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Cobalt-Catalyzed Carbonylation of Benzyl Halides Using Polyethylene Glycols as Phase-Transfer Catalysts

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Hydroxycarbonylation of benzyl and substituted benzyl chloride and bromide derivatives was achieved in good yields (up to 97.6%) and quantitative chemoselectivity, in the presence of $Co_2(CO)_8$ as the transition metal and polyethylene glycols as the phase-transfer catalyst in an organic solvent/20% aqueous NaOH two-phase system under mild conditions (1 bar CO, room temperature). η^1-Benzyl-, η^3-benzyl-, and (η^1-phenylacetyl)cobalt carbonyls were investigated as intermediates of this catalytic process.

Introduction

The carbonylation of benzyl halides and their derivatives is one of the most widely investigated transition metal catalyzed carbonylation reactions.[2−4] This reaction is one of the first examples of the combination of phase-transfer catalysis with transition metal chemistry (TM-PTC) and is the most promising in terms of industrial application.[5] Surprisingly, while a number of complexes were tested in TM-PTC studies ($Fe(CO)_5$,[3w,y] $[PhC(O)Fe(CO)_4]^-$,[4f] $Co_2(CO)_8$,[4b,d] $Na[Co(CO)_4]$,[3w,4c] $[Co(CO)_4]^-$/resin,[4g] $Co(CO)_3(NO)$,[4e] $[Co(CN)_6]^{3-}/[Co(CO)_4]^-$,[4h] $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$[4a]) as transition metal catalysts (or precursors), quaternary ammonium salts were used almost exclusively as PT agents for these reactions.

The practical application of this reaction is still limited on economic grounds.[5,6] Our main goal was to achieve some progress in this respect, aiming therefore to use (i) mild conditions, (ii) an inexpensive transition metal complex, (iii) a cheap PT agent, which moreover should be effective in low concentration, and (iv) an economical solvent, which results in good separation during workup or no solvent at all, and (v) to avoid environmental and safety problems.

We now report on the cobalt-catalyzed hydroxycarbonylation of benzyl halides using biphasic (BP) and phase-transfer catalytic (PTC) reaction conditions. Polyethylene glycols were chosen as PT agents in the latter

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case. There are surprisingly few reports on the use of these cheap and efficient[7] phase-transfer agents in TM-PTC.[8]

The other goal set by this study was to utilize some recently accumulated knowledge[9] on possible organometallic intermediates of the hydroxycarbonylation reactions[10] to gain additional insight into the mechanism.

Experimental Section

Starting materials were of commercial origin, their purity was determined by GLC, and they were distilled, if necessary, before use. $Co_2(CO)_8$ was either made by the method of Szabó et al.[11] or purchased from Aldrich Chemical Co. Fusel oils were distillery waste and were distilled before use, using a 1.3 m column filled with glass rings; the first drop generally appeared at 118 °C, and practically all material came over below 132 °C headspace temperature. The fractions above 120 °C were used; their composition varied slightly and were determined by GLC[12a] (3-Me-butan-1-ol 80−85%, 2-Me-butan-1-ol 15−20%).

All operations, until completion of the catalytic reactions, were performed according to standard Schlenk techniques.[13] CO was treated with 10% KOH before use.

Infrared spectra were recorded with an IR 75 (Carl Zeiss, Jena, Germany) and Bruker FT-IR IFS 113V or Perkin-Elmer 283 spectrometer, and ^{1}H- and ^{13}C-NMR spectra were recorded with 80-MHz BS-487 (Tesla, Brno, CSFR), Varian EM-360, Bruker WP-80 (FT, 80 MHz), and Bruker AMX-400 (FT, 400 MHz) instruments; GLC measurements were made with a Hewlett-Packard HP-5830 A or Varian 6000 gas chromatograph with a 1.3 m × 3 mm Porapak P column.

Table 1. Carbonylation of Benzyl Halides and Their Substituted Derivatives

	mmol	PEG, M (mmol)	org phase[a]	yield, %[b]	TON[c]
$PhCH_2Cl$	15[d]	400 (1)	*t*-AmOH	97.6	14.6
	15[d]	400 (0.5)	*t*-AmOH	83	12.5
	12[e]	400 (1)	*t*-AmOH	80	9.6
	12[e]	400 (1)	MP	37	4.4
	15[d]		*t*-AmOH	67	10
	15[d]	600	*t*-AmOH	85	12.8
	25[d]	400 (1)	*t*-AmOH	89.7	22.4
	50	400 (1)	*t*-AmOH	67.6	33.8
	15	2000 (1)	*t*-AmOH	78.3	11.7
	25	400 (1)	FO	82	20.5
	30		FO	85	25.5
	30	400 (1)	FO	80	24.0
	90		FO	80	72
	30	400 (2)	none	70	20.8
	30		none		
$PhCH_2Br$	15[e]	400 (1)	*t*-AmOH	65	24.4
p-$MeC_6H_4CH_2Cl$	15[d]	400 (1)	*t*-AmOH	71	10.7
m-$MeC_6H_4CH_2Cl$	15[d]	400 (1)	*t*-AmOH	52	7.8
o-$MeC_6H_4CH_2Br$	12[d]	400 (1)	*t*-AmOH	22	6.6
	12[d]	400 (1)	Mp	64	19.2
$Me_5C_6CH_2Cl$[f]	7.5[g]	400 (1)	*t*-AmOH	9.6	1.4
	7.5[g]	400 (0.5)	MP	14.6	2.2
	7.5[g]		*t*-AmOH	18.9	2.8
p-$BrC_6H_4CH_2Br$	12[e]	400 (1)	*t*-AmOH	63	18.9
p-$ClC_6H_4CH_2Cl$	15[d]	400 (1)	*t*-AmOH	66	9.9
m-$ClC_6H_4CH_2Cl$	7.5[g]	400 (1)	*t*-AmOH	35	5.2
	7.5[g]		*t*-AmOH	29	4.4
o-$ClC_6H_4CH_2Cl$	7.5[g]	400 (1)	*t*-AmOH	30	4.5
	7.5[g]		*t*-AmOH	44	6.6
p-$FC_6H_4CH_2Br$	7.5[g]	400 (1)	*t*-AmOH	24	3.6
	7.5[g]		*t*-AmOH	39	5.8
m-$FC_6H_4CH_2Br$	7.5[g]	400 (1)	*t*-AmOH	26	3.9
o-$FC_6H_4CH_2Br$	7.5[g]	400 (1)	*t*-AmOH	27	4.0
	7.5[g]		*t*-AmOH	34	5.1
1-$C_{10}H_7CH_2Cl$	15[d]	400 (1)	*t*-AmOH	52	7.8
	15[d]		*t*-AmOH	14	2.1
2-$C_{10}H_7CH_2Br$	12[d]	400 (1)	*t*-AmOH	63	18.9

