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On the mechanism of the hydrocarbalkoxylation of olefins catalyzed by palladium complexes

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Abstract

The acyl complex $PdCl(COR)(PPh_3)_2$ (R = Et, n-Hex), isolated during the course of hydrocarbalkoxylation reactions catalyzed by the precursor system $PdCl_2(PPh_3)_2$–PPh_3 (95 °C, P(CO) 100–120 atm; Pd : P = 1 : 3–4), in ethanol or higher alkanols as solvents, reacts with an alkanol R′OH in the presence of added PPh_3 (Pd : P = 1 : 3) to yield the ester RCOOR′ and a mixture of $PdCl_2(PPh_2)_2$ and $Pd(PPh_3)_{3or4}$. Moreover, when it is employed as catalyst precursor (R = n-Hex; Pd : P = 1 : 4) in the hydrocarbalkoxylation of ethylene, it is recovered as its ethyl analog and it yields almost stoichiometric amounts of n-HexCOOR′. When thedi carbomethoxy complex $PdCl(COOMe)(PPh_3)_2$, isolated in mixture with $PdCl(COR)(PPh_3)_2$ in hydrocarbomethoxylation experiments, is treated with 1-hexene in methanol (Pd : P : 1-hexene : MeOH = 1 : 3 : 40 : 125), under nitrogen, in the absence of carbon monoxide, at 95 °C, methyl heptanoate ester is not formed, and the starting complex is recovered almost quantitatively (92%). When $PdCl_2(PPh_3)_2$ or $PdCl(COOMe)(PPh_3)_2$ are used as catalyst precursors for the carbonylation of 1-hexene in MeOH, in the absence of added PPh_3 and in the presence of NEt_3 or of carboxylic acid anions (both of them are known to favor the formation of the carbomethoxy complex), no catalytic activity is observed and the precursors are recovered as palladium(0)carbonylphosphine complexes, ultimately mixed with the carbomethoxy complex.

The results support the view that, of the two commonly accepted mechanisms for the catalytic hydrocarbalkoxylation of olefins, involving M–H or M–COOR′ addition to the olefinic double bond, only the first one, in which a key intermediate is a Pd-acyl species, is probably involved.

When n-BuOH is used as solvent the catalytic activity remains high even after 5–6 reuses of the catalyst, whereas in MeOH the activity falls significantly below its initial value because of decomposition of the catalyst into inactive palladium(0) complexes and palladium metal, probably via a carbomethoxypalladium complex.

Introduction

It has been proposed that the hydrocarbalkoxylation of olefins to ester, catalyzed by transition metal complexes, occurs via addition to the double bond of a M–H [1–3] or of a M–COOR′ [4–9] intermediate, as depicted below:

$$\underset{(a)}{\mathrm{M{-}H}} \xrightarrow{\mathrm{C{=}C}} \underset{(b)}{\mathrm{M{-}C{-}C{-}H}} \xrightarrow{\mathrm{CO}} \underset{(c)}{\mathrm{M{-}CO{-}C{-}C{-}H}} \xrightarrow{\mathrm{R'OH}} \mathrm{R'OCO{-}C{-}C{-}H + M{-}H} \quad (1)$$

$$\mathrm{M{-}CO} \xrightarrow[-\mathrm{H}^+]{\mathrm{R'OH}} \underset{(x)}{\mathrm{M{-}COOR'}} \xrightarrow{\mathrm{C{=}C}} \underset{(y)}{\mathrm{M{-}C{-}C{-}COOR'}} \xrightarrow{\mathrm{H^+/CO}} \mathrm{H{-}C{-}C{-}COOR' + M{-}CO} \quad (2)$$

Scheme 1

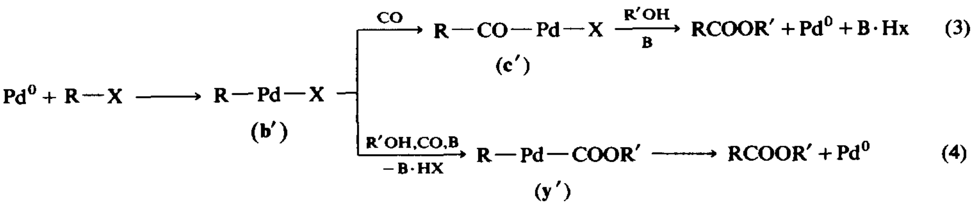
Mechanism 1 involves formation of a M-alkyl intermediate **b**, which adds to carbon monoxide to yield a M-acyl intermediate **c**, which, upon nucleophilic attack of the alkanol, yields the final product with return of M–H to the catalytic cycle.

