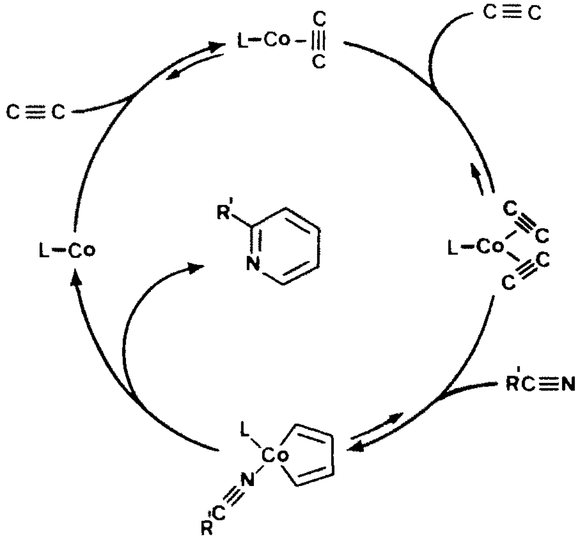
(2)

Extensive studies on Rh(diene)(cyclopentadienyl) [10] and Fe(CO)$_3$(diene) complexes [11] in the Zürich group have shown that the ^{103}Rh and ^{57}Fe resonances are very sensitive to the geometry of the olefinic ligands. This indicates that stereoelectronic effects in the p_π–d_π bonds, which showed to affect the stabilizing influence of the diolefin ligand, are also important for the chemical shift of the metal in these series.

Blockage of the central metal by cyclobutadiene is reflected in the exceptionally high shielding of the ^{59}Co nucleus in this complex (-2888 ppm). The chemical shift range of Cp-Co(diene)-16-electron complexes investigated in the Zürich laboratory [12] extends from -602 ppm Co(η^4-COD)(η^5-Cp) to -1880 ppm Co(η^4-cyclohexa-1,3-diene)(η^5-Cp) relative to K$_3$Co(CN)$_6$. The cyclobutadiene complex is thus about 1000 ppm more shielded. An analogous behaviour was found for cyclobutadienecyclopentadienylrhodium and (cyclobutadiene)dicarbonyliron, which are also very stable and whose metal resonances are also observed towards the high-field limit of the corresponding chemical shift ranges for complexed dienes [10,11]. Since metal shielding in the Fe, Co and Rh series decreases with increasing size of the ring incorporating the 1,3-diene and reaches a minimum for Co and Rh complexes with 1,5-diene systems, it can be concluded that the efficient p_π–d_π overlap leads to high shielding in the chemically stable cyclobutadiene complexes. Conversely, low shielding of the metal should correlate with decreasing stability and ease of activation of the complex.

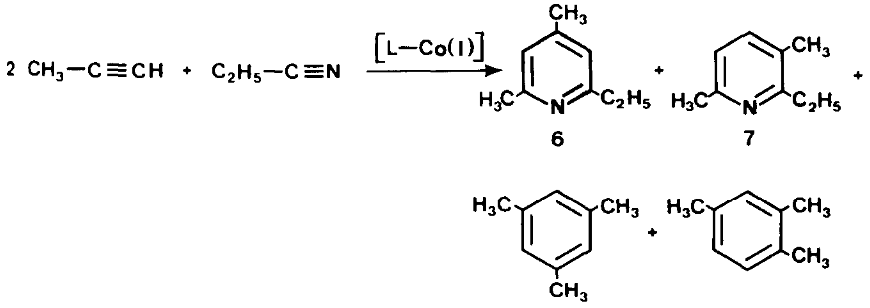
Influence of the ligand L upon the catalysis

(a) Activity. The activity of the L-Co catalysts is strongly dependent upon the nature of the ligand L, enabling the cobalt catalysts to be optimized for technical applications [13]. The turnover number at a given temperature can be regarded as a measure of the activity of any given complex (eq. 3). However, the complexes investigated have widely differing thermal stabilities and some decompose at temperatures at which others are not even active. We therefore used a continuous flow reactor to compare the activities of the catalysts measuring the temperature at which a particular turnover value is reached: the lower this temperature, the more active the catalyst under consideration.



(3)

The apparatus [14] that was used to determine the composition of the product mixture formed at a constant turnover rate is described in the experimental section. Since the external reaction conditions and the temperature and contact time are controlled precisely, kinetic effects can be eliminated, and the product distribution can be used to derive information about the properties of the catalyst. The reaction studied was that of propyne with propionitrile in the presence of L-Co systems. The extent of conversion of propyne, the concentrations of catalyst, alkyne and nitrile in the educt and the average contact time were carefully monitored for each experiment (eq. 4). The influence of the η^3-allyl or η^5-Cp ligands can be seen in Table 1; further results are given in Table 2.



(4)

Standard conditions

Propyne conversion	:	65%		
Mean reaction time	:	82	min	
Catalyst concentration	:	4	mmoles/l	Educt-solution
Propyne concentration	:	262	g/l	"
Propionitrile concentration	:	214	g/l	"
Toluene	:	345	g/l	"

(b) Chemical selectivity. The choice of L has a decisive effect upon the chemical selectivity of the catalyst. As can be seen from Table 1, the η^3-allyl cobalt catalyst **2** gave carbocycles as the major product under standard conditions whereas the Cp-Co catalyst **3** produced mostly pyridine derivatives. This result indicates that the ligand L does indeed remain bonded to the cobalt atom during the catalytic cycle. In the standard conditions defined in eq. 4, the chemical selectivity of the L-Co catalyst in question is given by the molar ratio of hetero- to carbo-cyclic products.

(c) Regioselectivity. The regioselectivity of the catalysts in the reaction of mono-substituted alkynes is also dependent upon the organic residue L attached to the cobalt atom (eq. 5).

