Cobalt chloride and phase-transfer catalyzed carbonylation of benzyl chlorides*

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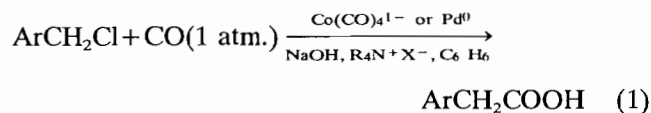
Abstract

A cobalt chloride–potassium cyanide system was found to catalyze carbonylation of benzyl chlorides into arylacetic acids under phase-transfer conditions The reaction takes place under mild conditions of temperature and carbon monoxide pressure. A catalytic cycle which includes complexes of the form $Co(CN)_{3-n}(CO)^{n-2}_{2+n}$ $(n=0-2)$ as active species is proposed.

Key words. Catalysis; Carbonylation; Cobalt complexes; Halide complexes; Cyanide complexes

Introduction

Transition metal catalyzed carbonylations are among the most important and useful methods for the synthesis of carboxylic acids. However these processes usually require high temperatures and pressures [1].

Recently [2] it has been shown that many of the classical metal-catalyzed reduction, oxidation, oligomerization and carbonylation reactions, require much milder reaction conditions when performed in two liquid phase systems in the presence of phase-transfer agents. For example, cobalt carbonyl [3, 4] or palladium complexes [5] were found capable of catalyzing the carbonylation of benzylic halides to the corresponding substituted acetic acids at ambient pressure and temperature (eqn. (1)).

$$ArCH_2Cl + CO(1 \text{ atm.}) \xrightarrow[\text{NaOH, } R_4N^+X^-, C_6H_6]{Co(CO)_4{}^{1-} \text{ or } Pd^0}$$

$$ArCH_2COOH \quad (1)$$

Recently [6] we have found that nickel cyanide complex is particularly efficient for the carbonylation of benzyl chlorides under phase-transfer conditions to arylacetic acid derivatives. The cobalt cyanide catalyst system has also proved to be very active for the car-

bonylation of a variety of other substrates**. We now wish to report that cobalt chloride–potassium cyanide catalyzes carbonylation of benzyl chlorides under phase-transfer conditions [8].

Experimental

General data

^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were recorded on a Nicolet 5ZDX FT-IR spectrometer. The progress of the reactions was monitored on a Packard model 417 gas chromatograph equipped with 5% DEGS on a Chromosorb W column. All solvents were distilled prior to use. $Co(CN)_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ were purchased from Strem Chemical Co. Benzyl chloride derivatives were obtained from Aldrich Chemical Co. Products were identified by comparison of their physical data (m.p., IR, NMR) with those of authentic samples.

General procedure for the carbonylation of benzyl chlorides

A 100 ml three-necked flask was charged under CO atmosphere with 2 mmol of KCN and 20 ml of 5 N NaOH. After stirring for 10 min, $CoCl_2 \cdot 6H_2O$ (1 mmol), Aliquat 336 (3 mmol) in 20 ml of toluene were added. The mixture was stirred under CO for 50 min in an oil bath held at 85 ± 3 °C. (Addition of the substrate before generation of the cobalt carbonyl complex leads

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*Dedicated to Professor J. Blum on the occasion of his sixtieth birthday. Part of this work was presented at the *55th Annual Meeting, Israel Chemical Society*, Tel-Aviv, Israel, Feb. 1990, p. 12.

**While this work was going, an article on the carbonylation of iodo compounds using $CoCl_2/KCN/BF_3 \cdot Et_2O/FeCl_2/PEG-400$ appeared [7].

TABLE 1. Carbonylation of benzyl chlorides catalyzed by the CoCl$_2$/KCN/Aliquat 336 system[a]

Substrate	Reaction time (h)	Conversion (%)	Isolated Yield[b] (%)
C$_6$H$_5$CH$_2$Cl	22	95	50
o-CH$_3$C$_6$H$_4$CH$_2$Cl	20	85	20
p-CH$_3$C$_6$H$_4$CH$_2$Cl	15	80	33
o-ClC$_6$H$_4$CH$_2$Cl	20	95	38
m-ClC$_6$H$_4$CH$_2$Cl	20	90	40
p-ClC$_6$H$_4$CH$_2$Cl	19	90	62
1-C$_{10}$H$_7$CH$_2$Cl[c]	20	90	40

[a]Reaction conditions: 20 mmol of substrate, 5 N NaOH (20 ml), CoCl$_2$·6H$_2$O (1 mmol), KCN (2 0 mmol), C$_6$H$_5$CH$_3$(20 ml), Aliquat 336 (2 mmol), CO (1 atm), 55 °C. [b]Yields of pure acetic acid derivatives. [c]1-Chloromethylnaphthalene.

mainly to hydrogenolysis of the benzyl chloride to give toluene derivatives owing to the formation of [Co(CN)$_5$R]$^{3-}$ complexes [9].) The temperature was lowered to 55 °C and the substrate (20 mmol) was then added. The stirring under CO was continued for 15–20 h (see Table 1) The reaction mixture was cooled to room temperature and the phases separated. The aqueous phase was acidified with 5% HCl and then extracted with ether (3×25 ml). The ether extracts were dried over MgSO$_4$ and concentrated to give the arylacetic acid derivatives. The organic phase was evaporated and the residue was chromatographed on silica gel and washed with 100 ml of a 1:1 ether/hexane mixture. Evaporation of the solvent gave the ketones and toluene derivatives.