In mechanism 2 the M–C σ-bond of a M-alkylcarbalkoxy intermediate **y** is split by H^+ with formation of the ester.

The above mechanisms have much in common with the two main mechanisms proposed for the carboalkoxylation of organic halides to give esters catalyzed by palladium complexes [7–9] (Scheme 2). Both mechanisms involve the initial oxidative addition of the organic halide to Pd^0. The reaction may proceed via CO insertion into a Pd–C bond to yield an acylpalladium intermediate which reacts with the alkanol to yield the ester (pathway 3), or may involve an alkyl-M-cabalkoxy intermediate (y′) which yields the ester and the Pd^0 precursor upon reductive elimination (pathway 4).

An account on aspects of intermediacy of M–H and M–COOR complexes in carbonylation reactions has recently appeared [10].

During the course of catalytic hydrocarbalkoxylation reactions (temperature ~ 100 °C, P(CO) 50–100 atm), involving the catalyst precursor *trans*-$PdCl_2(PPh_3)_2$ (**A**), it was possible to isolate the acyl complex *trans*-$PdCl(COR)(PPh_3)_2$ (**B**), when ethanol or a higher alkanol was used as solvent and a mixture of the carbomethoxy complex *trans*-$PdCl(COOMe)(PPh_3)_2$ (**C**) [3,11,12] together with **B** when MeOH was used as solvent.



$$\mathrm{Pd^0 + R{-}X} \longrightarrow \underset{(b')}{\mathrm{R{-}Pd{-}X}} \xrightarrow{\mathrm{CO}} \underset{(c')}{\mathrm{R{-}CO{-}Pd{-}X}} \xrightarrow[\mathrm{B}]{\mathrm{R'OH}} \mathrm{RCOOR' + Pd^0 + B\cdot Hx} \quad (3)$$

$$\underset{(b')}{\mathrm{R{-}Pd{-}X}} \xrightarrow[-\mathrm{B\cdot HX}]{\mathrm{R'OH,CO,B}} \underset{(y')}{\mathrm{R{-}Pd{-}COOR'}} \longrightarrow \mathrm{RCOOR' + Pd^0} \quad (4)$$

(B = base)

Scheme 2

We present here some observations on the reactivity of complexes **A**, **B**, and **C** that are relevant to the mechanism of the catalytic hydrocarbalkoxylation of olefins.

Results and discussion

Catalytic reactions were carried on for 3 hours in n-BuOH or MeOH as solvents, at 95 °C under 100–120 atm of carbon monoxide, with catalyst and reagents in the ratios palladium : olefin : alkanol = 1 : 100 : 1500–3000, and, unless otherwise stated, in the presence of additional amounts of PPh_3, (2 moles/mole of palladium precursor) to prevent decomposition to the palladium metal.

With complex **B** (R = n-Hex) as catalyst precursor for the carbonylation of ethylene in n-BuOH as a solvent, the precursor is recovered as *trans*-$PdCl(COC_2H_5)(PPh_3)_2$ (85%) and the reaction mixture contains significant amounts of butyl n-heptanoate (ca. 60% of the starting complex) and large amounts of n-butyl propionate (Pd : ester ≈ 1 : 60).

The formation of the propionyl complex can be represented as follows:

$$PdCl(COHex\text{-}n)(PPh_3)_2 + n\text{-}BuOH \longrightarrow n\text{-}BuOCOHex\text{-}n + \underset{(I)}{[PdHCl(PPh_3)_2]}$$

$$I + C_2H_4 + CO \longrightarrow PdCl(COC_2H_5)(PPh_3)_2$$

Thus, the possibility that under catalytic conditions the accumulation of complex **B** in the reaction medium might be due to its inertness, can be ruled out.