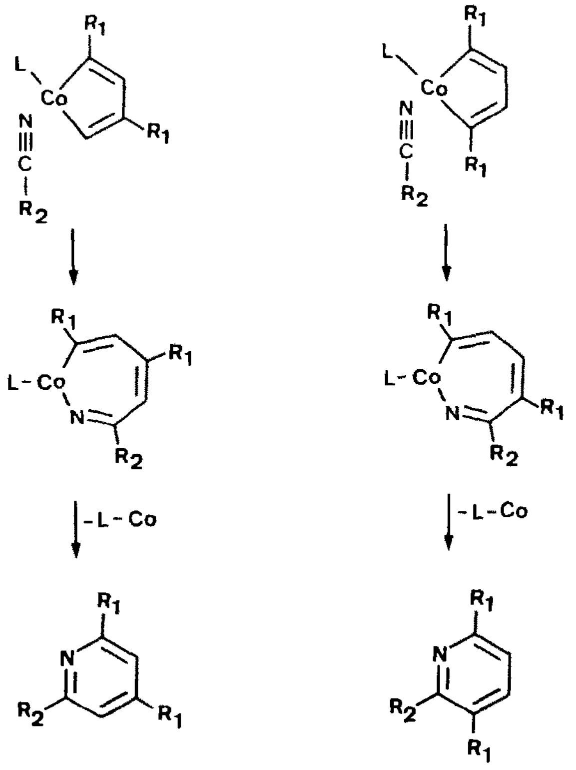
Symmetrically- or unsymmetrically-substituted pyridine derivatives are formed by either head-to-tail coupling or tail-to-tail coupling of the monosubstituted alkynes at the transition metal. The regioselectivity is defined as the molar ratio **6**/**7** in the product mixture obtained under the standard conditions in eq. 4.

3. NMR

(a) ^{13}C NMR

Measurement of the ^{13}C NMR spectra showed that considerable changes are observed in the chemical shift of the olefinic –CH= carbons in the COD complexed to cobalt on changing the substituent R on the cyclopentadienyl ring (see Table 2). In all cases, the olefin resonance is shifted to lower field in the derivatives relative to the unsubstituted Co(η^4-COD)(η^5-Cp).

The chemical shifts of the methyl-substituted derivatives are proportional to the



2,4,6-isomer 2,3,6-isomer

6 **7**

(5)

number of methyl groups, i.e., the chemical shift relative to the simplest compound of the series, Cp-Co-COD ($\delta_{rel}(^{13}C)$) for a single methyl substituent **10** is approximately a fifth of that for the pentamethyl derivative **8**, while **9**, which is analogous to a dimethyl-substituted Co(η^4-COD)(η^5-Cp), has a value of $\delta_{rel}(^{13}C)$ approximately double that of the mono-methyl compound **10**.

TABLE 1

REGIOSELECTIVITY AND ACTIVITY UNDER STANDARD CONDITIONS

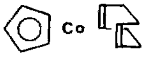
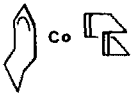
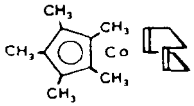
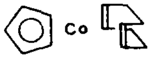
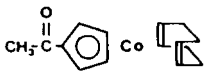
catalyst	(**6**) : (**7**) ratio	T
	1.71	147°
	2.32	130°

TABLE 2

^{13}C CHEMICAL SHIFTS OF THE OLEFINIC CARBON ATOMS OF COMPLEXED COD IN R-Cp-Co-COD AND REGIOSELECTIVITY AND ACTIVITY OF THE CATALYSTS UNDER STANDARD CONDITIONS

(δ_{rel} (^{13}C) = $\delta_{R\text{-}Cp\text{-}Co\text{-}cod} - \delta_{Cp\text{-}Co\text{-}cod}$; T = reaction temperature for 65% propyne conversion)

No.	Complex	δ [ppm]	δ_{rel} [ppm]	(6):(7) ratio	T
8		70.53	+ 7.2	3.51	220°
9		66.50	+ 3.1	2.50	180°
10		64.73	+ 1.4	2.02	162°
3		63.37	0	1.71	147°
11		63.45	+ 0.1	1.77	152°
12		63.95	+ 0.6	1.67	144°
13		66.09	+ 2.7	1.73	140°
14		68.33	+ 5.0	1.46	123°
	TMS	0			

A direct influence of the substituents R upon the COD resonances, similar to the γ-substituent effect in alkenes, can be disregarded since substitution produces a downfield shift. It is perhaps surprising that the t-butyl group has no significant influence upon the ^{13}C resonance of the complexed COD. This is reminiscent of the observation by Davies, Barker and Fisher [15] who studied the ESR of substituted

Cp radicals, and observed that the t-butyl group had practically no influence in comparison with a methyl group. Nesmeyanov and co-workers have reported that for monosubstituted ferrocene derivatives, not only is the proton NMR shift of the unsubstituted ring influenced by substituents on the other [16], but that the shift changes are dependent upon the type of alkyl substituent: a methyl group produces a large change in shift compared to that of the unsubstituted ferrocene, while a t-butyl group produces almost none.

(b) ^{59}Co NMR

Whereas the ^{13}C NMR shows the influence of the substituents on the η^5-Cp ring upon the complexed olefin, the ^{59}Co NMR data allow the changes at the metal centre to be followed. The ^{59}Co chemical shift of eight Co(η^5-R-Cp) half sandwich compounds are given in Table 3. The ^{59}Co shifts relative to Co(η^4-COD)(η^5-Cp) can be taken as a measure of the substituent influence.

In contrast to the ^{13}C NMR results, the ^{59}Co resonances may lie to lower or higher field than Co(η^4-COD)(η^5-Cp). The values of $\delta_{rel}(^{59}Co)$ correlate with the electronic properties of the substituents: alkyl groups act as electron donors and a greater shielding of the metal centre is observed while electron-withdrawing groups such as phenyl or acetyl cause reduced shielding. As observed with the ^{13}C chemical shifts, the ^{59}Co chemical shifts for the alkyl-substituted derivatives are additive and $\delta_{rel}(^{59}Co)$ for the pentamethylcyclopentadienyl compound is approximately five times that of the monomethyl-Cp-Co-COD **10**, while the dialkyl derivative **9** has approximately double this value. The substituent effect of the t-butyl group in **11** ($\delta_{rel}(^{59}Co)$ 10 ppm) is again negligible.

(c) Correlation between ^{13}C and ^{59}Co NMR data and catalytic effect

If the values of $\delta_{rel}(^{13}C)$ are plotted against the isomer ratio **6**/**7**, for R = alkyl a nearly linear relationship is found. A similar result is found if the reaction temperature for the catalytic conversion of 65% of the propyne is plotted against $\delta_{rel}(^{13}C)$. However, a correlation is found only among compounds having chemically related substituents.

