*Journal of Organometallic Chemistry*, 348 (1988) 123–134
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# Unusual type of catalysis by paramagnetic cobalt(0) complexes. Isolation of catalytically active 17-electron intermediate, $(Ph_3P)_2Co(CH_2{=}CHCH_2CH_2CHO)$, in the 4-pentenal intramolecular hydroacylation

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(Received December 24th, 1987)

## Abstract

The kinetics and mechanism of intramolecular hydroacylation catalyzed by complexes $Co_2(\mu\text{-}N_2)(PPh_3)_6$ (III) and $(PPh_3)_2Co(dppe)$ (IV) (dppe-1,2-bis(diphenylphosphino)ethane) were studied. The active monomeric 17-electron intermediate, $(Ph_3P)_2Co(CH_2{=}CHCH_2CH_2CHO)$ (Vb) was isolated in the cyclisation of 4-pentenal (I), catalyzed by complex III. Crystals of Vb are stable in an inert atmosphere at room temperature for a month. A well defined EPR spectrum of Vb in toluene glass at 77 K was obtained. According to the IR spectrum of complex Vb aldehyde I is bonded to the metal as a bidentate $\pi,\pi$-ligand. The ligand exchange reaction was found to proceed readily between Vb and dppe to form free I (85%) and $Co(dppe)_2$. The complex Vb is the first example of a cobalt(0) complex with a coordinated aldehyde group. The analogous intermediate, $(dppe)Co(CH_2{=}CHCH_2\text{-}CH_2CHO)$ (Va) was identified by EPR in solution during the 4-pentenal cyclization, catalyzed by complex IV. For the 4-pentenal hydroacylation reaction, catalyzed by complex Vb, zero and first order kinetic laws were found for the aldehyde I and the catalyst concentrations respectively in accordance with the equation: $W_0 = k[\text{Vb}]$, $k = (8.5 \pm 0.5) \times 10^{-4}$ $s^{-1}$ at 70 °C. It is suggested that the reaction mechanism involves oxidative addition of coordinated I to cobalt(0) within the complex Vb to give an acyl hydride intermediate (rate-determining step). The subsequent rearrangement of the acyl hydride complex to the acylalkylcobalt derivative, followed by a reductive elimination reaction yields the ketone II and the parent cobalt(0) complex. Unlike well-known catalytic processes, in which diamagnetic $Co^{I}$ and $Co^{III}$ species are key intermediates, the catalytic cycle of the intramolecular hydroacylation reaction seems to involve only mononuclear paramagnetic $Co^{0}$ and $Co^{II}$ species. Chelation of the cobalt atom by an unsaturated aldehyde was found to be an important requirement for this reaction to occur.

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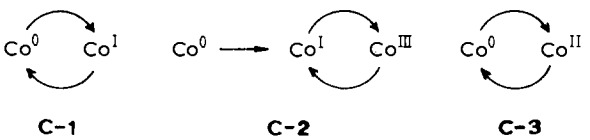
## Introduction

We reported earlier that cobalt(0) complexes, formed in $CoCl_2L_2/C_{10}H_8Na/L$ and $Co_2(\mu\text{-}N_2)L_2$ (III)/L′ systems (L = $PPh_3$, L′ = another phosphorus ligand) catalyze the intramolecular hydroacylation (*IH*) reaction, namely 4-pentenal (I) cyclisation to give cyclopentanone (II) [1–3].

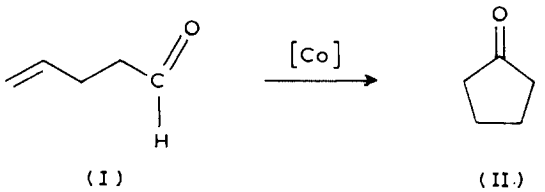
By analogy with the well-known hydrogenation and hydroformylation processes [4–6] we previously proposed [2,3], that $Co^{I}$ and $Co^{III}$ species could participate as active intermediates in the *IH* reaction (catalytic cycles **C-1** and **C-2**). However, the




new data presented here made us revise the previous suggestion based on traditional catalysis schemes in favour of the unusual pathway **C-3**, involving only $Co^{0}$ and $Co^{II}$ species as intermediates in the *IH* process. In contrast to the commonly accepted schemes **C-1** and **C-2**, no attention was paid to cycle **C-3** to explain the catalytic action of cobalt complexes, except for a single speculation [7] and no evidence was found in the literature for considering the catalytic cycle of type **C-3** as a real one.

## Results

4-Pentenal (I) cyclisation was found to proceed in benzene-acetonitrile solution, containing 3 mol% of complex $(PPh_3)_2Co(dppe)$ (IV), in which dppe is 1,2-bis(diphenylphosphino)ethane, at 70 °C for 1 h to yield cyclopentanone (II) with 100% selectivity and 95% conversion of I:




(1)

EPR was used to clarify the nature of the organocobalt species which are responsible for the catalytic cyclization (eq. 1). The EPR spectrum of the original cobalt complex IV is presented in Fig. 1a. The quantitative EPR measurements (see experimental part) showed that this compound exists in solution as a mononuclear complex (cf. [8–11]). After aldehyde I had been added to a toluene solution of IV, the amplitude of the original EPR signal sharply decreased and simultaneously a new well resolved spectrum appeared consisting of 3 sets of 8 lines owing to interaction of an unpaired electron with a single cobalt nucleus ($S_I = 7/2$) (Fig. 1b).