Complex **B** (R = n-Hex) reacts with n-BuOH in the presence of PPh_3 (Pd : P : n-BuOH = 1 : 3 : 100) under nitrogen and in the absence of carbon monoxide and 1-hexene, to give butyl n-heptanoate (ca. 50% of the starting complex) together with a yellowish solid, whose IR spectrum shows the presence of $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_n$ ($n = 3$ or 4). The products are probably formed through the reactions shown below:

$$PdCl(COHex\text{-}n)(PPh_3)_2 + n\text{-}BuOH \longrightarrow n\text{-}BuOCOHex\text{-}n + \underset{(I)}{[PdClH(PPh_3)_2]}$$

$$I \xrightarrow{PPh_3} PdCl_2(PPh_3)_2 + Pd(PPh_3)_{3\,or\,4}$$

These experiments indicate that catalysis is likely to proceed via the intermediacy of a Pd-acyl species formed by successive insertion of olefin and carbon monoxide into a preformed Pd–H species, as represented in mechanism 1, Scheme 1.

It is of interest that in the carbonylation of olefins catalyzed by a $PdCl_2(PPh_3)_2$–PPh_3 system, the catalytic activity is higher in the presence of molecular hydrogen [2,13–17]. In the light of the results reported above, the beneficial effect of hydrogen can probably be attributed to the possibility that this gas favors the formation of a Pd–H intermediate.

If after a catalytic reaction the reaction mixture is kept under carbon monoxide pressure at room temperature for several hours, complex **B** can be isolated as well-shaped crystals. If immediately after the catalytic reaction is complete the autoclave is cooled to room temperature and depressurized, the reaction mixture does not contain the complex **B** as a precipitate. This complex is formed after most of the dissolved carbon monoxide is removed. These observations, considered together with the fact that the regioselectivity depends on the pressure of carbon monoxide (for example the butyl n-heptanoate/2-methylexanoate ratio is 4.0 under 110 atm and 4.9 under 55 atm), as has been found for the carbonylation of other olefins [2,13–17], suggest that the observed catalytic activity involves several active acyl intermediates arising from the equilibria between complex **B** and carbon monoxide and having different numbers of coordinated CO ligands as the result of displacement by CO of the chloride and/or the PPh_3 ligands. For example, it has been found that under ambient conditions carbon monoxide displaces the chloride ligand from the closely related complex *trans*-$[PtCl(COEt)(PPh_3)_2]$ to yield the cationic complex *trans*-$[Pt(CO)(COEt)(PPh_3)_2]^+Cl^-$ [18].

When complex **C** is treated at 95°C with 1-hexene in methanol (Pd : P : 1-hexene : MeOH = 1 : 3 : 40 : 125) under nitrogen in the absence of carbon monoxide methyl heptanoate ester is not formed in detectable amounts, (in contrast to what is observed when complex **B** is treated with n-BuOH), and the starting complex is recovered almost quantitatively (92%).

When complex **A** or complex **C** is used as the catalyst precursor for the carbonylation of 1-hexene in MeOH in the absence of added PPh_3 and in the presence of NEt_3 (Pd : N = 1 : 2), no methyl heptanoate is detected and the precursors are recovered as yellow-orange solids showing $\nu(CO)$ IR bands at 1955 cm^{-1} and two bands centered at 1830 cm^{-1} due to $Pd(CO)(PPh_3)_3$ and $Pd_3(CO)_3(PPh_3)_4$ [19].

No catalytic activity is observed even when the carbonylation of 1-hexene is carried out in the presence of n-PrCOONa (Pd : Na = 1 : 5), in place of NEt_3. In this case the precursor is recovered as a mixture of complex **C** together with some palladium(0) carbonyl phosphine complexes, as suggested by the presence of an strong wide band in the $\nu(CO)$ region centered at ca. 1865 cm^{-1} [19].

In the light of these facts and of the knowledge that the formation of carbalkoxy species is favored by the presence of a base such as trialkylamine or carboxylic acid anions [20,21], it seems unlikely that the carbonylation of olefins occurs via reaction pathway 2, although this possibility cannot be ruled out under catalytic conditions.