For the ^{59}Co chemical shifts, a regular variation of $\delta_{rel}(^{59}Co)$ as a function of the substituent is observed. For all Cp-Co complexes, a nearly linear relationship is found between $\delta_{rel}(^{59}Co)$ and the regioselectivity as given by the isomer fraction of **6** or **7** (Fig. 2).

The pentamethyl-substituted compound **8** produces mainly the symmetrical isomer **6**, while the acetyl-substituted Co(η^4-COD)(η^5-Cp) catalyst produces the largest amount of the unsymmetrical isomer **7** and the isomer yield obeys the following relationships:

$$\mathbf{6}: c_{sym}(\%) = 65.24 - 0.05 \cdot \delta_{rel}(^{59}Co) \tag{6}$$

$$\mathbf{7}: c_{unsym}(\%) = 34.76 + 0.05 \cdot \delta_{rel}(^{59}Co) \tag{7}$$

where $\delta_{rel}(^{59}Co) = \delta_{R\text{-}Cp\text{-}Co\text{-}COD} - \delta_{Cp\text{-}Co\text{-}COD}$

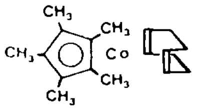
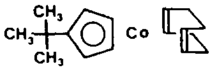
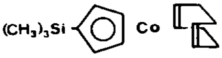
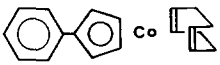
(Significance level 95%, Fisher Test)

The more negative the value of $\delta_{rel}(^{59}Co)$, the greater the fraction of the symmetrical derivative **6** in the product. Each additional alkyl substituent increases

TABLE 3

^{59}CO CHEMICAL SHIFTS IN η^5-R-Cp-Co-COD COMPOUNDS (in toluene-d_8, 23°C)

($\delta_{rel}(^{59}Co) = \delta_{R\text{-}Cp\text{-}Co\text{-}cod} - \delta_{Cp\text{-}Co\text{-}cod}$)

No.	Complex	δ [ppm]	δ_{rel} [ppm]
8		- 1413	- 237
9		- 1261	- 85
10		- 1227	- 51
3		- 1176	0
11		- 1166	+ 10
12		- 1149	+ 27
13		- 1088	+ 88
14		- 1055	+ 121
	$K_3Co(CN)_6$	0	

the temperature required for 65% conversion of propyne by ca. 15°C. In Fig. 3, a plot of the reaction temperatures against $\delta_{rel}(^{59}Co)$ is shown. Again a nearly linear relation for all eight cases is observed.

Those systems for which the ^{59}Co resonance lies to higher field (i.e., $\delta_{rel}(^{59}Co)$ is negative) are less active than Co(η^4-COD)(η^5-Cp), while those for which the resonance lies to lower field ($\delta_{rel}(^{59}Co)$ positive) are catalytically more active. The linear

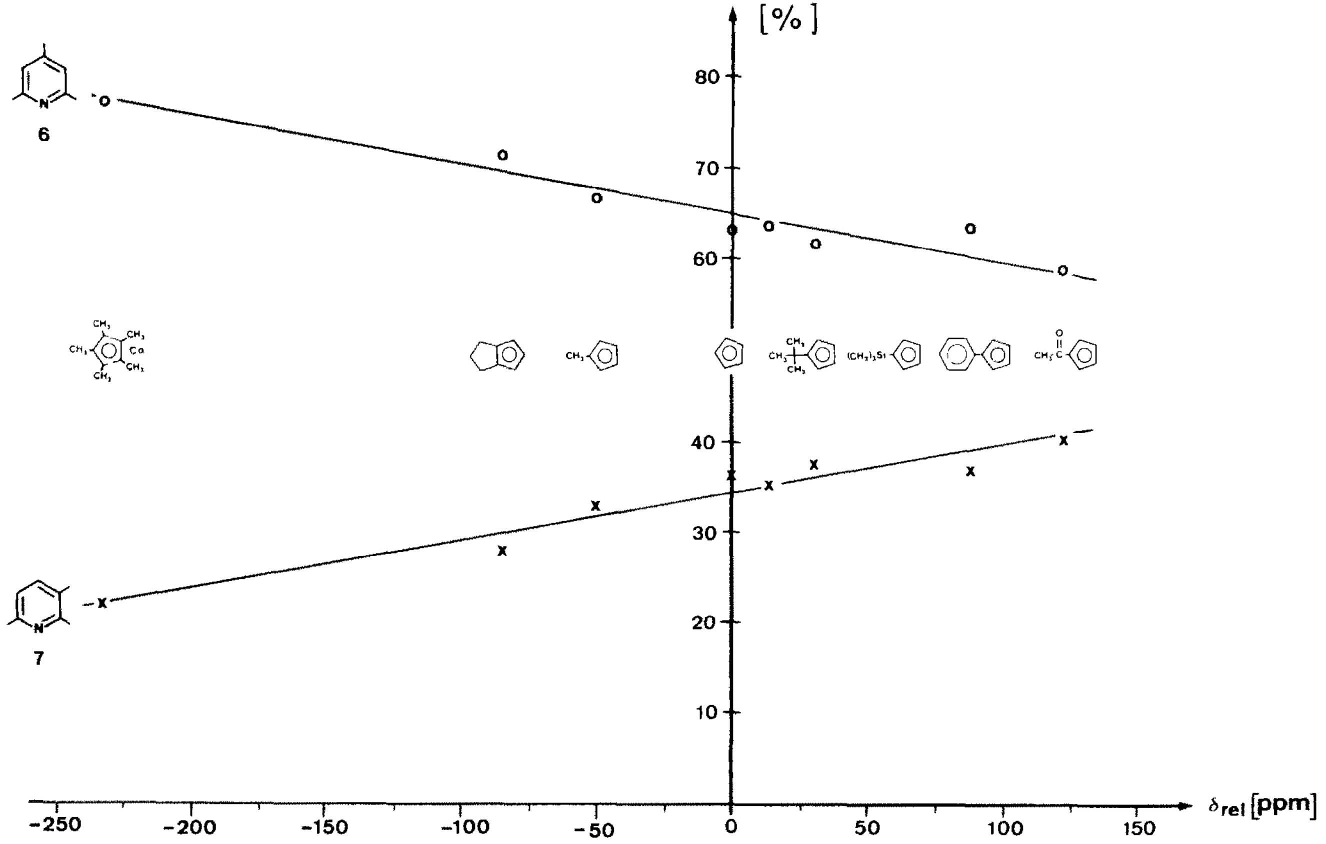


Fig. 2. Regioselectivity of R-Cp-Co catalysts under standard conditions as a function of the ^{59}Co chemical shift.