As it will be shown below, the new complex Va arises as result of a ligand exchange reaction 2:

$$\underset{\text{(IV)}}{(dppe)Co(PPh_3)_2} + I \rightleftarrows \underset{\text{(Va)}}{(dppe)Co(CH_2{=}CHCH_2CH_2CHO)} + 2PPh_3 \qquad (2)$$

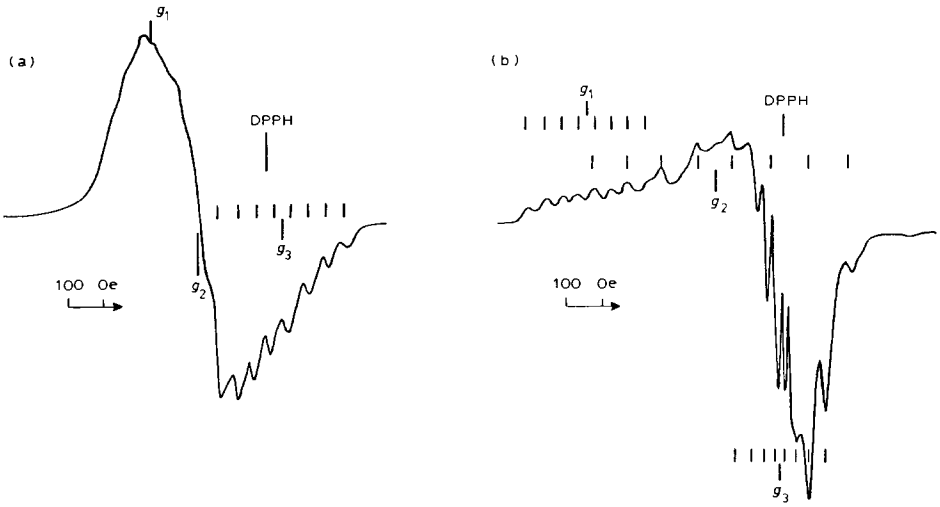



Fig. 1. EPR spectra of cobalt(0) complexes in a toluene matrix at 77 K, 20 mmol/l. DPPH = diphenylpicrylhydrazyl. (a) $(PPh_3)_2Co(Ph_2PCH_2CH_2PPh_2)$ (IV), (b) $(Ph_2PCH_2CH_2PPh_2)Co(CH_2{=}CHCH_2CH_2CHO)$ (Va).

More than 80% of complex IV (based on EPR data) is converted into complex Va at an initial ratio of I/IV = 5/1. The equilibrium 2 is achieved in 1 h at room temperature or in 3–5 min at 60 °C. Note, that only a few examples of ligand substitution for paramagnetic cobalt(0) complexes, in which the valence state of the metal remains unchanged, have been reported [8–10].

For reaction 1, catalyzed by complex IV, an induction period was observed (Fig. 2), the duration of which was equal to the time required to reach the equilibrium 2. Thus, the formation of complex Va is a necessary step for the *IH* reaction to

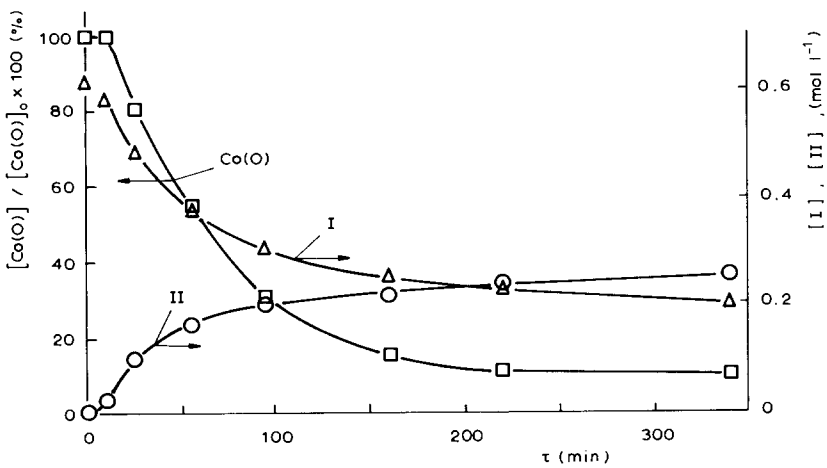
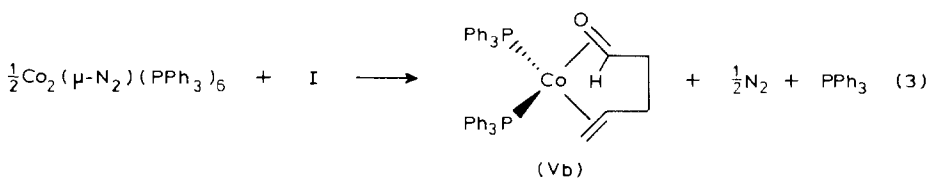