When complex **B** (R = n-hexyl) is used as catalyst precursor in the carbonylation of 1-hexene (Pd : hexene = 1 : 100) in MeOH in the presence of NEt_3 (Pd : N = 1 : 2), significant amounts of methyl heptanoate (ca. 60% of the starting complex) are formed although not as much as espected if complex **B** acts as a catalyst. The starting complex is recovered as a mixture of $Pd(CO)(PPh_3)_3$ and of $Pd_3(CO)_3(PPh_3)_4$ [19], the latter probably being formed through the following sequence:

$$PdCl(COHex\text{-}n)(PPh_3)_2 \xrightarrow{MeOH} MeOCOHex\text{-}n + \underset{(\mathbf{I})}{[PdClH(PPh_3)_2]}$$

$$\mathbf{I} \xrightarrow{NEt_3} Pd^0 + HCl \cdot NEt_3$$

This result suggests that use of preformed complex **B**, leads to the ester, whereas in methanol as solvent and in the presence of NEt_3 no catalysis is observed because of the formation of inactive palladium(0) complexes.

When complex **C** is employed as catalyst precursor in MeOH, catalysis occurs (See Fig. 1) and the precursor is recovered as a mixture of complexes **B** and **C**. Probably, the catalytic activity is due only to acyl complexes, although the possibility that, under these conditions catalysis may occur via reaction pathway 2 cannot be ruled out.

It has been reported that $PdCl(PhCH_2)(PPh_3)_2$, which is related to intermediates **b** and **b′** of Schemes 1 and 2, reacts with carbon monoxide (ca. 3 atm; room temperature) in methanol in the presence of NEt_3 to yield methyl phenyl acetate, but that no intermediates could be isolated or observed. Under the same conditions, the closely related complex $PdCl(CH_2Ph)(PMe_3)_2$ yields the corresponding acyl complex $PdCl(COCH_2Ph)(PMe_3)_2$, with no detectable $Pd(CH_2Ph)(COOMe)(PMe_3)_2$. When the reaction solution was kept at 80 °C for 1 h there was quantitative formation of $PhCH_2CO_2Me$, together with $Pd(PMe_3)_4$ and palladium metal [22]. Interestingly, it was found that $Pd(CH_2Ph)(COOMe)(PMe_3)_2$, prepared by treatment of $PdCl(CH_2Ph)(PMe_3)_2$ with HgCl(COOMe) at 25 °C, is thermally stable, and heating at 80 °C does not result in reductive elimination of $PhCH_2COOMe$.

Under actual catalysis conditions (ca. 3 atm, 80 °C, $MeOH/NEt_3 = 1:1$; $PhCH_2Cl : Pd(PMe_3)_4 = 50:1$) only complex $PdCl(COCH_2Ph)(PMe_3)_2$ was observed by ^{31}P NMR spectroscopy. It was concluded that the product-forming step for the catalytic methoxycarbonylation of benzyl chloride is the alcoholysis of an acylpalladium intermediate and not reductive elimination of a methoxy carbonyl palladium benzyl species [22]*. Thus, this system has much in common with the one described in this paper.

Further insight into the product-forming step has been provided by studying the carbalkoxylation of aryl iodides catalyzed by $PdPPh_3$ complexes, in which the esters are formed by reductive elimination of a $(PhCO)Pd(OR)(PPh_3)$ intermediate rather than by direct nucleophilic attack on the acyl ligand [23].

It is noteworthy that carbonylation of (π-allyl)palladium complexes occurs practically quantitatively at low pressure and temperature to give β,γ-unsaturated esters when carried out in the presence of carboxylic acid anions. Other bases, such as ammines and alkoxides, have do not promote such carbonylation. It has been suggested that a (π-allyl)carboalkoxypalladium complex is a key intermediate, since carboxylic acid anions are thought to have a unique effect in promoting formation of carbalkoxy palladium intermediates [21] in which other bases are inactive. This was supported by the fact that (π-allyl)palladium chloride dimer reacts with (carbomethoxy) mercuric chloride to afford 3-butenoate [24].

In addition to a mechanism of the type just described for the carbonylation of allylic ethers catalyzed by (π-allyl)palladium complexes in the presence of M^+Y^- cocatalysts ($M = H, R_4N$; $Y =$ Halide, BF_4), it has also been proposed that catalysis occurs via addition of carbon monoxide to a (π-allyl)palladium moiety followed by reductive elimination of the resulting acyl ligand and a halide ligand [25].

Reuse of the catalytic system

The catalytic system, $PdClX(PPh_3)_2$–PPh_3 (X = Cl, COHex-n, COOMe; $Pd:P = 1:4$), was reused for several carbonylation experiments of 1-hexene, under usual experimental conditions. After each experiment, the reaction mixture was analyzed

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* It was found that complex C also reacts with methyl iodide or benzyl bromide to yield methylacetate or methyl phenylacetate quantitatively [20].