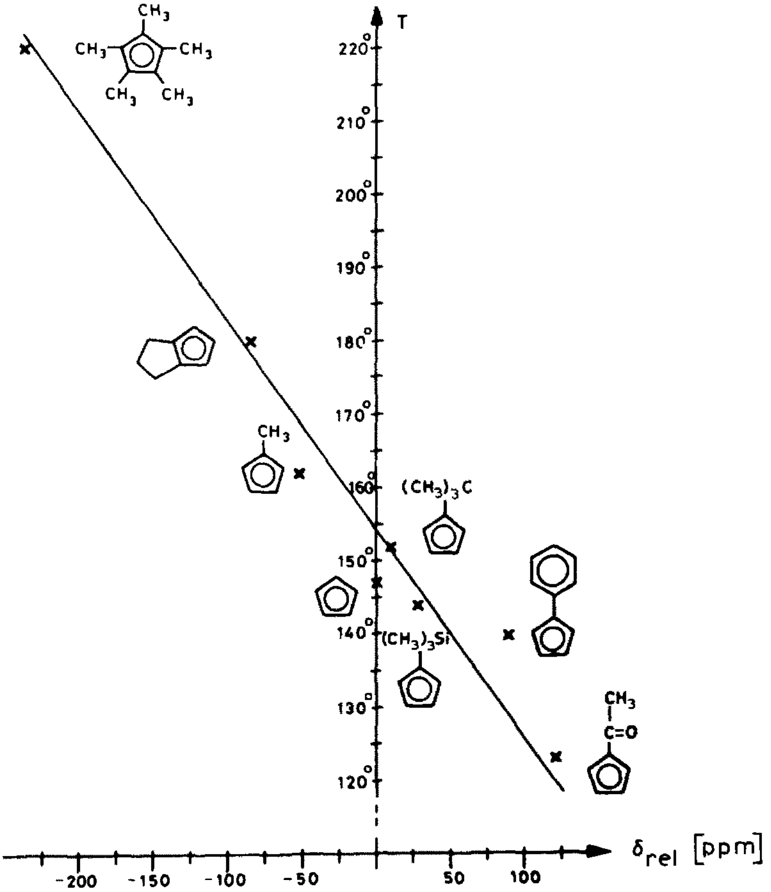


Fig. 3. Reaction temperature under standard conditions as a function of the ^{59}Co chemical shift.

relationship between the reaction temperature T, and $\delta_{\mathrm{rel}}(^{59}\mathrm{Co})$ is described by the regression equation (eq. 8). Thus those complexes with the largest (positive) $\delta_{\mathrm{rel}}(^{59}\mathrm{Co})$

$$T\,(\mathrm{K}) = 427.4 - 0.28 \cdot \delta_{\mathrm{rel}}(^{59}\mathrm{Co}) \tag{8}$$

are the most active.

Discussion

The influence of various substituted cyclopentadienyl groups on the metal and the substrate in the catalytic intermediates cannot be investigated directly by NMR. However, while the Co(η^4-COD)(η^5-Cp) complexes are not the actual catalytically active species, they can be taken as model compounds. It is reasonable to expect that the influence of Cp-residues upon the metal and upon the metal-substrate interaction in the intermediates will be similar to that upon the metal and the metal–COD bonding in the corresponding Co(η^4-COD)(η^5-Cp) complexes.

Since the olefinic carbon atoms are well separated from the substituents (R) on the Cp ring, and the olefin itself is not varied within the series, the ^{13}C chemical shift of the COD olefinic carbon might be expected to reflect changes in electron density in the COD double bond, as well as in the bond orders and electronic excitation energies. The first two factors will play a major role in the catalysis and this first suggested to us that there may be a correlation between the catalytic properties of the complexes and the NMR data obtained from the COD ligand. The experiments described show that while the ^{13}C NMR shift for the alkyl-substituted compound do correlate with the catalytic properties, this breaks down with other substituents.

Similar considerations apply to the metal centre. In this case, however, a good correlation between the ^{59}Co chemical shift and the catalytic properties is found for all the substituents investigated.

The regression equations 6, 7 and 8 are valid only for the substituted Co(η^5-R-Cp) catalysts. However, catalysts containing other organic ligands such as the η^3-allyl, η^5-indenyl or η^6-borinato systems can be expected to show similar relationships.

The greater shielding of the cobalt in the alkyl-substituted complexes suggests that there is an increase in the electron density at the metal; it is accompanied by a reduction in the activity of the Co(η^4-COD)(η^5-Cp) system in the test-reaction (eq. 4). Electron-withdrawing substituents, in contrast, which should cause a reduction in the electron density at the cobalt, reduce the shielding of the ^{59}Co nucleus, and lead to increased catalytic activity.

In view of the subtile interrelationships between the electronic structure of these complexes and the complexation of the substrates, their coupling and displacement, we have not attempted to give a detailed explanation for the observed correlations, but this does not detract from their empirical value.

The experiments described here show that there is a good correlation between the ^{59}Co spectra of Co(η^5-R-Cp) complexes for a particular series and their catalytic properties in the synthesis of pyridine. The nuclear magnetic resonance of transition metal nuclei appears to be particularly suitable for such studies, because of their large chemical shift ranges and great sensitivity to substitution. It is anticipated that NMR will find wider application in the future for the direct screening of potential catalysts.

Experimental

Preparation of complexes

All experiments were carried out under argon using carefully dried solvents and starting materials.

Co(η^4-COD)(η^5-bicyclo[3.3.0]octadienyl) (**9**) was prepared according to the procedure given by Lehmkuhl et al. [3d]. Since no details of the preparation of Natta's complex **1** have been published in ref. 2, we have included a description below. Otsuka's complex **2** is obtained in yields as high as 70% from Co(acac)$_3$, COD and triethylaluminium. The reduction of cobalt salts by organoaluminium compounds in the presence of the corresponding olefins was also used for the preparation of Co(η^4-COD)(η^5-Cp) (**3**) and the substituted compound **12**. "Organically solvated" magnesium [17] was used to prepare **10**, **11** and Co(η^5-C_6H_5-Cp)$_2$, which was subsequently treated with lithium metal to give **13** analogous to data in ref. 9, 18. The pentamethyl- (**8**) and the acetyl-Cp-Co-COD derivatives **14** were obtained from the corresponding dicarbonyl compounds by irradiation in an excess of COD.