[a] t-AmOH = 2-methylbutan-2-ol; MP = 4-methylpentan-2-one; FO = fusel oil; none = only substrate represented organic phase. [b] Isolated yields; the products were identified by their melting point and ^{1}H-NMR spectra. [c] Turnover number: molecule of acid per starting Co atom. [d] 12.5 mL of aqueous NaOH/12.5 mL of organic solvent; r.t., 1 bar CO; 0.5 mmol of $Co_2(CO)_8$. [e] 10 mL of 15−20% aqueous NaOH/10 mL of organic solvent; r.t., 1 bar CO; 0.2 mmol of $Co_2(CO)_8$. [f] The reaction mixture becames gelatinous as the carbonylation proceeds. [g] 6.25 mL of aqueous NaOH/6.25 mL of organic solvent; r.t., 1 bar CO; 0.25 mmol of $Co_2(CO)_8$.

Carbonylation Experiments. All carbonylation reactions were performed in three-necked reaction vessels equipped with a gas inlet (through a sintered glass end), outlet, and a GC septum fixed into a glass tube (to enable injecting the reagents without opening the reaction vessel). External magnetic stirring was applied. This reaction vessel was flushed 3 times with CO before starting the experiments. Since the conditions used in all the carbonylation experiments were the same, a representative procedure is described below. Variations in the experimental parameters are given in Table 1.

Carbonylation of Benzyl Chloride in 2-Methylbutan-2-ol/Water. 1. Biphasic Reaction Conditions. A mixture of dicobalt octacarbonyl [170 mg (0.5 mmol)], 12.5 mL of 2-methylbutan-2-ol, and 12.5 mL of 20% aqueous NaOH was

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stirred at room temperature while 0.2−0.5 mL/s CO gas was bubbled into the liquid mixture. The dark brown-red mixture turned light blue after 3−5 min, benzyl chloride (or bromide) (1.73 mL, 15 mmol) was injected, and after being stirred for 5 min, the solution became deep brown-red again. Stirring, under carbon monoxide, was continued for an additional 5 h and the conversion determined by taking aliquots every 0.5 h and analyzing these by GC. After 5 h GC analysis showed complete conversion of benzyl chloride and at the same time the color of the reaction mixture changed again, now to lemon-yellow. After the yellow color developed the reaction mixture was no longer handled in an inert atmosphere. The reaction mixture was transferred to a separatory funnel, the aqueous and organic phases were separated, and the aqueous phase was subsequently washed with 10 mL of benzene (or toluene) and then acidified with 36% aqueous HCl (until pH ∼ 1 was reached). During acidification a precipitate was formed, which was separated by filtration or decantation. The (wet) precipitate was then extracted with Et_2O (3 × 10 mL), and the extract was dried over anhydrous Na_2SO_4 or $MgSO_4$. Finally the ether was removed at reduced pressure and white crystalline phenylacetic acid was obtained (identified by ^{1}H-NMR (δ, DMSO-d_6) 3.56 (s, 2H), 7.24 (s, 5H), and 10.5 (s, br, 1H) and mp 77.0 °C (measured) lit. (76−77 °C[12b])). Yield: 1.37 g (67%).

2. Phase-Transfer Conditions. In these experiments the phase-transfer agent (PEG) was placed in the reaction vessel after $Co_2(CO)_8$ had been added. All other conditions were as described above and in Table 1. The substituted arylacetic acid products were identified by melting points[13c] and ^{1}H- and ^{13}C-NMR spectra.[13d]

Infrared Spectroscopic Investigation of the Reaction Mixtures. Reaction of Dicobalt Octacarbonyl with Sodium Hydroxide. In a thermostated (25 °C) reaction vessel, equipped with a magnetic stirrer, gas buret (paraffin oil), injection neck and gas inlet/outlet tube, 170 mg (0.5 mmol) of dicobalt octacarbonyl was dissolved in 10 mL of 2-methylbutan-2-ol (CO atmosphere). The solution was stirred for 5 min, 10 mL of 20% aqueous NaOH was added, and stirring was continued for ∼1.5 h. At the beginning 4.4 mL gas was evolved, and then gas absorption was observed with the volume change at the end being +2.1 mL. Samples were taken for infrared analysis from the liquid and for GLC from the gas phase. Infrared analysis showed $[Co(CO)_4]^-$ (∼1900 cm^{-1}, vs) as the only cobalt carbonyl species present, distributed in a 70:30 ratio between the aqueous and organic phase. GC analysis showed 1.5% H_2 and 98.5% CO in the gas phase, the amount of H_2 corresponding to 0.124 H atoms/Co atom.