Fig. 2. Plots of concentrations of cobalt(0) species (□), determined by EPR, 4-pentenal (I) (△) and cyclopentanone (II) (○) versus reaction time for $[(PPh_3)_2Co(Ph_2PCH_2CH_2PPh_2)]_0 = 20$ mmol/l in benzene at 60 °, $[I]_0/[Co(0)]_0 = 30$.

proceed. Figure 2 shows that in the course of the cyclisation of aldehyde (I) the rate of ketone (II) formation decreases as the concentration of the cobalt(0) species determined by EPR falls. After the disappearance of the EPR signal of complex Va only slow conversion of I to by-products was observed [2,3]. The remaining broad EPR signal (~ 10% of the initial intensity) which is different from that of Va corresponds to a cobalt(0) complex inactive in reaction 2. Its nature was not examined.

Reaction 3 was found to be the most convenient route for preparation of the cobalt(0) complex containing coordinated aldehyde I. Unlike reaction 1, this one is irreversible owing to nitrogen evolution:




Green crystals of complex Vb were thus obtained. They remained unchanged when exposed to air for a short time (1–2 min) or kept in an inert atmosphere for a month at room temperature. The IR spectrum of Vb does not show any typical C=C absorption bands and there is only a single broad band of medium intensity at 1515 $cm^{-1}$, which can be assigned to carbonyl stretching. The pronounced $\nu$(C=O) shift observed is obviously not the result of metal–carbonyl $\sigma$-bonding, since it is known that frequency lowering for such $\sigma$-complexes does not exceed 100 $cm^{-1}$ [12]. There are only a few examples of $\pi$-bonding of a carbonyl group to a central metal atom, and in all the cases known a considerable $\nu$(C=O) lowering (200–700 $cm^{-1}$) was observed. Thus, the IR spectrum of Vb is in accordance with bidentate $\pi,\pi$-bonding of aldehyde I to the cobalt atom.

The EPR spectrum of compound Vb is presented in Fig. 3, and the EPR parameters are given in Table 1. The EPR spectrum consists of 3 groups of 8 lines in each. In addition, the $g_2$-group is split into doublets due to unpaired electron interaction with the phosphorus atom. The three $g$-values spectrum of Vb indicates considerable distortion of the tetrahedral environment of the central cobalt atom. The hyperfine splitting constants show that the unpaired electron is largely localized on the cobalt atom. The same EPR spectrum was directly observed for the organometallic species arising in the course of reaction 1, catalyzed by complex III. Since complex Vb and complex Va, obtained in situ from IV and aldehyde I (see above), show similar EPR spectra, the compounds obviously have analogous structures. It should be noted that these compounds are the first representatives of cobalt(0) complexes with a coordinated aldehyde group.

Some chemical properties of the new complex Vb were examined. It was found that all ligands of Vb can be displaced by bisphosphine (dppe) to yield 4-pentenal (85%), $Co(dppe)_2$ and triphenylphosphine. This reaction (eq. 4) proceeds smoothly at room temperature.

$$Vb + 2\ dppe \rightarrow Co(dppe)_2 + I + 2\ PPh_3 \qquad (4)$$

Heating complex Vb in benzene solution up to 70 °C gives rise to formation of 4-pentenal (I), cyclopentanone (II) and diphenyl in a molar ratio of 35/55/10

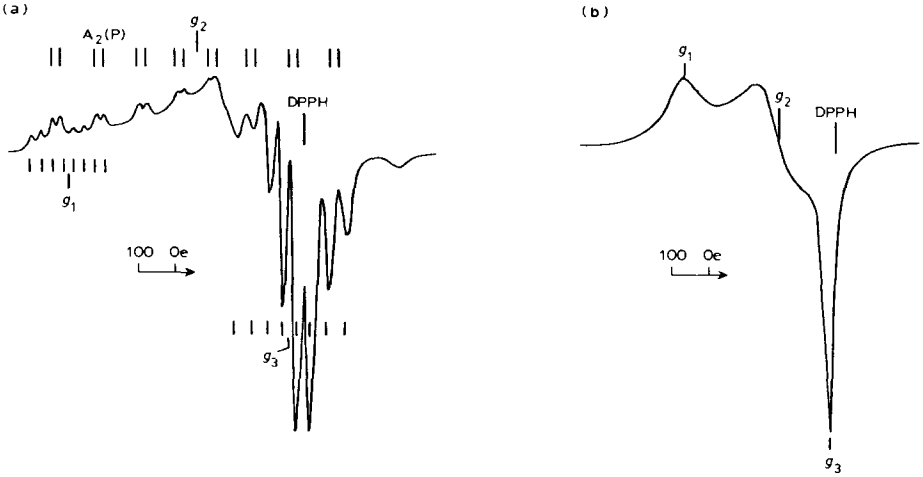



Fig. 3. EPR spectra of complex $(PPh_3)_2Co(CH_2{=}CHCH_2CH_2CHO)$ (Vb) at 77 K. (a) in a toluene matrix, 20 mmol/l, (b) polycrystalline sample.