(η^4-Butadiene)($\eta^{2,3}$-5-methylheptadienyl)cobalt (1). Anhydrous $CoCl_2$ (65 g, 0.5

mol) is suspended at −30 °C under argon in 1.5 l liquid butadiene in a 4 l three-necked flask. 500 ml dry ethanol are added from a dropping funnel over 15 min. The resulting dark blue suspension is stirred rapidly at −30 °C and a freshly prepared solution of $NaBH_4$ (38 g, 1 mol) in 1.5 l dry ethanol is added over 4 h. During the reaction gas is evolved and the colour changes first to pink, then to greenish-grey and finally becomes brown. Stirring is continued for 2–3 h and the mixture is then allowed to stand for 15 h at −30 °C. The supernatant liquid is carefully separated from the precipitate (NaCl), concentrated under high vacuum at −80 to −30 °C during which part of the red-brown product usually begins to precipitate. Crystallization is completed at −90 to −100 °C and the crude product is collected and washed with dry pentane (4 × 100 ml). The resulting red-brown crystals of **1** are dried at −30 °C under high vacuum. Yield: 77.7 g of **1** (350 mmol; 70% theory). The compound is air sensitive, decomposes at about −30 °C and should be stored at −80 °C.

(η^4-Cyclooctadiene)(η^3-cyclooctenyl)cobalt (2). Cobalt(III) acetylacetonate (112 g, 0.31 mol), COD (123 g, 1.1 mol) (dried over $NaAlEt_4$) and 1 l of pentane are vigorously stirred in a 2 l three-necked flask under argon. The resulting green suspension is cooled at 0 to −5 °C and triethylaluminium (107 g, 0.94 mol) is added from a dropping funnel over 45 min. After 10% of the reducing agent has been added, the colour changes to brown and vigorous gas evolution is observed. At the end of the addition a dark brown solution is obtained which is stirred for a further 2.5 h at +20 °C. $Al(acac)_3$, unreacted $Co(acac)_3$ and a brown residue are removed by filtration through a glass-frit. The clear filtrate is held at −30 °C for 14–16 h which causes small, colourless crystals of $Al(acac)_3$ to precipitate and these are filtered off at −30 °C. Cooling the solution over 2 h to −65 °C causes the product to crystallize (if necessary this can be initiated by scratching or by seeding with a dry crystal). Temperatures below −65 °C cause the co-precipitation of $Et_2Al(acac)$ and should be avoided. The supernatant liquid is filtered off and the product washed at −65 to −70 °C (3 × 150 ml pentane). The brown-black crystals of **2** obtained after drying for 3.5 h at +20 °C in high vacuum are analytically pure. Yield: 59.8 g of **2** (216.7 mmol, 69.9% theory).

(η^4-Cyclooctadiene)(η^5-cyclopentadienyl)cobalt (3). A mixture of cyclopentadiene (6.8 g, 103 mmol), COD (27 g, 250 mmol) and triethylaluminium (42.2 g, 370 mmol) in 200 ml pentane is vigorously stirred under argon at 0 to −10 °C. Cobalt(III) acetylacetonate (35.6 g, 100 mmol) is added in small portions. A vigorous gas evolution occurs. After the addition of the cobalt salt, the mixture is allowed to warm up to room temperature over 2 h and is then filtered through a glass frit and the filtrate cooled to −50 °C. The orange-brown product crystallizes out in about 16 h. The supernatant liquid is removed, and the crystals washed with pentane (2 × 50 ml) at −50 °C and dried under vacuum. Yield: 17.8 g of **3** (76.7 mmol, 76.7% theory).

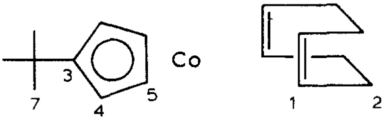
(η^4-Cyclooctadienyl)(trimethylsilyl-η^5-cyclopentadienyl)cobalt (12). The application of the one-pot reduction by triethylaluminium used for **3** (see above) gave the following results: Starting materials: $Co(acac)_3$ 33.5 g (94.0 mmol), pentane 200 ml, COD 22.9 g (212.0 mmol), 1-Me_3SiCpH 13.0 g (94.0 mmol), and $AlEt_3$ 34.0 g (298.0 mmol). Yield: 12.2 g of **12** (40.1 mmol, 42.7% theory) m.p. 64–66 °C. For characterization of **12** see Lit. 1c.

(η^4-Cyclooctadiene)(t-butyl-η^5-cyclopentadienyl)cobalt (11). Experimental proce-

dure: 0.55 g (3.1 mmol) of anthracene, 150 ml of THF and 0.05 ml of methyl iodide are added with stirring in an inert gas atmosphere at 20 °C to 3.6 g (150 mmol) of magnesium powder (particle size 0.15 mm). After about 2 h, the reaction mixture is activated by suspending the reaction vessel for 3 h in an ultrasonic bath (continuous peak HF output 240 Watt, 35 kHz). The mixture of orange magnesium anthracene is then heated with stirring to 60 °C. After the addition of 13.5 g (125 mmol) of COD and 7.0 g (57.4 mmol) of t-BuCpH, the source of heat is removed and 17.8 g (50 mmol) of solid cobalt(III) acetylacetonate added over 30 min. An exothermic reaction takes place and the temperature increases to 70 °C, the mixture becoming deep red-brown. After cooling to 20 °C, the reaction mixture is filtered through a G-3 glass-frit and evaporated to dryness (max. bath temperature 30 °C). The residue is taken up in 500 ml of pentane, filtered and washed with a total of 500 ml pentane in several portions. The clear red filtrate is evaporated to dryness (max. bath temperature 30 °C) under vacuum. The complex is isolated by sublimation at a bath temperature of 80 to 150 °C/0.15 Pa, and recrystallization from pentane at −80 °C. Solutions of **11** are very air sensitive. Yield: 6.0 g of **11** (20.83 mmol, 41.7% theory).

Characterization of 11. Elemental analysis: Found: C, 70.93; H, 8.62; Co, 20.52. $C_{17}H_{25}Co$ calcd.: C, 70.82; H, 8.74; Co, 20.44%.