Results and discussion

When benzyl chloride was treated for 22 h at 55 °C with catalytic amounts of hydrated cobalt chloride, potassium cyanide and carbon monoxide (1 atm.), under phase-transfer conditions using benzene and quaternary ammonium or phosphonium salts as the organic phase and 5 N of sodium hydroxide as the aqueous phase phenyl acetic acid was isolated in 50% yield (95% conversion) from the basic solution, toluene and 1,3-diphenylpropanone accumulated in the organic phase in 35% yield. Similar results were obtained with substituted benzyl halides.

The results given in Table 1 indicate that electron-withdrawing substituents (i.e. p-Cl, o-Cl) are beneficial relative to electron-donating groups (i.e. p-CH$_3$, o-CH$_3$).

(i) Effect of the phase-transfer agent
In the absence of phase-transfer agent the reaction was very slow (56% conversion of benzyl chloride after 5 h and 15% isolated phenyl acetic acid). A series of

TABLE 2 Carbonylation of benzyl chloride by CoCl$_2$/KCN in the presence of various quaternary onium salts[a]

Quaternary onium salt	Maximum reaction rate (mM h^{-1})
	2 11[b]
(C$_{10}$H$_{21}$)$_4$N$^+$Br$^-$	4 46
(C$_6$H$_{13}$)$_4$N$^+$Br$^-$	5 14
(C$_5$H$_{11}$)$_4$N$^+$Br$^-$	5 73
(C$_4$H$_9$)$_4$N$^+$Br$^-$	6 00
(C$_4$H$_9$)$_4$P$^+$Br$^-$	6 00
C$_{16}$H$_{33}$N(CH$_3$)$_3$$^+Br^-$	3 12
(C$_{12}$H$_{25}$)$_2$N(CH$_3$)$_2$$^+Br^-$	5.60
(C$_8$H$_{17}$)$_3$NCH$_3$$^+Cl^-$[c]	6.30
C$_6$H$_5$CH$_2$N(C$_2$H$_5$)$_3$$^+Cl^-$	2.54

[a]Reaction conditions: 10 mmol substrate, 5 N NaOH, CoCl$_2$ 6H$_2$O (1 mmol), KCN (2 mmol), C$_6$H$_5$CH$_3$ (20 ml), quaternary onium salt (3 mmol), CO (1 atm), 80 °C [b]Without phase transfer catalyst [c]As Aliquat 336
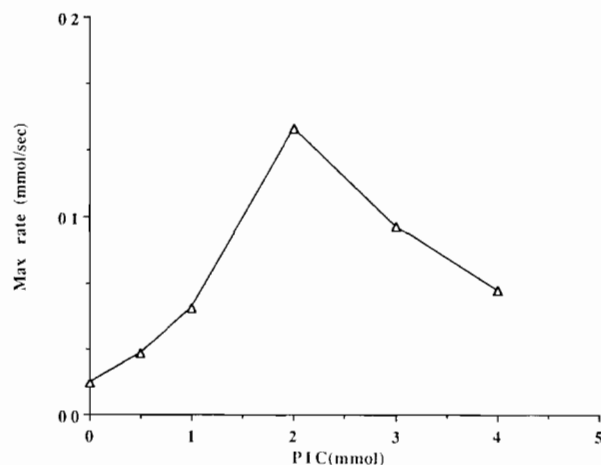

Fig. 1. Dependence of the maximum rate of carbonylation of benzyl chloride on the concentration of the phase-transfer catalyst (Aliquat 336) Reaction conditions as in Table 2

quaternary ammonium and phosphonium salts were used as phase-transfer agents in the carbonylation process (Table 2). In contrast to nickel cyanide catalyzed carbonylation of benzyl chlorides [6], methyltrioctyl- or tetrabutylammonium salts were found to be the most efficient phase-transfer agents. The rate of carbonylation was not only affected by the structure of the onium salt but also by its concentration (Fig. 1). The best results were obtained when the ratio between the ammonium salt and cobalt chloride was 2.