The aqueous phase was analyzed for Co(II) by adding 70% aqueous $HClO_4$ until pH = 1, and the $HCo(CO)_4$ formed from the $[Co(CO)_4]^-$ present was removed by bubbling CO through the solution for 30 min. The Co(II) content was determined by complexometry photometrically. Found: 4.5 mg of Co(II) (7.6% with respect to the starting $Co_2(CO)_8$).

The above experiment was repeated except that, after the addition of aqueous NaOH, the mixture was stirred for an additional 5 min and then 1.73 mL (15 mmol) of benzyl chloride was added. At the end of the reaction (end of gas volume change) 1.37 g of $PhCH_2COOH$ was isolated (67%) and 31.5% unreacted $PhCH_2Cl$ was determined by GLC. The gas volume changes and GLC analysis showed 10.35 mmol of CO consumed (69−67% for PhCOOH and 2% for the formation of carbonate, the latter corresponding to ∼30% of the reactant Co atoms in $Co_2(CO)_8$). The final gas phase contained 7% H_2, which corresponds to 0.54 H atoms/Co atom.

In experiments investigating the *fate of the catalyst during the catalytic* reactions (BP or PTC) an identical experimental technique was used but samples were taken for IR analysis after each 10−15 min.

Characterization of the Intermediates. Preparation of (η^3-Naphth-2-ylmethyl)cobalt Tricarbonyl. $Co_2(CO)_8$ (680 mg, 2 mmol) was transformed into $Na[Co(CO)_4]$ in 60 mL of Et_2O. Naphth-2-ylmethyl chloride (670 mg, 3.8 mmol) was added at 0 °C to the filtered solution under Ar atmosphere. The reaction mixture was stirred for 6 h at r.t. under Ar atmosphere, and then the solution was cooled to ∼0 °C and an Ar stream (∼80 mL/min) was bubbled through it for 5−6 h until the solvent was completely evaporated. The remaining dark brown oily product was extracted with 20 mL of *n*-pentane, and the solution was filtered and analyzed by IR spectroscopy. The IR ν(C−O) spectrum was similar to those of (η^3-benzyl)cobalt tricarbonyl compounds. Then the *n*-pentane was evaporated with an Ar stream as described above and a reddish-brown dense oil was obtained (yield 669 mg, 62%). This material could not be obtained in crystalline form from various solvents and their mixtures at temperatures ranging between 0 and 80 °C. Anal. Found: C, 59.3; H, 3.4; Co, 20.5. Calcd for $C_{14}H_9O_3Co$: C, 59.18; H, 3.19; Co, 20.74. ^{1}H- and ^{13}C-NMR and IR spectra are reported in Tables 2−6.

(η^3-Naphth-1-ylmethyl)cobalt tricarbonyl was prepared similarly, and the yield of the brownish-red oily product was 76%. Anal. Found: C, 59.2; H, 3.5; Co, 20.7. Calcd for $C_{14}H_9O_3Co$: C, 59.18; H, 3.19; Co, 20.74. ^{1}H- and ^{13}C-NMR and IR spectra are reported in Tables 2−6.

Preparation of η^3-(2-Methylbenzyl)cobalt Tricarbonyl. $Na[Co(CO)_4]$ (2 mmol) was prepared in 50 mL of Et_2O and cooled to 0 °C. To this solution, under Ar atmosphere, while being stirred, 2-methylbenzyl bromide (348 mg, 1.9 mmol) was added at once. The reaction mixture then left to warm to r.t. after 30 min, and it was stirred for additional 5 h at r.t. Then a sample was taken and analyzed by IR spectroscopy, which showed the disappearance of the characteristic strong band of $[Co(CO)_4]^-$ and emergence of a new band system, which could be assigned to a mixture of approximately 20% RC(O)-$Co(CO)_4$, 40% $RCo(CO)_4$, and 40% η^3-benzyl$Co(CO)_3$. Then the reaction mixture was cooled to 0 °C and an Ar stream (50 mL/min) was bubbled through it for 10 h, while the solvent was completely evaporated. The brown residue was extracted by 2 × 10 mL of *n*-hexane, and the combined extracts were filtered and chilled to −80 °C overnight. A dark brown microcrystalline substance was isolated which turned to be oily when it was left to warm at ∼−60 °C; yield 0.15 g (32%). Anal. Found: C, 53.6; H, 3.8; Co, 23.4. Calcd for $C_{11}H_9O_3Co$: C, 53.25; H, 3.66; Co, 23.75. NMR and IR spectra are reported in Tables 2−6.