^{13}C NMR (toluene-d_8)



C(1) 63.5; C(2) 32.4; C(3) –; C(4) 83.6; C(5) 80.4; C(6) 31.8; C(7) 32.3 ppm. Mass spectrum: m/z: 288 (M^+, 61%); 231 (93%); 229 (100%); 164 (54%); 137 (28%); 125 (31%); 59 (47%).

(η^4-Cyclooctadiene)(methyl-η^5-cyclopentadienyl)cobalt (10). Procedure analogous to the above method applied for the synthesis of **11**. Starting materials: magnesium 7.2 g (300.0 mmol), anthracene 1.1 g (6.2 mmol), THF 300 ml, methyl iodide 0.1 ml, 1-MeCpH 8.8 g (110.0 mmol), COD 27.0 g (250.0 mmol), $Co(acac)_3$ 35.6g (100.0 mmol). Yield: 17.5 g of **10** (71.1 mmol, 71.1% of theory). Yellow-brown crystals (m.p. −15 °C) from pentane by recrystallization at -80 °C. For further characterization of **10** see Lit. 13,19.

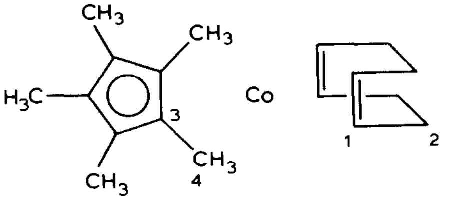
(η^4-Cyclooctadiene)(phenyl-η^5-cyclopentadienyl)cobalt (13). Step 1: preparation of $Co(\eta^5\text{-PhCp})_2$ (**15**). Magnesium powder (7.2 g, 300 mmol, particle size 0.1 mm) is treated with 1.1 g (6.2 mmol) anthracene, 300 ml THF (purified over $NaAlEt_4/LiAlH_4$) and 0.1 ml methyl iodide. On stirring at 23°C a yellow-green solution is formed, from which orange coloured magnesium anthracene separates in ca. 1–2 h. The mixture is subjected to an ultrasonic bath treatment for 3 h and heated with stirring to 65 °C. After addition of 28.5 g (264 mmol) COD and 12.5 g (88 mmol) 1-phenylcyclopentadiene, the source of heat is removed and solid cobalt(III) acetylacetonate (35.5 g, 99.7 mmol) is added portionswise to the continually stirred solution over 15 min, whereby the solution vigorously boils.

After cooling to 20 °C and filtration through a G-3 glass-frit, the clear filtrate is evaporated to dryness in a high vacuum. The residue is taken up in 300 ml pentane and the solution refiltered through a G-3 glass-frit. The low boiling part of the filtrate is removed under vacuum (0.15 Pa) and a viscous dark-red oil is distilled from the residue at 160–200 °C (0.015 Pa). This crystalline crude product is purified by extraction with 100 ml pentane. Yield: 1.3 g of **15**. Mass spectrum: *m/z*: 341 (M^+, 100%); 141 (18%).

Step 2: **14** (1.7 g, 4.98 mmol) are dissolved in 100 ml THF, 1.07 g (9.1 mmol) of COD and elemental lithium (44 mg, 6.29 mmol) are added and the mixture is refluxed for 18 h. The solvent is removed in vacuum and the residue dissolved in 100 ml pentane. Chromatography using a 40 cm SiO_2 column (eluent: pentane) followed by recrystallization from pentane at −50 °C gives pure **13**. Yield: 700 mg of **13** (2.27 mmol, 45.6% theory) m.p. 61–62 °C. For spectral data see lit. 13, 20.

*(η^4-Cyclooctadiene)(η^5-pentamethylcyclopentadiene)cobalt (**8**).* $Co(CO)_2(\eta^5$-$Me_5Cp)$ (1.49 g, 5.6 mmol) [21] are dissolved in 150 ml COD and irradiated (Hg UV-lamp). 236.8 ml (10.57 mmol) CO are evolved over 3 h and the colour of the solution changes to bright orange-brown. COD is removed in vacuo, the yellow-brown crystalline residue extracted with a 1/1 ether/pentane mixture and the solution cooled to −80 °C. Complex **8** precipitates as orange crystals (m.p. 166 °C) which were dried in vacuo. Yield: 1.3 g of **8** (4.3 mmol, 76.7% theory).

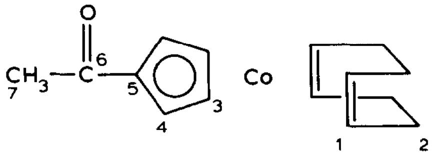
*Characterization of **8**.* Elemental analysis: Found: C, 71.67; H, 8.83; Co, 19.46. $C_{18}H_{27}Co$ calcd.: C, 71.52; H, 8.94; Co 19.53%. ^{13}C-NMR (toluene-d_8):



C(1) 70.5; C(2) 32.6; C(3) 91.6; C(4) 9.2 ppm. Mass spectrum: *m/z*: 302 (M^+ 100%); 285 (94%); 272 (84%) 194 (57%); 192 (72%); 133 (78%); 59 (34%).

*(η^4-Cyclooctadiene)(acetyl-η^5-cyclopentadienyl)cobalt (**14**).* $Co(CO)_2(\eta^5$-acetylCp) [22] (2.96 g, 13.3 mmol) are dissolved in 70 ml COD and irradiated 36 h (Hg UV-lamp). COD is removed in vacuo, the orange residue is dissolved in 40 ml diethyl ether and filtered. The solution is cooled to −80 °C and the complex is isolated as dark red needles. Yield: 2.35 g (8.55 mmol, 64.3% theory) m.p. 102–103 °C.

*Characterization of **14**.* Elemental analysis: Found: C, 65.81; H, 6.98; Co. 21.42. $C_{14}H_{19}CoO$, calcd.: C, 65.69; H, 6.93; Co, 21.53%. ^{13}C-NMR (toluene-d_8)



C(1) 31.99; C(2) 68.33; C(3) 83.42; C(4) 88.20; C(5) 97.90; C(6) 192.64; C(7) 26.88 ppm. Mass spectrum: *m/z*: 274 (M^+, 100%); 231 (63%).

Process chromatographic investigation of the catalysts. The apparatus we have developed for the evaluation of the catalyst properties under stationary conditions is shown in Fig. 4 [14] and consists of a continuous flow reactor linked to process chromatography equipment consisting of the analytical instruments, a control panel and the data processor. Solutions of the educts and catalysts are pumped through the system which is controlled by electronic balances. All the catalysts were tested in the standard reaction under identical conditions (eq. 4).