(ii) Effect of the cyanide
In the absence of cyanide absolutely no carbonylation reaction occurred. In this case brown solids separated in the aqueous phase. The concentration of the cyanide anion proved to have a significant influence on the rate of the carbonylation (Fig. 2). The highest maximum
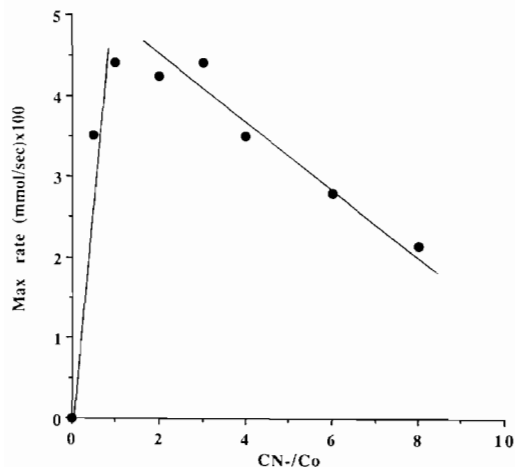
Fig. 2 Dependence of the maximum rate of carbonylation of benzyl chloride, on the ratio of KCN/CoCl₂ Reaction conditions as in Table 2.

Fig. 3. Dependence of the maximum rate of carbonylation of benzyl chloride on the base concentration. Reaction conditions as in Table 2.

rates were reached with a 2:1 ratio of $KCN/CoCl_2 \cdot 6H_2O$. Lower ratios caused partial extraction of the cobalt chloride into the organic phase and brown or pink solids separated*. Higher ratios gave low carbonylation rates in spite of complete cobalt extraction. It seems that at high ratios of $KCN/CoCl_2 \cdot 6H_2O$, complexes of the type $Co(CN)_5^{3-}$ and $Co(CN)_6^{3-}$ that have no catalytic activity are formed. By using $Co(CN)_2 \cdot 2H_2O$ instead of the $CoCl_2 \cdot 6H_2O/2KCN$ system no reaction took place. It is noteworthy that $Co(CN)_2 \cdot 2H_2O$ could not be extracted into the organic phase.

(iii) Effect of the base

The concentration of the aqueous phase was found to have a strong influence on the rate (Fig. 3). A 5 N NaOH solution gave the best results. Lower concentrations cause lower rates of the carbonylation process and at higher concentrations the catalyst system suffered poisoning after a short time.

(iv) The nature of the organic phase

The nature of the organic medium significantly affected both the conversion and the yield (Fig. 4). The results reported in Fig. 3 indicate that polar solvents promote faster reactions than non-polar ones, but the polar ones were not as selective. While in 4-methyl-2-pentanone the yield was only 25% of phenylacetic acid, in toluene or in benzene the yield increased to 50%.

Mechanistic considerations

A possible mechanism for the carbonylation reaction is illustrated in Scheme 1. Cobalt chloride with potassium cyanide forms cobalt(II) or cobalt(III) cyano complexes [11]. These complexes may react with carbon monoxide
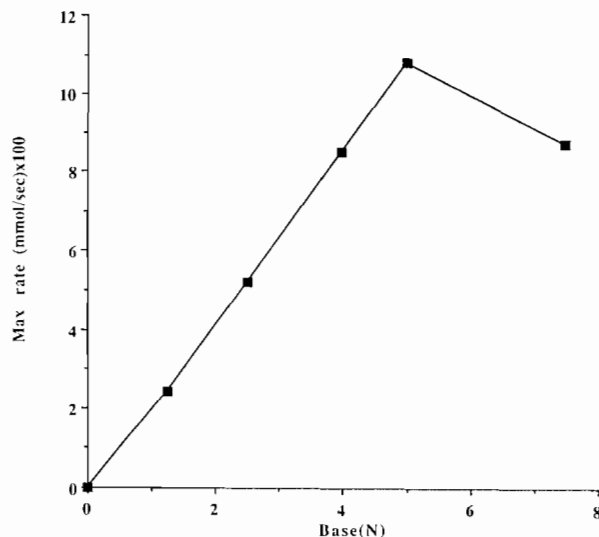