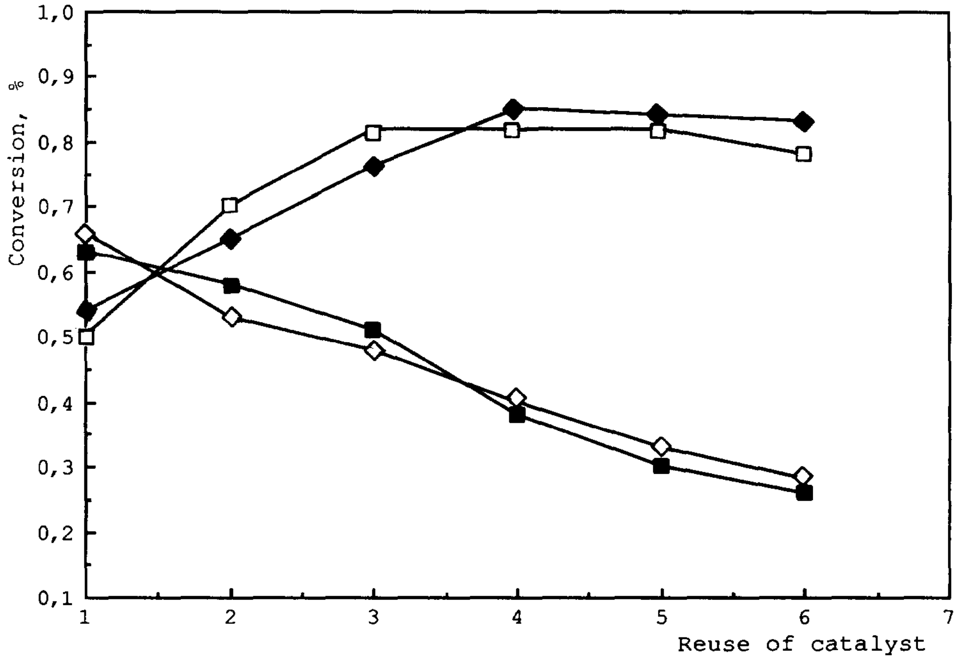

Fig. 1. Run conditions: temperature 95 °C; P(CO) 120 atm; 3 h; [$PdClX(PPh_3)_2$] = 10^{-2} M; [PPh_3] = 2 · 10^{-2}; Pd : 1-hexene = 1 : 80; ◆ X = Cl in n-BuOH; □ X = COHex-n in n-BuOH; ■ X = Cl in MeOH; ◇ X = COOMe in MeOH.

by GC to determine the amount of 1-hexene consumed. This amount was then added to the reaction mixture, and a new carbonylation experiment was carried out. The results are summarized in Fig. 1.

When the precursor is used with X = Cl or COHex-n in n-BuOH, the catalytic activity remains high even after 5–6 experiments. No palladium metal is observed at the end of this series of experiments. When the precursor is used with X = Cl or COOMe in MeOH, the catalytic activity after 5 experiments falls to ca. 1/3 of the initial value. After 3 experiments, decomposition of the palladium(II) complex to metallic palladium is noticed; at the end of the fifth experiment much metallic palladium is observed on the walls of the reaction vessel as a shiny mirror (see Experimental Section). At the end of the first experiment, even when starting from complex **C**, the precursor is recovered as a mixture of complexes **B** and **C**.

These results, together with those described earlier, suggest that in n-BuOH precursor **A** is transformed mainly to complexes of type **B**, which is stable and shows practically the same catalytic activity when reused several times. With methanol as solvent, precursor **A** gives rise to a mixture of complexes of type **B** and **C**. The latter decomposes to palladium(0) complexes and to metallic palladium, which are inactive, so that the catalytic activity falls below the initial value when methanol is used as solvent.

The fact that under catalytic condition it has been possible to isolate a Pd-carbalkoxy complex only in MeOH, whereas with higher alkanols only complex **B** can be isolated, is probably connected to the relative stabilities of complexes **B** and $PdCl(COOR)(PPh_3)_2$ (R = Me, Et, Pr, Bu). For the closely related system

$$\mathrm{PtCl(PPh_3)(CO)^+ + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtCl(PPh_3)_2(COOR) + H^+}$$

it has been found that the equilibrium constants, K_{eq} ($= k_1/k_{-1}$), determined from kinetic measurements on both the forward and reverse reactions, decrease with increase in the bulk of the alkanol (MeOH > EtOH > i-PrOH) [26]. The same order of stability has been found for complexes of the type (diene)PtCl(COOR) [27].