Since all measurements in the continuous flow reactor were carried out for 65% conversion of propyne and since the rate of formation of the pyridine derivatives is independent of the nitril concentration [14a], a concentration dependence of the results can be excluded. Kinetic effects are therefore eliminated.

A careful analysis of the catalytic reaction in the continuous flow reactor indicated that the isomer ratio **6**/**7** was independent of the temperature of the reaction. The effects are therefore not thermodynamic in origin. Thus differences in activity and regioselectivity measured in the continuous flow reactor can be attributed to the catalyst themselves.

The results of the experiments carried out in the reactor under the conditions described in equation 4 are given in Table 4 together with the relevant catalysts.

^{13}C and ^{59}Co NMR spectra. ^{13}C NMR spectra were recorded at 75.46 or 25.16

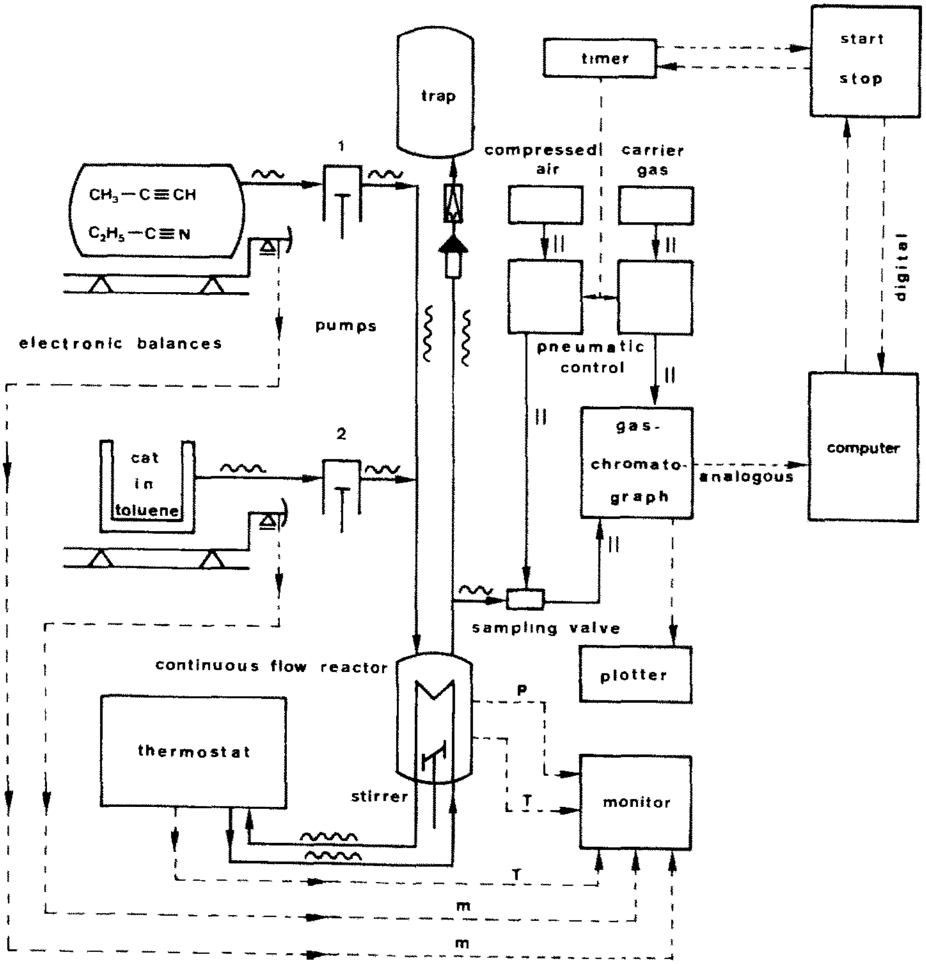
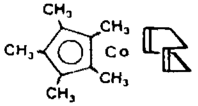
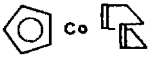


Fig. 4. Process chromatographic evaluation of the catalysts.

TABLE 4

SUBSTITUENT EFFECTS IN η^5-R-Cp-Co-COD CATALYSTS ON THE REACTION TEMPERATURE T AND THE RATIO OF THE ISOMERIC PYRIDINES **6** AND **7** UNDER STANDARD CONTINUOUS-FLOW CONDITIONS [a]

No.	Catalyst	T	ΔT^b	6 : 7	% 6	% 7
8		220°	73	3.51	77.8	22.2
9		180°	33	2.50	71.4	28.6
10		162°	15	2.02	66.9	33.1
3		147°	0	1.71	63.1	36.9
11		152°	5	1.77	63.9	36.1
12		144°	- 3	1.67	62.5	37.5
13		140°	- 7	1.73	63.4	36.6
14		123°	-24	1.46	59.3	40.7

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[a] For standard conditions see eq. 4. [b] $\Delta T = (T_{\text{R-Cp-Co}} - T_{\text{Cp-Co}})$.

MHz on Bruker WM-300 or Varian XL-100 spectrometers, respectively. The CD_3 signal of the perdeuterotoluene solvent was taken as reference and the chemical shifts converted to the TMS scale ($\delta(CD_3)$ 20.43 ppm). Assignments were made using the multiplicities and values of J(CH) in the proton-coupled spectra and by comparison with other compounds in the series. The allylic and olefinic –CH= resonances in the ^{13}C NMR spectrum of Otsuka's complex (eq. 2), for which the proton NMR assignment is known [3b], were assigned by means of a ^{13}C–^{1}H shift-correlated 2D NMR spectrum.

^{59}Co NMR spectra were recorded at 71.2 MHz on a Bruker WM-300 NMR spectrometer at 23°C: chemical shifts are given in the δ-scale relative to external $K_3[Co(CN)_6]$ in D_2O. Typical linewidths were 12–25 kHz. The free induction decays were submitted to Gauss multiplication in order to narrow the signals to between a half and a third of their natural linewidths so that the peak position could be determined more accurately. The ^{59}Co NMR spectra of (η^4-Cyclobutadiene)(η^5-cyclopentadienyl)cobalt and (η^4-cyclooctadiene)(η^5-cyclopentadienyl)cobalt were measured at 47.7 MHz in acetone-d_6 solution at 23°C on a Varian XL-200 spectrometer, (η^4-cyclohexa-1,3-diene)(η^5-cyclopentadienyl)-cobalt in methanol-d_4 solution.