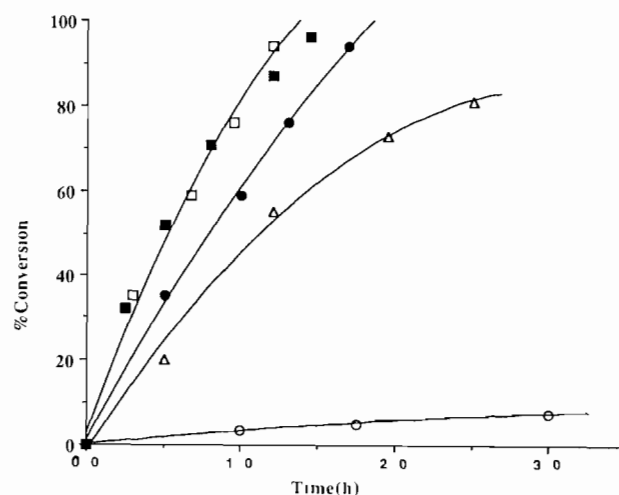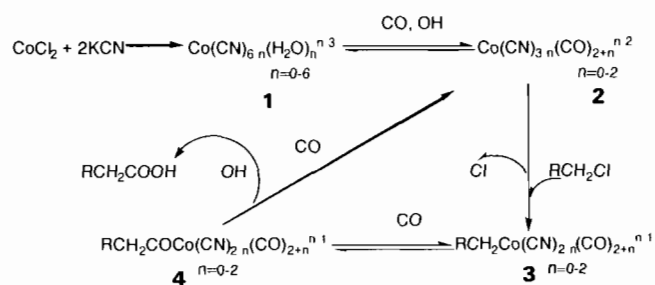*These solids should be $Co(OH)_2$ or $CoO(OH)$ [10].

Fig. 4 Conversion–time profiles for carbonylation of benzyl chloride in: 1,2-dichloroethane (○), hexane (△), toluene (●), t-amyl alcohol (■), 4-methyl-2-pentanone (□). Reaction conditions as in Table 2.

Scheme 1

under basic conditions to form cyanocarbonyl cobalt (1) complexes. The existence of such complexes was demonstrated by following the progress of the reaction

by FT-IR (under N_2 or Ar). We found that under N_2 the system $CoCl_2 \cdot 6H_2O/2KCN/Aliquat$ 336/5 N NaOH (at 80 °C), forms initially a cobalt cyanide complex that absorbs at 2117.1 and 2075.9±4 cm^{-1}. We attribute these absorptions to $Co(CN)_6^{3-}$ and $Co(CN)_5^{3-}$ or the analogs $Co(CN)_5OH_2^{3-}$ and $Co(CN)_5OH^{3-}$ [10, 11]. By replacement of the nitrogen atmosphere by carbon monoxide for 10 min, three new absorptions at 1922.8, 1983.1 and 2091.9 cm^{-1} appeared. The formation of these new absorptions was completed after 1 h. By that time, a shoulder at 1888.7 cm^{-1} began to appear which indicated the formation of a cobalt carbonyl anion $Co(CO)_4^{1-}$ [12, 13]. By addition of 1.5 mmol of α-chloro-p-xylene new absorptions at 1950.4, 1815.8 and 1713 ± 4 cm^{-1} appeared. The absorption at 2117.1 and 1887.7 ± 4 cm^{-1} of $Co(CN)_6^{3-}$ and $Co(CO)_4^{1-}$ did not disappear. The band at 1713 cm^{-1} indicates the formation of the acyl cobalt complexes 4 [13]. By following the experiment mentioned above by ^{13}C NMR (under N_2, Ar or CO) in C_6D_6 the ammonium cyanide resonance peak appeared at 165.74 ppm ($C \equiv N$) [14]. Addition of $CoCl_2 \cdot 6H_2O$ resulted in formation of four peaks at 143.86, 143.37, 134.13 and 133.52 ppm The carbonylation of the cobalt cyanide complex gave only two peaks at 203.68 and a broad one at 143.95 ppm. Addition of α-chloro-p-xylene to the carbonyl complex led to the disappearance of the former peaks and formation of new ones at 155.31, 148.97, 138.17, 133.31, 130.87, 46 ($-CH_2-$) and 21.23 ($-CH_3$) ppm.

As we assumed that initially the cyano Co^{III} or Co^{II} complexes 1 are formed*, carbonylation of these complexes leads under the reaction conditions to the low valent cyano carbonyl cobalt compounds 2. Reaction of benzyl chloride with 2 furnishes the alkyl or acyl complexes 3 or 4, respectively. Nucleophilic attack by hydroxy anion on 4 then liberates the acid in the aqueous phase and regenerates 2. The effect of the concentration of the base and CN$^-$ on the rate of formation of 2 is in agreement with the observation given by Halpern et al. [15].

The role of the ammonium salt is to transfer the cobalt cyano complexes and the OH$^-$ to the organic phase while the carbonylation reactions are proceeding. The fact that ammonium salts that are also surfactants (i.e. those having one long chain and three short alkyl groups) are not effective, suggests that our reaction is

proceeding by an extraction rather than an interfacial mechanism [16]. This behavior is similar to cobalt carbonyl catalyzed carbonylation of benzyl bromides under phase-transfer conditions [17].

In conclusion we found that under phase-transfer conditions the cyano–carbonyl–cobalt system is a useful system for the carbonylation of benzyl chlorides and other substrates.

*Under very complete inert conditions we were able to detect only the cyano Co^{II} complex by IR spectroscopy (2075.9±4 cm^{-1}).

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