Preparation of (η^1-(4-Fluorophenyl)methyl)cobalt Tricarbonyl. $Na[Co(CO)_4]$ (2 mmol) was prepared in 50 mL of Et_2O, and to this solution, 4-fluorobenzyl bromide (359 mg, 1.9 mmol) was added at once under Ar atmosphere at −20 °C. This solution was stirred and left to warm to r.t. after 30 min. Samples were taken after each 1 h, which were analyzed by IR spectroscopy. A fine white precipitate (NaBr) was formed and the solution became yellow after 2 h, when IR ν(CO) spectra indicated the disappearence of the characteristic strong absorption due to $[Co(CO)_4]^-$ and a band system corresponding mainly to $RCo(CO)_4$ (together with some minor bands, due most probably to an $RC(O)Co(CO)_4$ type complex). Then the solvent was evaporated at r.t. and reduced pressure. The brown residue was extracted by 2 × 10 mL of *n*-hexane, and the combined extracts were filtered and chilled to −80 °C. A light yellow microcrystalline substance was separated, yield 0.24 g (46%). Anal. Found: C, 47.3; H, 2.5; Co, 20.9. Calcd for $C_{11}H_6O_4CoF$: C, 47.17; H, 2.16; Co, 21.04. NMR and IR spectra are reported in Tables 2−6.

Preparation of (η^1-(2-Chlorophenyl)acetyl)cobalt Tetracarbonyl. $Na[Co(CO)_4]$ (4 mmol) was prepared in 60 mL of Et_2O, and to this solution 2-chlorobenzyl chloride (612 mg, 3.8 mmol) was added under CO atmosphere at 0 °C. This solution was stirred and left to warm to r.t. after 30 min. Then samples were taken after each 1 h, which were analyzed by IR spectroscopy. IR ν(C−O) spectra indicated after 7 h the disappearance of the strong band of $[Co(CO)_4]^-$ and a band system which corresponds approximately to the mixture of 20%

Table 2. ^{1}H-NMR Spectra of Acyl-, Alkyl-, and (η^3-Benzyl)cobalt Carbonyls (C_6D_6, δ Value Relative to δ_{TMS} 0)

R	RC(O)Co(CO)$_4$	RCo(CO)$_4$	(η^3-benzyl)Co(CO)$_3$
PhCH$_2$	7.19−6.97 (m, Ph); 3.92 (s, 2H, CH$_2$)	7.19−6.97 (m, Ph); 3.16 (s, 2H, CH$_2$)	6.65, 6.58, 6.48, 6.15, 6.05, 2.33, 2.12
p-MeC$_6$H$_4$CH$_2$	7.16−6.93 (m, Ph); 3.93 (s, 2H, CH$_2$); 2.05 (s, 3H, Me)	7.1−6.9 (m, Ph); 3.23 (s, 2H, CH$_2$); 2.13 (s, 3H, Me)	6.54, 6.44, 6.19, 6.09 (ab, 27.65, 7.87 CH), 2.38, 1.81, 2.02 (s, CH$_3$)
m-MeC$_6$H$_4$CH$_2$	7.05−7.00, 6.90−6.84 (m, Ph), 3.96 (s, 2H, CH$_2$); 2.08 (s, 3H, Me)	7.05−7.00, 6.90−6.84 (m, Ph); 3.20 (s, 2H, CH$_2$); 2.13 (s, 3H, Me)	6.38, 6.29, 5.97, 5.88, 5.38, 2.57, 1.95
o-MeC$_6$H$_4$CH$_2$	7.02−6.84 (m, Ph); 4.06 (s, 2H, CH$_2$); 2.04 (s, 3H, Me)	7.02−6.84 (m, Ph); 3.20 (s, 2H, CH$_2$); 2.09 (s, 3H, Me)	7.31 (dd, 6.86, 1.77 1H,CH), 6.66 (t, 7.07 1H,CH), 6.50 (d, 7.08 1H,CH), 5.02 (d, 6.64 1H,CH), 2.89, 1.61 (2d, 2.6 CH$_2$) 1.82 (s CH$_3$)
Me$_5$C$_6$CH$_2$	4.43 (s,2H,CH$_2$); 2.05, 1.99 (2s, 12H, 4CH$_3$); 1.69 (s, 3H, CH$_3$)		2.85; 2.02, 1.95 (2s, 12H, 4CH$_3$); 1.81 (s, 3H, CH$_3$)
p-BrC$_6$H$_4$CH$_2$	7.20−7.11, 6.82−6.80, 6.60−6.55 (m, Ph); 3.72 (s, 2H, CH$_2$)	7.20−7.11, 6.82−6.80, 6.60−6.55 (m, Ph); 2.89 (s, 2H, CH$_2$)	*a*
p-ClC$_6$H$_4$CH$_2$^{b}	7.06−6.88, 6.79−6.63 (m, Ph); 3.77 (s, 2H, CH$_2$)	7.16, 7.98−6.71 (m, Ph); 2.94 (s, 2H, CH$_2$)	*a*
m-ClC$_6$H$_4$CH$_2$^{b}	7.16, 7.98−6.71 (m, Ph); 3.80 (s, 2H, CH$_2$)	7.16, 7.98−6.71 (m, Ph); 2.90 (s, 2H, CH$_2$)	*a*
o-ClC$_6$H$_4$CH$_2$^{b}	7.08−7.04, 6.84−6.70 (m, Ph); 4.19 (s, 2H, CH$_2$)	7.08−7.04, 6.84−6.70 (m, Ph); 3.21 (s, 2H, CH$_2$)	*a*
p-FC$_6$H$_4$CH$_2$^{b}	7.08−7.06 (m, Ph); 3.8 (s, 2H, CH$_2$)	7.0−6.9 (m, Ph); 3.0 (s, 2H, CH$_2$)	*a*
o-FC$_6$H$_4$CH$_2$^{b}	7.08−7.06, 6.81−6.67 (m, Ph); 4.19 (s, 2H, CH$_2$)	7.08−7.06, 6.81−6.67 (m, Ph); 3.21 (s, 2H, CH$_2$)	*a*
1-NaphtCH$_2$	7.32−7.06 (m, 7H, CH); 4.41 (s, 2H, CH$_2$)	*a*	7.79 (dd, 8.4, 0.88), 7.58 (d, 7.96), 7.54 (d, 8.18), 7.32−7.06 m, 6.69 (d, 5.97), 6.66 (d, 5.98), 4.587 (d, 5.97), 3.68 (d, 2.43) 1.70 (dd, 2.43, 0.66)
2-NaphtCH$_2$	*a*	7.49−7.16 (m, 7H, CH); 4.08 (s, 2H, CH$_2$)	7.49−7.16, 6.9−6.58 m, 5.07 (d, 1.43), 3.02 (d, 1.67), 1.82 (d, 1.67)