respectively, the total product yield being 90%. Diphenyl seems to arise via oxidative addition of the triphenylphosphine ligand to cobalt(0) within the coordinatively unsaturated intermediate **F** followed by reductive coupling of the phenylcobalt species according to eq. 5 and 6 (cf. [15]):

$$\mathrm{Vb} \rightarrow \mathrm{I} + \mathrm{II} + \underset{(\mathbf{F})}{[\mathrm{Co(PPh_3)_2}]} \tag{5}$$

$$2[\mathbf{F}] \rightarrow 2\left[(\mathrm{PPh_3})\mathrm{Co}\begin{matrix}\mathrm{Ph}\\ \mathrm{PPh_2}\end{matrix}\right] \rightarrow \mathrm{Ph_2} + 2[(\mathrm{PPh_3})\mathrm{CoPPh_2}] \tag{6}$$

The kinetics of 4-pentenal cyclization have been studied using complex Vb as a catalyst. The results shown in Fig. 4a and 4b suggest that the *IH* reaction 1 obeys a zero order kinetic law in the [aldehyde I] ([I] = 20–150 mmol/l) and a first order

Table 1

Characteristics of the EPR spectra of cobalt(0) complexes in a toluene matrix [a]

| Complex | $T$ (K) | $g_{av.}$ | $g_1$ | $g_2$ | $g_3$ | $A_1$ (Oe) | $A_2$ (Oe) | $A_3$ (Oe) |
|---|---|---|---|---|---|---|---|---|
| $(dppe)Co(CH_2{=}CHCH_2CH_2CHO)$ (Va) | 77 | 2.182 | 2.397 | 2.136 | 2.013 | 44 (Co) | 90 (Co) | 34 (Co) |
| $(PPh_3)_2Co(CH_2{=}CHCH_2CH_2CHO)$ (Vb) | 298 | 2.128 | – | – | – | – | – | – |
| | 77 | 2.209 | 2.445 | 2.171 | 2.012 | 29 (Co) | 106 (Co) 22 (P) | 41 (Co) |
| | 77 [b] | 2.139 | 2.294 | 2.104 | 2.017 | – | – | – |
| $(PPh_3)_2Co(dppe)$ (*IV*) | 77 | 2.108 | 2.223 | 2.118 | 1.983 | – | – | 54 (Co) |
| $Co(dppe)_2$ | 77 | 2.122 | $g_{\parallel}$ 2.335 | $g_{\perp}$ 2.015 | | – | – | – |

[a] 20 mmol/l. [b] Polycrystalline sample.

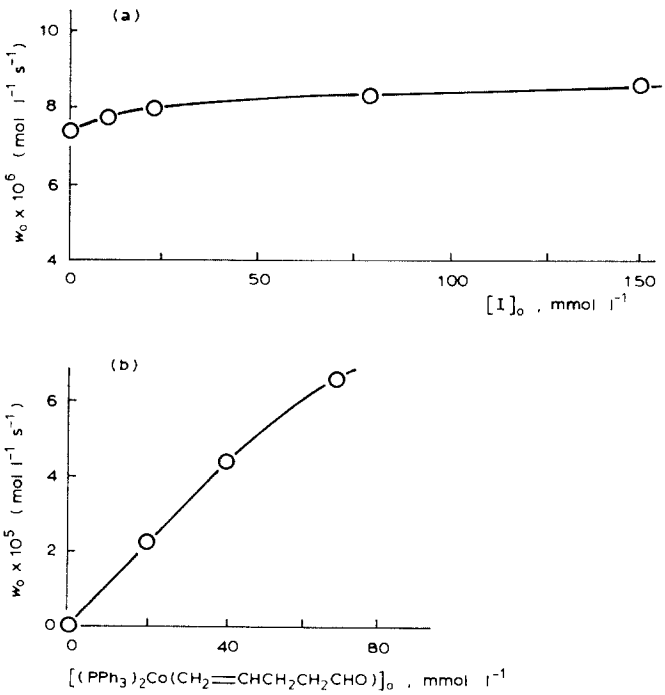



Fig. 4. Plots of initial rate ($w_0$) of reaction 1 in benzene at 70 °C. (a) vs. 4-pentenal (I) concentration at $[(PPh_3)_2Co(CH_2{=}CHCH_2CH_2CHO)]_0$ 10 mmol/l, (b) vs. $(PPh_3)_2Co(CH_2{=}CHCH_2CH_2CHO)$ (Vb) concentration at $[I]_0$ 700 mmol/l.

