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Catalytic carbonylation of benzylic and allylic bromides by a rhodium zwitterionic complex under phase transfer catalysis conditions [☆]

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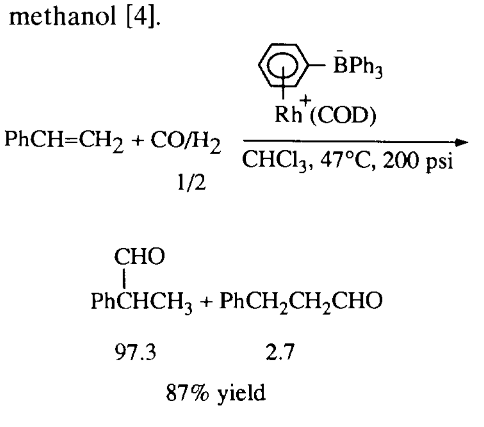
Abstract

The zwitterionic rhodium complex, (COD)Rh(η^6-$C_6H_5BPh_3$) (**1**), can catalyze the carbonylation of benzylic and allylic bromides in the presence of 5 N NaOH and CH_2Cl_2 at atmospheric pressure and 40°C, with $(C_6H_{13})_4N^+HSO_4^-$ as the phase transfer catalyst, to give carboxylic esters as the major products.

Keywords: Rhodium; Carbonylation; Zwitterionic complex; Phase transfer catalysis

1. Introduction

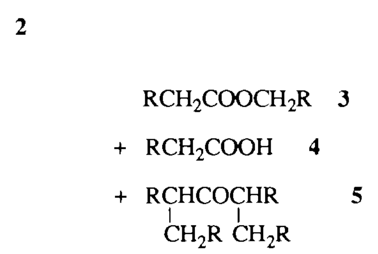
Metal complex and phase transfer catalyzed carbonylation of halides has been the subject of many publications and patents, with carboxylic acids being the usual reaction products [1]. There are no reports of rhodium complexes being used as the metal catalyst in phase transfer catalyzed carbonylation reactions. It has been recently reported that the zwitterionic rhodium complex **1** shows excellent catalytic activity towards the homogeneous hydroformylation of olefins (Eq. (1)) [2,3].It was of interest to investigate the activity of this catalyst under phase transfer conditions. Complex **1** is readily obtained from rhodium chloride, sodium tetraphenylborate and 1,5-cyclooctadiene in aqueous methanol [4].



(1)

2. Results and discussion

The catalytic activity of **1** under phase transfer conditions was first examined with benzylic halides as substrates. Treatment of a benzylic bromide (**2**, R = Ar) with carbon monoxide and **1** in methylene chloride, and 5 N sodium hydroxide, with tetra-n-hexylammonium hydrogen sulfate as the phase transfer agent, usually afforded the ester **3** as the major product with the acid **4** and/or ketone **5** as by products (Eq. (2)). Small amounts (< 5%) of the dimer RCH_2CH_2R and the ether RCH_2OCH_2R were formed in some cases. The results are presented in Table 1.



$$\underset{\mathbf{2}}{RCH_2Br} + CO \xrightarrow[40°\,C,\ 1\ atm,\ 24-48\ h]{\mathbf{1},\ CH_2Cl_2,\ (C_6H_{13})_4N^+HSO_4,\ 5\ N\ NaOH} RCH_2COOCH_2R\ \mathbf{3} + RCH_2COOH\ \mathbf{4} + \underset{CH_2R\quad CH_2R}{RCHCOCHR}\ \mathbf{5} \qquad (2)$$

Benzyl bromide and *p*-methylbenzyl bromide gave the corresponding ester **3** in good yield. The *p*-fluoro-substituted reactant did not afford the ester in the presence of tetrahexylammonium hydrogen sulfate, as it did when palladium catalysts were used [5]. Instead, it gave the ketone **5** as the major product. When tetrahexylammonium bromide was used as the phase

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[☆] Dedicated to Fausto Calderazzo, a warm and sensitive person, who has made pioneering contributions in Chemistry.