[a] Could not be sufficiently enriched in NMR solvent (probably because of insufficient solubility or transformation during the measurement). [b] Some unidentified bands were also observed.

Table 3. ^{13}C-NMR Spectra of Acylcobalt Carbonyls, RC(O)Co(CO)$_4$ (C_6D_6 δ Value Relative to δ_{TMS} 0)[a]

R	CO$_{acyl}$	CO$_{carb}$	C$_{quat}$		CH$_{ar}$		CH$_2$	CH$_3$
PhCH$_2$	224.1	196.9	ipso	133.4	*p*-	127.6	69.0	
					o-, *m*-	129.8, 128.8		
p-MeC$_6$H$_4$CH$_2$	224.3	196.9	ipso	130.5	*o*-	129.8	68.8	21.0
			4-C	138.1	*m*-	129.6		
m-MeC$_6$H$_4$CH$_2$	224.0	197.0	ipso	133.3		130.5, 128.7	69.0	21.1
			3-C	138.3		128.4, 126.9		
o-MeC$_6$H$_4$CH$_2$	223.6	197.1	ipso	133.5		130.7, 130.5	68.3	19.5
			2-C	136.9		128.0, 126.3		
Me$_5$C$_6$CH$_2$	222.9	197.5	ipso	129.3	*p*-	133.3	67.7	18.2, 17.1
					o-, *m*-	132.4, 131.9		17.0, 16.8
								16.7
p-BrC$_6$H$_4$CH$_2$	223.7	196.7	ipso	121.9		131.9	68.1	
			4-C	132.4		131.4		
p-ClC$_6$H$_4$CH$_2$^{b}	223.9	196.7	ipso	132.0		131.1	68.0	
			4-C	133.7		128.9		
m-ClC$_6$H$_4$CH$_2$^{b}	223.9	196.6	ipso	127.5		130.0, 129.9	69.0	
			3-C	135.5		127.8, 126.7		
o-ClC$_6$H$_4$CH$_2$^{b}	222.1	196.8	ipso	133.5		131.5, 129.6	67.2	
			2-C	134.5		129.1, 126.9		
p-FC$_6$H$_4$CH$_2$	224.2	196.7	ipso	129.2 (3.0)	*o*-	131.4 (8.0)	67.9	
			4-C	162.6 (246.1)	*m*-	115.7 (12.1)		
o-FC$_6$H$_4$CH$_2$^{b}	215.6	198.5	ipso	123.0 (16.0)	4-C	132.3 (4.2)	65.9	
			2-C	161.9 (245.8)	5-C	130.3 (7.6)		
					6-C	124.5 (2.5)		
					3-C	116.2 (21.7)		
1-NaphtCH$_2$	223.7	197.0	C$_{junction}$	134.1		129.0 128.9	67.3	
				132.5		128.7 126.7		
			1-C	130.9		126.1 125.5		
						124.3		
2-NaphtCH$_2$	224.2	196.9		*c*		*c*	69.2	

[a] Tentative assignment. [b] Some unidentified bands were also observed. [c] Could not be sufficiently enriched in NMR solvent (probably because of insufficient solubility or transformation during the measurement).

RCo(CO)$_4$ and 80% RC(O)Co(CO)$_4$ compound. Then the solvent was evaporated at r.t. and reduced pressure, and the brownish residue was extracted by 20 mL of *n*-hexane. The extract was filtered and then chilled to −30 °C. A light yellow microcrystalline substance was obtained, yield 0.75 g (61%). Anal. Found: C, 44.5; H, 2.1; Co, 17.8; Cl, 10.6. Calcd for $C_{12}H_6O_5CoCl$: C, 44.41; H, 1.86; Co, 18.16; Cl, 10.92. NMR and IR spectra are reported in Tables 2−6.

Additional (η^1-benzyl)cobalt tetracarbonyl, (η^3-benzyl)cobalt tricarbonyl, and (η^1-phenylacetyl)cobalt tetracarbonyl derivatives, with different substituents in the phenyl ring were prepared by essentially similar methods as described above.