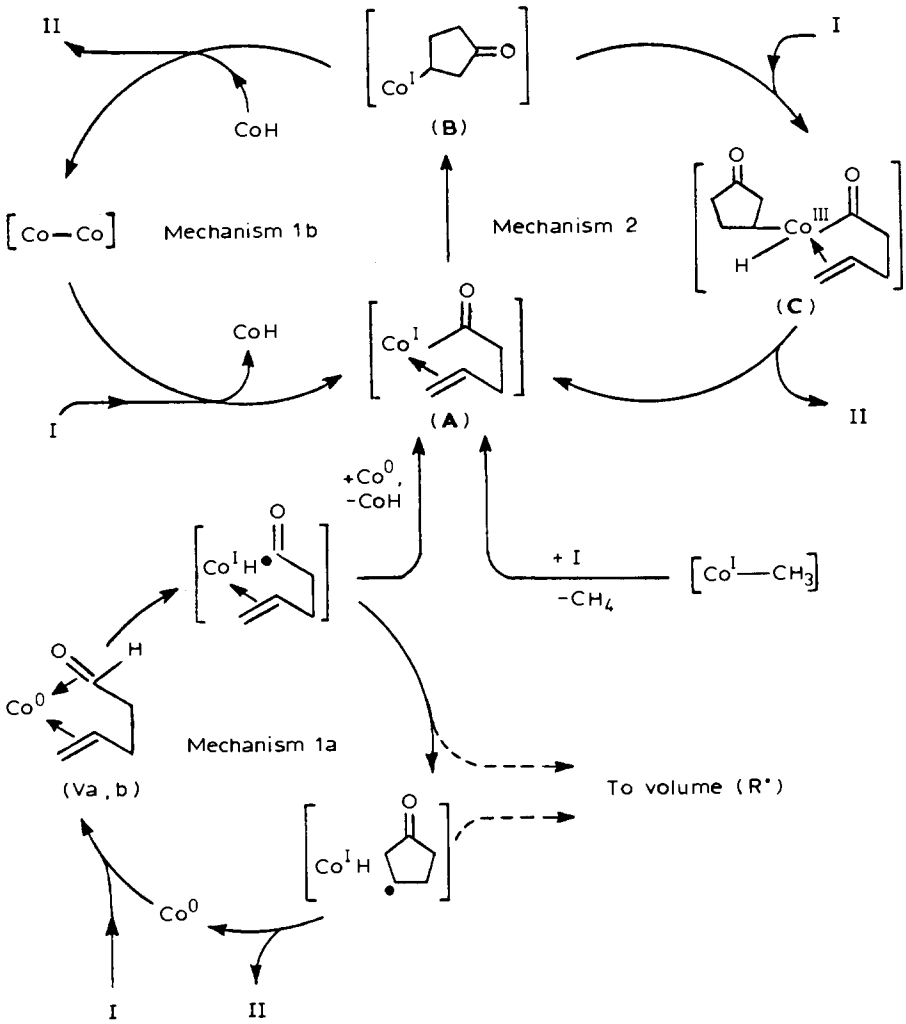
kinetic law in [complex Vb] ([Vb] = 0–50 mmol/l). Accordingly, the kinetic equation may be written as

$$w_0 = k[Vb] \tag{7}$$

The rate constant ($k$) in eq. 7 was found to be $(8.5 \pm 0.5) \times 10^{-4}$ s$^{-1}$ at 70 °C. The observed small deviation from zero order law at low aldehyde I concentrations is apparently due to partial decomposition of complex Vb in accordance with eq. 5. Indeed, a marked amount of diphenyl was detected as a by-product at $[I]_0 < 10$ mmol/l, but no diphenyl was found at $[I]_0 > 40$ mmol/l.

## Discussion

We first tried to explain the results obtained in the framework of the catalytic schemes **C-1** and **C-2** developed earlier for the well-known catalytic processes (see Introduction). However, the data presented above together with those described previously [2,3] were not consistent with generally accepted schemes of catalysis by cobalt complexes. Thus, mechanism 1a (Scheme 1), assuming free radical participation in the catalytic cycle [16–18], seems not to be valid, as no product of induced

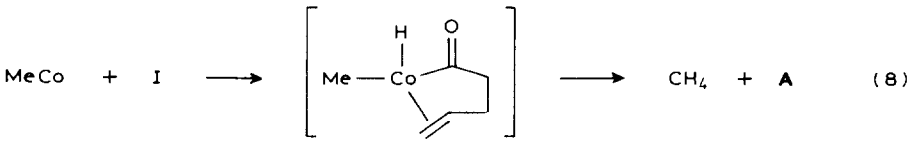



Scheme 1

free radical addition to the 4-pentenal double bond has been found when another aldehyde (butyraldehyde) is added to initial reagents [2]. Binuclear mechanism 1b contradicts the kinetic data obtained, because both initial and intermediate cobalt(0) complexes are present in solution in mononuclear form and a first order kinetic law for the catalyst concentration was found. In addition, it is difficult to assume that the cobalt(I) hydride species can act as a hydrogen donor towards free radicals [17,18] or alkyl cobalt intermediates **B** [18,19], since the complex $CoH(N_2)(PPh_3)_3$ is known to reduce easily 4-pentenal to 4-pentenol even at room temperature [2]. Therefore the concentration of "cobalt(I) hydride" is expected to be negligibly small under real *IH* reaction conditions (60–70 °C).