It is noteworthy that the initial catalytic activity is slightly higher in MeOH than in BuOH (Fig. 1), in spite of the fact that in MeOH part of the precursor is converted to the inactive complex C. Since in this paper we present strong evidence that catalysis involves reaction 1 (Scheme 1), the fact that catalytic activity is higher in MeOH than in BuOH suggests that the rate of the nucleophilic attack on the Pd–COR intermediate decreases when the bulk of the alkanol is increased, as found in reactions of $PdCl(COMe)(PPh_3)_2$ with MeOH and EtOH, and for the closely related termination reactions in the palladium(II)-catalyzed copolymerization of carbon monoxide with ethylene, for which the mechanism depicted below has been proposed [28]:

$$\mathrm{Pd{-}H \xrightarrow{C_2H_4} Pd{-}C_2H_5 \xrightarrow{CO} Pd{-}(COC_2H_5) \xrightarrow[CO]{C_2H_4}}$$

$$\mathrm{Pd{-}(COCH_2{-}CH_2)_nH \xrightarrow{ROH} RO({-}COCH_2{-}CH_2{-})_nH}$$

Experimental

General procedure

Yields and compositions of products were determined by GC, with a Hewlett-Packard gascromatograph model 5830 equipped with a Hewlett-Packard GC terminal model 18850. A 6 ft column of 5% Carbowax 20 *M* or a 6 ft column of 5% OV 17 was used, with helium as carrier gas.

IR spectra were recorded on Perkin Elmer Model 683 spectrometer. NMR spectra were recorded on a Varian T-60 instrument in $CDCl_3$ solution with TMS as internal standard. Mass spectra were recorded on a Hitachi Perkin Elmer RMU-6L spectrometer.

Materials

Carbon monoxide, quality N 37, was purchased from the S.I.O. Company. EtOH was commercial grade. 1-Hexene was passed through a column of neutral Al_2O_3 and distilled before use.

trans-$PdClX(PPh_3)_2$ (X = Cl, COHex-n, COOMe) were prepared as described previously [3,12,20,29].

Synthesis of trans-*$PdCl(COEt)(PPh_3)_2$*

A mixture of 70 mg of *trans*-$PdCl_2(PPh_3)_2$ (0.1 mmol) and 53 mg of PPh_3 (0.2 mmol) in 10 ml of EtOH was placed in a bottle which was introduced into an autoclave, which was then purged with carbon monoxide and pressurized with 20 atm of ethylene and 80 atm of CO at room temperature. The autoclave was then placed in a oil bath thermostated at 100 °C. After 4 h the autoclave was cooled in an ice bath then after ca. 1 day at room temperature depressurized. White microcrystals of the complex were filtered off, washed with EtOH, and dried under vacuum. Yield 80%. Found: C, 64.66; H, 4.91; Cl, 4.68 $C_{39}H_{35}ClOP_2Pd$ calcd.: C, 64.72; H, 4.88; Cl, 4.90%.

Catalytic experiments

Carbonylations were carried out in a 100 ml stainless steel autoclave immersed in a thermostated oil bath. Catalyst, substrate and solvent were contained in a Pyrex bottle placed in the autoclave in order to prevent contamination of other metallic species. Carbon monoxide pressure was maintained approximately constant.

In a typical experiment, 0.1 mmol of $PdCl_2(PPh_3)_2$, 0.2 mmol of PPh_3, 8.0 mmol of 1-hexene (1.0 ml), and 9 ml of alkanol were introduced into a Pyrex bottle which was placed in the autoclave, free volume of which was reduced to ca. 50 ml. The autoclave was purged with carbon monoxide. Carbon monoxide was introduced (100 atm), and the autoclave placed in a thermostated oil bath, in which it reached the working temperature in ca. 10 min. At the end of the reaction period (3 h) the autoclave was cooled in anice bath and slowly depressurized. The solid at the bottom of the bottle was filtered off and the reaction mixture analyzed. In some cases precipitation of complex **B** occured after most of dissolved carbon monoxide was removed.

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