Table 4. ^{13}C-NMR Spectra of Alkylcobalt Carbonyls $RCo(CO)_4$ (C_6D_6 δ Value Relative to δ_{TMS} 0)[2]

R	CO_{carb}	C_{quat}		CH_{ar}		CH_2	CH_3
$PhCH_2$	199.2	ipso	147.7	*p*-	126.1	19.9	
				o-, *m*-	128.9, 128.6		
p-$MeC_6H_4CH_2$	201.2	ipso	137.4		*b*	20.4	20.9
		4-C	*b*				
m-$MeC_6H_4CH_2$	199.3	ipso	138.2		129.4, 128.8	20.1	21.3
		3-C	147.5		126.4, 125.8		
o-$MeC_6H_4CH_2$	199.3	ipso	134.6		142.0, 131.1	16.1	18.5
		2-C	146.5		127.7, 126.9		
p-$BrC_6H_4CH_2$	198.8	ipso	119.7		132.0	18.5	
		4-C	146.7		130.1		
p-$ClC_6H_4CH_2$[c]	198.9	ipso	134.6		130.0	18.5	
		4-C	146.3		128.5		
m-$ClC_6H_4CH_2$[c]	198.7	ipso	134.6		130.1, 128.5	17.9	
		3-C	139.7		126.5, 126.0		
o-$ClC_6H_4CH_2$[c]	199.0	ipso	131.0		130.5, 130.3	14.9	
		2-C	146.0		129.9, 127.1		
p-$FC_6H_4CH_2$	199.2	ipso	*b*	*o*-	130.1 (7.8)	18.8	
		4-C		*m*-	115.8 (21.5)		
o-$FC_6H_4CH_2$[c]	204.4	ipso	115.5 (14.0)	4-C	130.6 (4.0)	15.4	
		2-C	160.3 (246.6)	5-C	127.7 (8.0)		
				6-C	124.6 (3.2)		
				3-C	115.9 (21.7)		
2-$NaphtCH_2$	201.2	$C_{junction}$	133.9		128.9, 128.6, 127.6	33.8	
			131.0		127.3, 126.9, 126.5		
		1-C	133.1		125.2		

[a] Tentative assignment. [b] Could not be sufficiently enriched in NMR solvent (probably because of insufficient solubility or unfavorable effect on the equilibria) to obtain (additional) assignable bands. [c] Some unidentified bands were also observed.

Table 5. ^{13}C-NMR Spectra of (η^3-Benzyl)cobalt Carbonyls $RCo(CO)_3$ (C_6D_6 δ Value Relative to δ_{TMS} 0)[a]

R	CO_{carb}	C_{quat}		CH			CH_2	CH_3
$PhCH_2$	203.8	100.2		138.9	129.6	128.9	35.6	
				126.9	120.1			
p-$MeC_6H_4CH_2$	203.9	97.2		140.7	127.0	122.3	35.2	21.6
				b				
o-$MeC_6H_4CH_2$	203.9	98.7		131.1	130.8	129.6	33.9	16.1
				126.4	99.8			
$Me_5C_6CH_2$	204.5	97.7	134.3, 131.3				34.6	32.0, 25.8
			136.8[b]					23.1, 17.3
								14.3
1-$NaphtCH_2$	203.5	$C_{junction}$	134.0	129.7	129.3	129.0	35.2	
			132.4	128.4	127.3	121.4		
		1-C	95.2	80.8				
2-$NaphtCH_2$	203.8	$C_{junction}$	135.4	129.7	128.8	127.6	40.2	
			132.9	126.7	*b*			
		2-C	95.9	80.8				

[a] Tentative assignment. *m*-$MeC_6H_4CH_2^-$ decomposed during NMR measurement. [b] Could not be sufficiently enriched in this solvent (probably because of insufficient solubility or unfavorable effect of solvent on the equilibria) to obtain (additional) assignable bands.

Experimental conditions in preparations of the model complexes varied as follows.

According to IR analysis of the reaction mixtures (substituted) benzyl chlorides need 3−10 h for (practically) quantitative conversion of the $[Co(CO)_4]^-$ anion, while benzyl bromides need 1−5 h reaction times.

Typical data are as follows: $PhCH_2Cl$, 4−5 h; 4-MeC_6H_4-CH_2Cl, 3−4 h; 1-$C_{10}H_7CH_2Cl$, 4−5 h; 2-$ClC_6H_4CH_2Cl$, 6−8 h; $PhCH_2Br$, 2 h; 2-$MeC_6H_4CH_2Br$, 1−2 h; 2-$FC_6H_4CH_2Br$, 2−3 h.

Yields (ratios) of the cobalt carbonyl complexes depend strongly on the substituents, the acyl- and the η^3-benzyl complexes being favored with electron donor substituents, while the acyl and alkyl derivatives are favored with electron acceptor (F, Cl) substituents. Typical compositions of the reaction mixtures at the end of the reaction are for the $RC(O)Co(CO)_4/RCo(CO)_4/\eta^3$-benzyl$Co(CO)_3$ ratio as follows: $PhCH_2$ (CO, 80/20/0; Ar, 70/25/5); 2-$MeC_6H_4CH_2$ (CO: 70/25/5); 3-$ClC_6H_4CH_2$ (CO, 60/40/0; Ar, 5/70/25); $Me_5C_6CH_2$ (CO, 80/20/0; Ar, 40/5/55) (approximate IR data).

The naphthylmethyl and pentamethylbenzyl derivatives represent particular cases: (i) At the former a characteristic predominance of the η^3-benzyl derivative (>80%) was observed (even using CO atmosphere), while (ii) at the latter under CO the acyl complex was predominant; under Ar atmosphere the η^3-benzyl derivative was predominant with almost no alkyl complex in both cases.