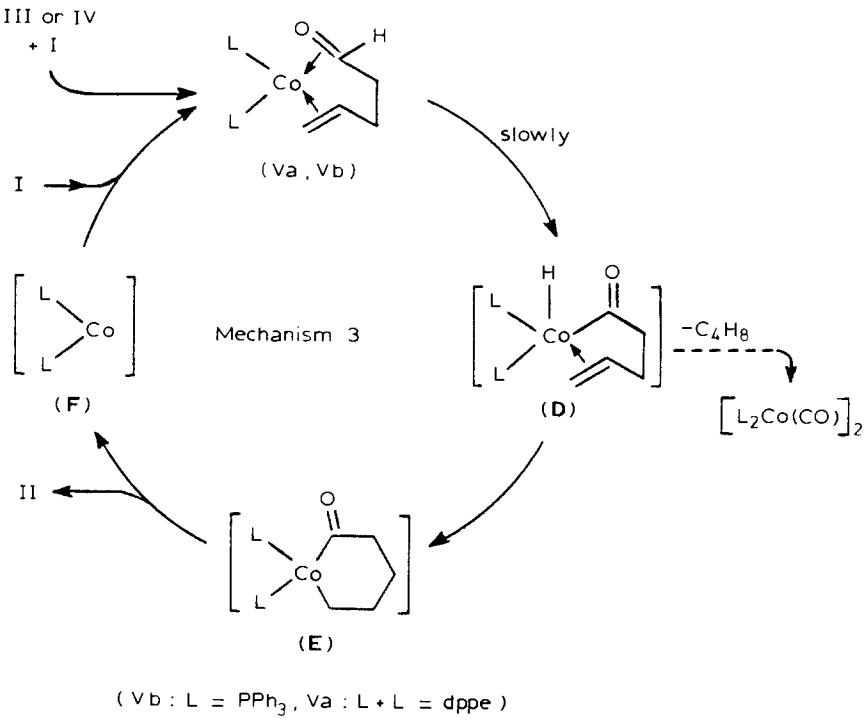
In order to check whether mechanism 2 takes any part in the real catalytic process, the possible acyl intermediate **A** was obtained in situ from $MeCo(PPh_3)_3$

and aldehyde I via the unstable acylcobalt(III) hydride derivative according to eq. 8 (triphenylphosphine ligands are omitted):




The occurrence of reaction 8 is confirmed by the formation of methane (87%) and butenes (15%). Butenes could arise only from acyl complex **A** as a result of a decarbonylation reaction. However, the reaction mixture contained no cyclopentanone even when aldehyde I was used in excess. Thus, intermediate **A** participation in the *IH* reaction is unlikely. This agrees with the fact that complex $(CO)_3CoC(O)(CH_2)_nCH{=}CH_2$ ($n = 2$) decomposes without acyl ligand cyclization. Note that cyclization of an unsaturated acyl ligand does occur in the case of a similar complex, in which $n = 3$ [6].

In our opinion, the results of this study as well those obtained earlier [2,3] may be best explained by mechanism 3 (Scheme 2). According to this the rate-limiting stage of the catalytic process is the oxidative addition of aldehyde I to cobalt(0) within complex V to produce the short lived acylcobalt(II) hydride intermediate **D**. The subsequent rearrangement of complex **D** into the acylalkyl intermediate **E** followed




Scheme 2

by a reductive elimination reaction (both stages are rapid) results in ketone II and parent complex regeneration.

The main arguments in favour of mechanism 3 are the following: (1) the induction period, observed in the catalytic cyclization (eq. 1), is equal to the time required for complex V formation from the original reagents; (2) the decomposition of the isolated complex Vb in the absence of aldehyde I gives cyclopentanone (II) as the main product, marked amounts of diphenyl being also obtained owing to irreversible transformation of active species of type **F**; (3) the kinetic data obtained indicate that the mononuclear cobalt species V are active intermediates.

The catalyst deactivation may be caused by aldehyde I decarbonylation via acyl hydride intermediate **D** (Scheme 2). Indeed, when the cyclisation (1) was carried out in ethanol, the red crystals, identified by IR spectra as $[Co(dppe)(CO)]_2$, were precipitated. Another possible route for catalyst deactivation, which probably prevails at low aldehyde I concentrations, involves decomposition of the active species **F** according to eq. 5 and 6.

As follows from mechanism 3, the key stage of the *IH* reaction is the oxidative addition of the CHO group to cobalt(0). The known examples of participation of cobalt(0) complexes in this reaction were found to give preferably cobalt(I) compounds [4–6, 16], but only a few examples are described, where cobalt(II) derivatives were obtained [9]. The main reason for this is the high lability of the Co–C bond in organocobalt(II) compounds, from which only cyclopentadienyl [21] and certain aryl- [22] organo-cobalt(II) complexes proved to be stable enough. Nevertheless a number of 5-coordinated phosphinecobalt(II) complexes have been synthesized [23,24]. It should be noted, that participation of acyl- and acylalkyl-cobalt complexes, similar to those of types **D** and **E**, was postulated in some stoichiometric reactions [25,26].