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Table 1
Products obtained from the rhodium zwitterionic complex **1** catalyzed carbonylation of **2** [a]

2, R =	Phase transfer catalyst [b]	Yields of products [c,d]		
		3	**4**	**5**
Ph	A	72	16	–
	B	65	21	–
2-Naphthyl	A	53	4	4 [f]
	B	76	5	–
p-$CH_3C_6H_4$	A	70	8	–
o-$CH_3C_6H_4$	A	20	35	–
m-$CH_3C_6H_4$	A	40	8	–
	B	60	15	–
p-FC_6H_4	A	–	27	34 [f]
	B	47	13	9
$C_6H_5CH=CH$ [g]	A	40 [f]	5	28 [f]

[a] See Experimental section for general procedure. [b] A = $(C_6H_{13})_4N^+HSO_4^-$, B = $(C_6H_{13})_4N^+Br^-$. [c] Products were identified by comparison of spectral data (IR, NMR, MS) and GC retention times with those of authentic samples. [d] Isolated yield. [e] 36% of the ketone RCH_2COCH_2R was isolated. [f] New compound. [g] The dimer $C_6H_5CH=CHCH_2CH_2CH=CHC_6H_5$ was formed in 17% yield.

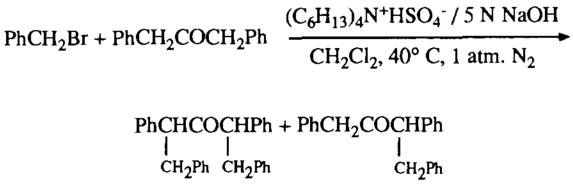
transfer catalyst, p-fluorobenzyl bromide was converted into the ester (**3**, 47% yield), acid (**4**, 13%), and the ketone (**5**, 9%). It should be noted that the yield of ester was also higher for 2-napthyl and m-methylbenzyl bromide when $(C_6H_{13})_4N^+Br$ was used rather than $(C_6H_{13})_4N^+HSO_4^+$ as the phase transfer catalyst. In the case of cinnamyl bromide, the reaction was complete within 24 h, giving the ester (**3**, R = PhCH=CH) as the major product, with the ketone (**5**, R = PhCH=CH) formed in 28% yield. Several solvents were used as the organic phase, of which methylene chloride was the best. This could be due to the fact that the rhodium zwitterionic catalyst is soluble in methylene chloride at 4°C. The catalyst is only soluble in benzene at higher temperature (80°C) and this results in complicated reactions. Use of amyl alcohol as the organic phase at 50°C afforded only 15% of the acid but no ester, while no carbonylated products were obtained at 100°C, when benzyl bromide was the starting material. Use of low base strength (0.5 N NaOH) resulted mainly in hydrolysis, product benzyl alcohol, from benzyl bromide. At high base strength (10 N NaOH), the alkylated ketone (**5**) was the major product. This is similar to the phase transfer catalyzed reaction of $Fe(CO)_5$ which gave the ketone (**5**) in considerable yield at high base concentrations [7].

The effectiveness of the phase transfer catalyst was examined in the carbonylation of benzyl bromide. The results in Table 2 show that whereas benzyltriethylammonium chloride (TEBA) was of little use, the tetrahexylammonium salts, $(C_6H_{13})_4N^+Br^-$ and $(C_6H_{13})_4N^+HSO_4^-$ afforded the ester, $PhCH_2COOCH_2Ph$, in 65–72% yield. The crown ether, 18-crown-6 in the presence of base, gave the ester in 60% yield. Ineffective phase transfer agents include PEG-400 and TDA-1.

In order to determine whether the ester **3** is formed via the acid **4**, and to see whether the alkylated ketone **5** is formed from the simple ketone RCH_2COCH_2R, by the phase transfer catalyzed reaction with RCH_2Br, the following reactions were carried out in the absence of **1** and carbon monoxide.

$$PhCH_2Br + PhCH_2COOH \xrightarrow[CH_2Cl_2,\ 40°\ C,\ 1\ atm.\ N_2]{(C_6H_{13})_4N^+HSO_4^-\ /\ 5\ N\ NaOH} PhCH_2COOCH_2Ph \quad (3)$$