Spectroscopic (^{1}H- and ^{13}C-NMR and IR) characterization of the model complexes is reported in Tables 2−6.

Solvent Effect Studies. In a Schlenk vessel under CO or Ar, $Na[Co(CO)_4]$ (2 mmol) was prepared in 30 mL of Et_2O and reacted with 1.9 mmol of (substituted) benzyl chloride (or bromide) as described earlier in this paper and ref 9c. After the reaction was completed (monitored by IR) Et_2O was evaporated at r.t. and reduced pressure and 30 mL of a solvent was added. The solution was stirred under CO at r.t. until equilibrium was reached (30−120 min) (monitored by IR), and then the IR spectrum was registered with an expanded wavenumber scale.

Model Experiments for Testing the Intermediacy of (η^3-Benzyl)cobalt Complexes in the Catalytic Cycle.[30] (η^3-Naphth-1-ylmethyl)cobalt tricarbonyl (1.14 g, 4 mmol) (prepared as described earlier in this paper) was dissolved in 12 mL of toluene. This solution was then divided into four equal parts (A−D) and treated according to the methods of the PTC carbonylation experiments as follows. To portion A (3 mL) 3

Table 6. FT-IR Spectra of Acyl-, Alkyl-, and (η^3-Benzyl)cobalt Carbonyls (*n*-Hexane, cm^{-1})

R	RC(O)Co(CO)$_4$	RCo(CO)$_4$	(η^3-benzyl)Co(CO)$_3$
$Me_5C_6CH_2$	2104 m 2045 s 2022 vs 2013 s 1722 m	*a*	2065 m 2002 vs 1980 s 1966 s
p-$ClC_6H_4CH_2$	2107 m 2020 vs, br 1717 m	2099 m 2035 s 2013 vs, br	2054 vs ~1990 s 1972 s
m-$ClC_6H_4CH_2$	2107 m 2042 s 2027 vs 1714 m	2101 m 2036 s 2018 vs	2063 s *a*
o-$ClC_6H_4CH_2$	2107 m 2049 s 2026 vs 2012 vs 1712 w	2100 m 2036 s 2023 vs 2012 vs	2062 s 2001 s 1987 s
o-$FC_6H_4CH_2$	2108 m 2049 s 2028 vs 2013 s 1713 w	2101 m 2036 s 2023 vs 2013 s	2063 s *a*
1-NaphthCH_2	*a*	*a*	2058 s 1999 s 1988 vs
2-NaphthCH_2	*2106 m* *a*	2098 m 2033 m 2015 vs	2058 s 2000 vs 1986 vs

[a] Could not be sufficiently enriched in this solvent (probably because of insufficient solubility or unfavorable effect of solvent on the equilibria) to obtain (additional) evaluable bonds.

mL of 20% aqueous NaOH solution and 60 μL of PEG 400 were added and stirred (for 20 h) until it became yellow; then it was treated as the samples in the carbonylation experiments.

To portion B 3 mL of 20% aqueous NaOH solution, 60 μL of PEG 400, and $Co_2(CO)_8$ (17 mg, 0.05 mmol) were added, and then the sample was treated as portion A.

To portion C was added 1-(choromethyl)naphthalene (5.28 g, 30 mmol), 3 mL of 20% aqueous NaOH solution, and PEG 400 (60 μL). Subsequently the sample was treated as portion A.

To portion D was added 1-(choromethyl)naphthalene (5.28 g, 30 mmol), 3 mL of 20% aqueous NaOH solution, $Co_2(CO)_8$ (17 mg, 0.05 mmol), and PEG 400 (60 μL). Then the solution was treated as portion A.

Experiments A, C, and D were repeated using (η^3-naphth-2-ylmethyl)cobalt tricarbonyl and 2-(bromomethyl)naphthalene.

Yields of 1-naphthylacetic acid (2-naphthylacetic acid in parentheses): A, 8.9% (18.6); B, 54%; C, 91.6% (55%); D, 93.4% (77.4%). (Yields of experiments C and D were calculated with respect to the sum of the starting η^3-complex and naphthylmethyl halide.)

Results and Discussion

Preparation of Arylacetic Acids. Excellent results were achieved in previous investigations in the preparation of phenylacetic acids[3g,r,v,z,aa,4a,c] and esters[3k,l,n,s,t] from benzyl halides. From the viewpoint of eventual practical realization, however, most of these methods have some drawbacks: (i) medium to high pressure (5–150 bar),[3n,s,z,aa,4a] (ii) a multicomponent catalyst "system" which appears to create handling and waste (recycling) problems,[3g,l] (iii) insufficient selectivity,[3rzaa,14] and (iv) the use of a corrosive promoter (HI)[3t] or halogenated solvent (CH_2Cl_2).[3v,15]

We regarded two procedures (ester, ref 3k; acid, ref. 4c) as standards. Our principal aim was to develop more economical techniques.

We used—if necessary at all—only polyethylene glycols as PT agents for two reasons. First, these are appreciably cheaper than "quats" or crown ethers, and second, the quaternary ammonium salts may suffer irreversible degradation under the conditions of catalytic carbonylation, as was demonstrated earlier by one of us.[16]

Essentially three procedures were found to be suitable to prepare phenylacetic acids from the corresponding benzyl chlorides or bromides.