The suggested mechanism (3) resembles one proved for the rhodium-catalyzed *IH* reaction. However, the electronic states of the metals taking part in the catalytic cycles are essentialy different in both cases. When rhodium complexes were used as catalysts, the key intermediates were found to be diamagnetic rhodium(I) ($d^8$) and rhodium(III) ($d^6$) species [27,28], while catalysis by cobalt complexes involves paramagnetic cobalt(0) ($d^9$) and cobalt(II) ($d^7$) centres. In contrast, the pathways, including cobalt(I) ($d^8$) and cobalt(III) ($d^6$), were found to be unlikely (see above). This is confirmed by comparison of the catalytic action of $RhCl(PPh_3)_3$ and $CoCl(PPh_3)_3$ in the *IH* reaction: if the former effectively catalyzes the cyclization (1) [29], the latter is inactive as a catalyst.

A final remark deals with the relationship between the structure of the unsaturated aldehyde and its reactivity in the *IH* reaction. The main requirement for the structure of the initial aldehyde apparently consists in its ability to form a chelate cycle with the cobalt atom. In the cases of 5-hexenal and 1-formylcyclohex-3-ene, the structures of which are less favourable for chelation, no ketones were obtained. On the other hand, 2,2-dimethyl-4-pentenal, 1-formyl-1(2-propenyl)cyclohex-3-ene and 2-endo-formylbicyclo[2.2.1]hept-5-ene are expected to be more prone to chelate cycle formation. Indeed, they cyclize in the presence of 3–10% mol of complex IV to yield 3,3-dimethylcyclopentanone, cyclopentanone-2-spiro-3′-cyclohexene and tricyclo[$3.2.1.0^{3,6}$]octan-4-one respectively with high selectivity. This part of the study is now in progress.

## Experimental

*Materials and methods*

4-Pentenal, synthesized from allyl vinyl ether [2], was dried (4 Å molecular sieve) and redistilled. 5-Hexenal [30], $CH_3Co(PPh_3)_3$ [31], $Co(Ph_2PCH_2CH_2PPh_2)_2$ [14] and $Co_2(\mu\text{-}N_2)(PPh_3)_6$ [3] were prepared by the literature methods referenced. THF, ether, benzene, toluene, pentane/diglyme (95/5) were distilled from sodium/benzophenone, MeCN and EtOH were distilled from $CaH_2$. All the other chemicals were at least reagent grade. All the experiments were performed under Ar unless otherwise stated. GC analyses were carried out on an LHM-8MD instrument, fitted with 3 m 5% carbowax-20M or SE-30 on chromaton-N-AW-DMDCS columns, undecane being the internal standard. IR spectra were obtained with a Specord M-80 instrument. EPR spectra were recorded with an X-band EPR spectrometer. The samples for EPR analysis were prepared in the following way: the solvent and aldehyde were frozen in vacuo in a test tube containing the cobalt complex, then allowed to melt and the resulting solution was transferred (20 °C) into ampules for EPR measurements, which were sealed in vacuo.

*$(PPh_3)_2Co(dppe)$ (IV).*

A mixture of $Co_2(\mu\text{-}N_2)(PPh_3)_6$ (3.44 g, 2 mmol), $Ph_2PCH_2CH_2PPh_2$ (1.59 g, 4 mmol) and benzene (35 ml) was stirred at room temperature for 1 h, $N_2$ being evolved. The dark red solution thus obtained was filtered, then ether (80 ml) and EtOH (80 ml) were added successively and the stirred solution was carefully evaporated in vacuo (20 torr) down to a volume of 40 ml. The dark brown crystals formed were filtered off, washed with EtOH (3 × 10 ml) and dried in vacuo to give complex IV (3.06 g, 78% yield). M.p.(dec.) 151–152 °C. (Found: C, 75,21; H, 5.75; P, 11.85; Co, 6.20. $C_{62}H_{54}P_4Co$ calcd.: C, 75.84; H, 5.54; P, 12.62; Co, 6.00%). Under inert gas or in vacuo complex IV is stable at 20 °C for an unlimited time, but it is oxidized in air in 1–2 min. It gives bright red benzene and toluene solutions, is only slightly soluble in ether and poorly soluble in EtOH and hydrocarbons. The EPR spectrum of IV is presented in Fig. 2. For the determination of paramagnetic species concentration in solutions of complex IV, two identical ampules were taken. Into one of them a 5 mmol/l solution of the complex in benzene was introduced and in the second ampule a 2 mmol/l solution of $Cu(acac)_2$ in benzene/pyridine (9/1) was placed. Taking into account the difference in concentrations of the complexes, the integral intensities of the EPR signals have been found in both cases to coincide within experimental error (approximately 20%), i.e. IV exists in solution as a mononuclear complex.

*Catalytic cyclization of 4-pentenal in the presence of complex IV*

The mixture of complex IV (0.0982 g, 0.1 mmol), 4-pentenal (0.252 g, 3 mmol) and benzene/MeCN (1/1) (5 ml) was heated in a sealed ampule at 70 °C for 1 h. The resulting mixture was analyzed by GC. Conversion of 4-pentenal was complete. The following products were obtained (yields in mg, % and mol/mol catalyst): cyclopentanone (244, 97, 29), 4-pentyl-4-pentenoate (5, 2, 0.3) together with minor amounts of 2-(2-propenyl)-2,6-heptadienal, 4-pentenol and diphenyl.