80° C



$$PhCH_2Br + PhCH_2COCH_2Ph \xrightarrow[CH_2Cl_2,\ 40°\ C,\ 1\ atm.\ N_2]{(C_6H_{13})_4N^+HSO_4^-\ /\ 5\ N\ NaOH} \underset{CH_2Ph}{PhCH}CO\underset{CH_2Ph}{CHPh} + PhCH_2CO\underset{CH_2Ph}{CHPh} \quad (4)$$

After 60 h, in the reaction of halide with acid conversion was not complete, whereas it was in the halide-ketone reaction, These results not only indicate that the ester **3** and ketone **5** are generated in the absence of the metal catalyst but that the formation of the ketone **5** is faster than that involving the ester **3**. When the carbonylation of benzyl bromide catalyzed by **1** was effected in the absence of a phase transfer catalyst, the carboxylic acid was obtained in 10% yield. It has been shown that crown ether is a good catalyst for the phase transfer catalyzed esterification of carboxylic acids [6].

The question arises as to whether other rhodium complexes could catalyze the carbonylation reaction under phase transfer conditions. The cationic complex $[Rh(COD)(PPh_3)_2]^+PF_6^-$ and the neutral compounds $RhCl_3 \cdot 3H_2O$ and $[Rh(COD)Cl]_2$ were used as catalysts for the carbonylation of benzyl bromide. Surprisingly, none of these complexes gave the ester, the major products being the acid **4**, and the ketone **5**. The results are presented in Table 3.

Table 2
Effect of phase transfer catalyst on the carbonylation of **2** R = Ph [a]

Phase transfer agent	Products (% yield)	
	$PhCH_2COOH$	$PhCH_2COOCH_2Ph$
$(C_6H_{13})_4N^+HSO_4^-$	16	72
$(C_6H_{13})_4N^+Br^-$	21	65
TEBA [b]	16	–
PEG-400	–	Trace
TDA-1 [c]	Trace	–
18-Crown-6/KOH [d]	–	60
$(PPh_3)_2NCl$	21	–
– [e]	10	–

[a] Reaction conditions are the same as the general procedure with 0.1 mmol used of the different phase transfer catalyst. [b] Benzyltriethylammonium chloride. [c] $N(CH_2CH_2OCH_2CH_2OCH_3)_3$ [d] 5 mmol KOH was used instead of 15 ml of 5 N·NaOH [e] No phase transfer catalyst.

Table 3
Phase transfer catalyzed carbonylation of benzyl bromide with different rhodium catalysts [a]

Rhodium complex	Products (%5 yield) [b]		
	$PhCH_2COOH$	$PhCH_2COOCH_2Ph$	$PhCH(CH_2Ph)COCH(CH_2Ph)Ph$ [c]
1	16	72	–
$RhCl_3 \cdot 3H_2O$ [c]	15	–	45
$[Rh(COD)(PPh_3)_2]^+ PF_6$	35	–	45
$[Rh(COD)Cl]_2$	30	–	20

[a] See experimental for general procedure. [b] Isolated yield. [c] Known compound. [7] [d] D benzyl other was isolated in 22% yield.

The following mechanistic scheme can account for the carbonylation of halides catalyzed by the rhodium zwitterion **1** (Scheme 1). The rhodium zwitterion **1** can react with carbon monoxide to give **6**. Reaction of the latter with $R_4N^+OH^-$ would result in the sequential formation of the hydride **7** (the formation of CO_2 was also detected by isolation of $BaCO_3$ after passage of the solvent gases through $Ba(OH)_2$) and the dianionic rhodium complex **8**. The halide can then convert **8** into **9**, which undergoes ligand migration to give **10**. Steps A and B would determine the product distribution. It was found that the phase transfer catalyzed reaction of halide with acid (Eq. (3)) is slower than the reaction of halide with ketone (Eq. (4)). Therefore if step B is favoured then the ketone will be formed and the halide will be consumed for the synthesis of **5**, thereby reducing the formation of the ester **3**. Rhodium complexes, irrespective of the oxidation state of the metal, catalyse the carbonylation of halides, but only the rhodium zwitterion **1** gives the ester **3**. It is conceivable that the η^6-coordinated benzene ring with the anionic triphenyl boron substituent hinders the formation of the intermediate **11**. In contrast, the other rhodium complexes (Table 2) are more susceptible to reaction with benzyl bromide to form an acyl alkyl rhodium intermediate, leading to the ketone **5**.