The ^{59}Co resonances of **9** and **12**, as well as (η^4-butadiene)(η^5-cyclopentadienyl)cobalt were observed for the first time by Benn and Rufińska [23].

References

1 (a) H. Bonnemann, R. Brinkmann and H. Schenkluhn, Synthesis, (1974) 575; H. Bonnemann and H. Schenkluhn, DBP 2416295 (4.4.1974); U.S.P. 4,006,149; (b) H. Bönnemann, Angew. Chem., 90 (1978) 517; Angew. Chem. Int. Ed., 17 (1978) 505. (c) H. Bonnemann and M. Samson, DBP 2840460 (16.09.1978) to Studiengesellschaft Kohle m.b.H.; H. Bonnemann and M. Samson, Europ. Patent Appl. 009685 (1980); U.S.P. 4,266,061 (05.05.1981) to Studiengesellschaft Kohle m.b.H.; H. Bonnemann and M. Samson, U.S.P. 4,266,061 (14.09.1979, 05.05.1981). (d) H. Bönnemann, DOS 3117363.2 (02.05.1981); Europ. Pat. Appl. 064268 (28.04.1982) to Studiengesellschaft Kohle m.b.H.; H. Bönnemann, U.S. Pat. Appl. 371,872 (26.04.1982). (e) H. Bonnemann and W. Brijoux, The Cobalt-catalyzed Synthesis of Pyridine and its Derivatives, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 5, D. Reidel, Dordrecht, in press (S. 22–24, 123).

2 G. Natta, U. Giannini, P. Pino and A. Cassata, Chim. Ind. (Milano), 47 (1965) 524.

3 (a) Ch. Grard, Thesis, University of Bochum 1967; G. Wilke, Kagaku Kogyo, 20 (1967) 1308, 1310; (b) S. Otsuka and M. Rossi, J. Chem. Soc. A, (1968) 2630; (c) S. Koda, A. Tanaka and T. Watanabe, J. Chem. Soc. Chem. Commun., (1969) 1293; (d) H. Lehmkuhl, W. Leuchte and E. Janssen, J. Organomet. Chem., 30 (1971) 407.

4 J.A. Connor, Top. Curr. Chem., 71 (1976) 71.

5 H. Bönnemann and W. Brijoux, The Cobalt-catalyzed Synthesis of Pyridine and its Derivatives, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 5, D. Reidel, Dordrecht, in press (p. 104 ff).

6 (a) T.S. Pieper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem. I, (1955) 165; (b) A. Nakamura and N. Hagihara, Bull. Chem. Soc. Japan, 33 (1960) 425; (c) Gmelins Handbuch der anorg. Chemie, Vol. 5, Cobalt-organische Verbindungen, Part 1, 359 ff.

7 (a) W. Meurers, Diplomarbeit RWTH Aachen 1982; (b) H. Bönnemann and W. Brijoux, The Cobalt-catalyzed Synthesis of Pyridine and its Derivatives, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 5, D. Reidel, Dordrecht, in press (p. 36–42).

8 (a) M. Radermacher, Diplomarbeit RWTH Aachen 1982; (b) H. Bönnemann, M. Radermacher, C. Krüger and H.-J. Kraus, Helv. Chim. Acta, 66 (1983) 185.

9 (a) D. Habermann, Thesis, University of Bochum 1980, p. 58 and 70; (b) K. Jonas and C. Krüger, Angew. Chem., 92 (1980) 513; Angew. Chem. Int. Ed., 19 (1980) 520; (c) K. Jonas, Advan. Organometal. Chem. Vol. 19 (1981) 112.

10 E. Maurer, S. Rieker, M. Schollbach, A. Schwenk, Th. Egolf and W. von Philipsborn, Helv. Chim. Acta, 65 (1982) 26.

11 T. Jenny, W. von Philipsborn, J. Kronenbitter and A. Schwenk, J. Organomet. Chem., 205 (1981) 211.

12 Th. Egolf and W. von Philipsborn, Helv. Chim. Acta, in preparation; Th. Egolf, PhD Thesis, University of Zürich, 1983.

13 H. Bönnemann, W. Brijoux, R. Brinkmann and W. Meurers, Helv. Chim. Acta, in press.

14 (a) W. Brijoux, Thesis, University of Dortmund, 1979; (b) H. Bönnemann, W. Brijoux and K.H. Simmrock, Erdöl und Kohle; Erdgas-Petrochemie vereinigt mit Brennstoffchemie, 33 (1980) 476; (c) H. Bönnemann and W. Brijoux. The Cobalt-catalyzed Synthesis of Pyridine and its Derivatives, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 5, D. Reidel, Dordrecht, in press (p. 94).

15 A.G. Davies, P.J. Barker, and J.D. Fisher, J. Chem Soc. Chem. Commun., (1979) 587.

16 A.N. Nesmeyanov, N.S. Kochetkova, E.V. Leonova, E.I. Fedin and P.V. Petrovskii, J. Organomet. Chem., 39 (1972) 173.

17 (a) H. Bonnemann and B. Bogdanović, Ger. Pat. Appl. 32 0550.1 (17.02.1982), Europ. Patent Appl. 83101246.3 (10.02.1983) to Studiengesellschaft Kohle m.b.H.; (b) H. Bönnemann, B. Bogdanovic, R. Brinkmann, D.-W. He and B. Spliethoff, Angew. Chem., 95 (1983) 728.

18 K. Jonas, E. Deffense and D. Habermann, Angew. Chem., 95 (1983) 729.

19 H. Bönnemann and W. Brjioux, The Cobalt-catalyzed Synthesis of Pyridine and its Derivatives, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 5, D. Reidel, Dordrecht, in press (p. 108).

20 H. Bonnemann and W. Brijoux, in R. Ugo (Ed.), Aspects of Homogeneous catalysis, Vol. 5, D. Reidel, Dordrecht, in press (p. 112).

21 R.B. King and A. Efraty, J. Am. Chem. Soc. 93 (1971) 4950.

22 W.P. Hart, D.W. Macomber, and M.D. Rausch, J. Am. Chem. Soc., 102 (1980) 1196.

23 R. Benn and A. Rufińska, unpublished results.