The kinetics of 4-pentenal cyclization were studied as follows. Two sets of glass tubes, containing a solution of 4-pentenal (0.252 g, 3 mmol) and complex IV (0.0982 g, 0.1 mmol) in benzene (5 ml) were prepared. Sealed ampules were heated in pairs

for a fixed time at 60 °C and then analyzed separately by GC and EPR methods. The results thus obtained are summarized in Fig. 2.

*Preparation of $(PPh_3)_2Co(CH_2{=}CHCH_2CH_2CHO)$ (Vb)*

4-Pentenal (0.252 g, 3 mmol) was added to a suspension of $Co_2(\mu\text{-}N_2)(PPh_3)_6$ (0.860 g, 0.5 mmol) in toluene (12 ml). Stirring the mixture for 30 min at 20 °C ($N_2$ was evolved) produced a homogenous brown-green solution, which was filtered and concentrated slowly at 10 °C down to a volume of 2 ml. The residue was treated with pentane (10 ml) under stirring at 10 °C. The microcrystalline precipitate formed was filtered off, washed with pentane (2 × 5 ml) and dried in vacuo to give the crude product (0.547 g, 82%). The product was purified by dissolving in toluene (about 10 ml per 1 mmol) at 10–15 °C, followed by addition of half the volume of decane. Concentration of the solution thus obtained in vacuo down to 1/3 of the initial volume, resulted in fine green crystals, m.p. (dec.) 123–124 °C. (Found: C, 74.04; H, 5.71; P, 9.57. $C_{41}H_{38}OP_2Co$ calcd.: C, 73.76; H, 5.74; P, 9.28%). The complex Vb is readily soluble in benzene and toluene, slightly soluble in ether and almost insoluble in saturated hydrocarbons. The complex decomposes in solution in several hours under an inert atmosphere and at once when exposed to air. The EPR spectra and spectral characteristics of complex Vb are presented in Fig. 3 and Table 1. The integral intensities of the EPR signals, obtained at 20 °C for a polycrystalline sample and at −196 °C for a solid toluene solution of Vb (glass) were found to be approximately equal. IR spectrum (nujol, $\nu$, $cm^{-1}$): 1515m, 1392m, 1248s, 1236m, 966m, 928w, 916w, 884m, 864w, 628w, 528w, 514s, 488w, 452w, 440w, 416m and bands which belong to $PPh_3$ ligands.

*The ligand exchange reaction between complex Vb and 1,2-bis(diphenylphosphino)ethane (dppe)*

When dppe (39.8 mg, 0.05 mol) was added to a solution of complex Vb (33.4 mg, 0.05 mol) in benzene (2.5 ml) the colour changed from green to dark red in 20 min. The solvent together with liquid products formed were removed in vacuo by recondensation into a trap cooled by liquid nitrogen. By GC analysis of the condensate the following products were found (mg, mol/mol Vb): 4-pentenal (3.58, 0.85), cyclopentanone (0.25, 0.06), 4-pentenol (0.17, 0.04). The EPR spectrum of the solid residue, dissolved in 1 ml of toluene ([Co] 50 mmol/l) was identical to that of $Co(dppe)_2$, synthesized as described in [14] (see Table).

*Decomposition of complex Vb in benzene*

A solution of complex Vb (33.4 mg, 0.05 mmol) in benzene (2.5 ml) was heated at 70 °C for 1 h. As GC analysis showed, the resulting mixture contained (mg, mol/mol Vb): 4-pentenal (1.47, 0.35), cyclopentanone (2.31, 0.55), diphenyl (0.77, 0.1) and 4-pentenol (traces).

*Kinetics of 4-pentenal cyclization, catalyzed by complex Vb*

Into a glass vessel, containing complex Vb, the required amounts of benzene, 4-pentenal and undecane (standard) were recondensed in vacuo. A set of ampules were filled with the solution thus prepared, sealed off and heated in turn for a fixed time at 70 °C. The reaction mixture was analyzed by GC. Initial reaction rates ($w_0$) were determined from the plots of cyclopentanone versus reaction time.

*Reaction of $CH_3Co(PPh_3)_3$ with 4-pentenal*

4-Pentenal (42.1 mg, 0.5 mmol) was added (20 °C) to $CH_3Co(PPh_3)_3$ (86.1 mg,

0.1 mmol), dissolved in benzene (2 ml), the resulting solution was kept at 20 °C for 1 h, then gaseous products were condensed in a cooled trap. Gaseous and liquid products were analyzed by GC. The following products were obtained (mol/mol methyl cobalt complex): 4-pentenol (0.22), 1-butene (0.15), 5-hexen-2-ol (0.023), methane (0.67), ethylene (0.062), propane (0.055) together with small amounts of ethane, propylene, 2-butenes and products of aldehyde I condensation. No cyclopentanone was detected.

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