When $Pd(PPh_3)_4$ is used as the catalyst for the carbonylation of secondary halides, esters and acids are formed in low yields [5], whereas with the rhodium zwitterion **1** there was no reaction when α-phenethyl bromide was exposed to carbon monoxide. There was no reaction with β-bromostyrene under the same conditions.

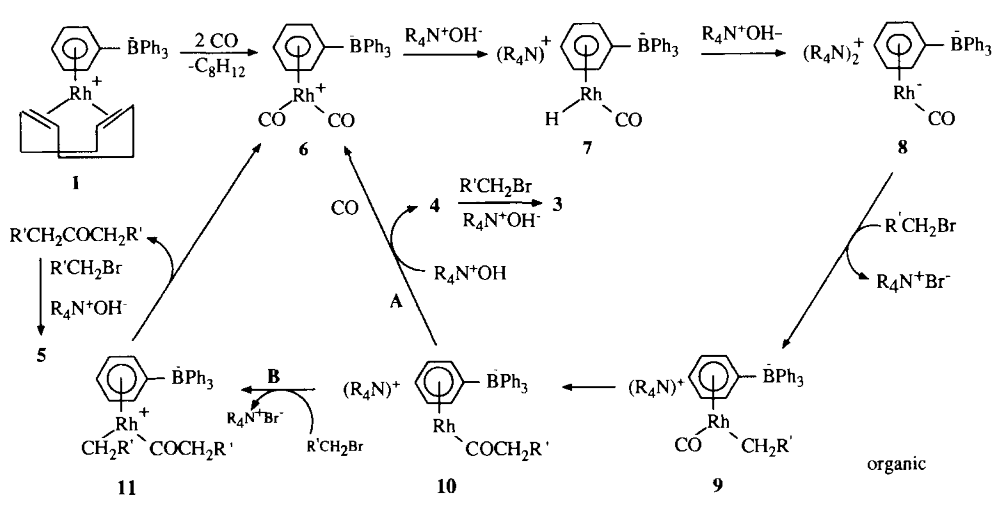
In conclusion, rhodium complexes catalyze the phase transfer catalyzed carbonylation of benzylic and allylic bromides. The zwitterionic rhodium complex brings about alkoxycarbonylation, while cationic and neutral rhodium complexes catalyze symmetrical ketone formation. These are the first examples of the use of zwitterionic rhodium complexes under phase transfer conditions, and the first report of any rhodium catalyzed carbonylation process under phase transfer conditions.

3. Experimental section

3.1. General

Infrared spectra were recorded on a Bomem-MB 100FT-IR spectrometer. Proton and carbon magnetic resonance spectra were recorded on a Gemini 200 or a Varian XL-300 spectrometer. Mass spectra were obtained on a VG 7070E mass spectrometer. Gas chromatographic determinations were carried out with an OV-17 packed column. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ. The benzylic and allylic halides were commercial products

$R_4N^+HSO_4^- + OH^- \longrightarrow R_4N^+OH^- + HSO_4^-$ aqueous



Scheme 1.

and were used as received. $[Rh(COD)(PPh_3)]_2^+PF_6^-$ was synthesized by a published procedure [8]. $[Rh(COD)Cl]_2$ and $RhCl_3 \cdot 3H_2O$ were commercial products.

3.2. General procedure for the rhodium complex catalyzed carbonylation of halides

The rhodium zwitterionic complex **1** (0.05 mmol) was stirred with methylene chloride (15 ml) under a slow stream of carbon monoxide at 40°C until **1** had dissolved, giving a yellow solution. To the latter was added 5 N NaOH (15 ml) and tetrahexylammonium hydrogen sulfate (0.1 mmol). The mixture was stirred at 40–45°C until the organic phase turned pale green (15 min). A methylene chloride (5 ml) solution of the halide (5 mmol) was added dropwise and stirring was continued, the reaction being monitored by gas chromatography. When the conversion was complete (24–48 h, reaction followed by NMR and GLC), distilled water (20 ml) was added and the organic phase was separated and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The ester **3** and the ketone **5** were isolated by column chromatography of the crude product(s) on silica gel with hexane and ethyl acetate as the eluant. The aqueous phase was acidified with dilute HCl and extracted with ethyl acetate (2 × 25 ml). The combined organic extract was dried ($MgSO_4$), and the solvent removed by rotary evaporation to give the carboxylic acid. The compounds were identified by comparison of their spectral data with those of authentic samples. The following compounds are new.

3: $R = C_6H_5CH{=}CH$. m.p. 67–69°C. IR ν(CO) 1730 cm^{-1}. ^1H NMR δ ($CDCl_3$): 3.20 (dd, 2H, $J = 0.9$ Hz, CH_2CO), 4.68 (dd, 2H $J = 0.9$ Hz $-OCH_2$), 6.23 (m, 2H, $2(CH{=}CHCH_2)$), 6.43 and 6.57 (dd, 2H, $J =$ 15.9 Hz; $2(CH{=}CHCH_2)$), 7.35 (m, 10H, aromatic protons). ^{13}C NMR δ ($CDCl_3$): 39.07 (CH_2CO), 66.04 (OCH_2), 122.23, 122.33, 123.62, 126.74, 126.94, 127.27, 128.21, 128.74, 128.85, 129.17, 129.24, 134.21, 135.03, 137.43 (aryl and olefinic carbons); 171.98 (CO). MS (m/e) 278 $[M]^+$, 135 $(M - RCH_2)^+$; 117 $(M - RCH_2CO)^+$. Anal. Calcd. for $C_{19}H_{18}O_2$; C, 81.97; H, 6.52. Found: C, 81.84; H, 6.20.

5: $R = C_6H_5CH{=}CH$, m.p. 145–147°C. IR ν(CO) 1702 cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.45 (m, 2H, $2(CH_2CH)$), 2.73 (m, 2H, $2(CH_2CH)$), 3.59 (m, 2H, 2(CHCO)), 6.14 (m, 4H, 4(=CH)), 6.36 and 6.56 (dd, 4H $J = 15.8$ Hz, $4(C_6H_5CH{=})$), 7.23 (m, 20H, aromatic protons) MS (m/e) 494 $[M]^+$, 261 $(M - RCH_2CHR)^+$, 233 $(M - RCH_2CH(CO)R)^+$. Anal. Calcd. for $C_{37}H_{34}O$ C, 89.83; H, 6.93. Found: C, 89.84; H, 6.60.

5: $R = p\text{-}FC_6H_4$. m.p. 146–148°C. IR ν(CO) 1706 cm^{-1}. ^1H NMR δ ($CDCl_3$). 2.68 (dd, 2H, $J = 6$Hz, (CH_2CH)), 3.17 (dd, 2H, $J = 8.65$ Hz, (CH_2CH)), 3.76 (dd, 2H, $J = 6.4$ Hz, 2(CHCO)), 6.81 (dd, 16H, $J = 7$ Hz, aromatic protons). MS (m/e) 462 $[M]^+$, 245 $(M - RCH_2CH)^+$, 217 $(M - RCH_2CH(CO)R)^+$. Anal. Calcd. for $C_{29}H_{22}F_4O$, C: 75.30; H, 4.80; F, 16.44. Found: C, 74.97; H, 5.08; F, 16.22.

5: $R = 2$-*naphthyl*. IR ν(CO) 1710 cm^{-1}. ^1H NMR δ ($CDCl_3$): 3.06 (dd, 2H, J = 8 Hz, (CH_2CH)), 3.49 (dd, 2H, $J = 10.1$ Hz, (CH_2CH)), 3.86 (dd, 2H, $J = 8$Hz, 2(CHCO)), 7.35 (m, aromatic protons). MS (m/e) 590 $[M]^+$, 309 $(M - RCH_2CHR)^+$, 281 $(M - RCH_2CH(CO)R)^+$. Anal. Calcd. for $C_{45}H_{34}O$: C, 91.48; H, 5.81. Found: C, 91.84; H, 6.01.

Acknowledgements

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