(a) A PTC system using the 2-methylbutan-2-ol/water solvent pair provided the best isolated yield for $PhCH_2$-COOH and acceptable yields for some substituted derivatives. An alternative to this method proved to be 4-methylpentan-2-one/water in some cases, but the available data are insufficient to interpret the observed differences. The BP variant of the *tert*-amyl alcohol containing system provides considerably lower yields, but the reaction takes place. Not even traces of phenylacetic ester and phenylpyruvic acid (or derivatives)[4b,d] were detected in these experiments.

(b) Seeking a more practical variant of these procedures, we found that fusel oil is also a suitable solvent both under BP or PTC reaction conditions. Fusel oils of various origins were tested, but no remarkable differences were observed with these distillates having only slightly different compositions. Good yields and turnover numbers could be achieved. There was practically no difference between the BP and PTC variant in these solvents—*i.e.* the PT agent had no detectable effect on the yields. The selectivity was found to be quantitative also in this case.

(c) A third variant, on the other hand, provided a dramatic demonstration of the effect of the PT agent. Using only the benzyl chloride/water system (*i.e.* no organic "solvent"), we found that in the absence of PEG no reaction occurs, while if PEG was added, acceptable yields of phenylacetic acid could be achieved.

Mechanistic Studies. We report in this section on the results of experiments (mainly monitored by IR spectroscopy) concerning (i) the fate of the catalyst precursor ($Co_2(CO)_8$), (ii) the identification of the organocobalt complexes formed and their distribution in the liquid phases, (iii) the influence of the nature of the organic phase on the equilibrium between the organocobalt complexes and the role of the phase-transfer agent, and (iv) the influence of the substituent on the aromatic ring on the equilibrium distribution of the organocobalt compounds. Since the best quality IR spectra could be obtained in *t*-AmOH, most of the

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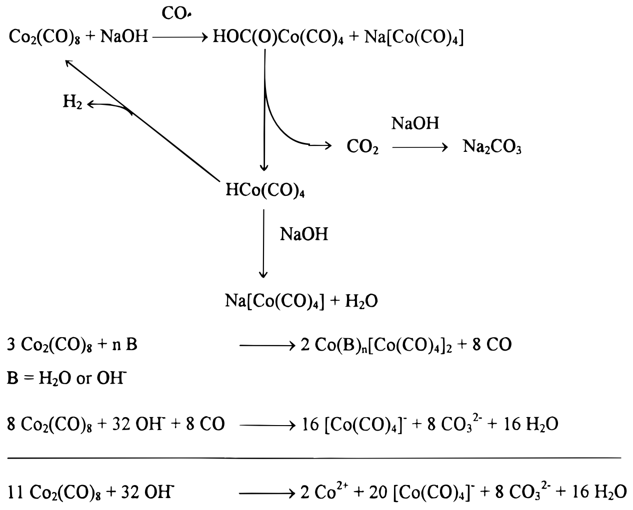
(14) With regard to preparation of phenylpyruvic acid or its derivatives.

(15) Low molecular weight halocarbons should be avoided in light of recent environmental results and regulations. Some leading references are as follows: (a) Fabian, P.; Gönner, D. *Fresenius Z. Anal. Chem* **1983,** *319*, 890. (b) Grob, K.; Habich, A**.** *J. High Resolut. Chromatogr.-Chromatogr. Commun.* **1983,** *6*, 11. (c) Grob, K.; Grob, G. *J. High Resolut. Chromatogr.-Chromatogr. Commun.* **1983,** *6*, 133. (d) Grob, K. *J. Chromatogr.* **1984,** *229*, 1. (e) Nunez, A. J.; Gonzales, L. F.; Janák, J. *J. Chromatogr.* **1984,** *300*, 127. (f) Ettre, L. S.; Di Cesare, J. L. *Am. Laboratory* **1984,** *16*, 76. (g) Ettre, L. S. *Anal. Chem.* **1985,** *57*, 1419A. (h) Croll, B. T.; Sumner, M. E.; Leathard, D. A. *Analyst* **1986,** *111*, 73. (i) Lakszner, K.; Szepesy, L. *J. High Resolut. Chromatogr.-Chromatogr. Commun.* **1986,** *9*, 441.

(16) Gambarotta, S.; Alper, H. *J. Organomet. Chem***. 1980,** *194*, C19.

Scheme 1



spectroscopic studies were made in the system with this alcohol as the organic phase. The identity of the organocobalt intermediates was ensured by ^{1}H- and ^{13}C-NMR and IR spectra (Tables 2−6) and by analogy of these spectra to those of isolated (benzyl- and (phenylacetyl)cobalt carbonyls where an X-ray diffraction structure could be obtained (c.f. Experimental Section and refs 9b,c, 18c, 21j, and 22).

Fate of the Catalyst Precursor. It is generally believed that in phase-transfer or biphasic systems dicobalt octacarbonyl undergoes a complicated reaction depicted in Scheme 1.[2dg,17−19] One of the most interesting points of this mechanism is the intermediacy of the hydroxycarbonylcobalt tetracarbonyl $HOC(O)Co(CO)_4$. Esters of this compound are known,[18] and decarboxylation of one of the esters was recently demonstrated.[18f,h] In the present work we controlled the stoichiometry, and in addition to earlier findings, we detected the evolution of H_2 even at an early stage of the reaction. This can be regarded[18h,19a−e] as indirect evidence for the formation and decomposition (via decarboxylation) of $HOC(O)Co(CO)_4$ in the apolar phase according to Scheme 1.

The dramatic increase of the quantity of H_2 evolved during the carbonylation of benzyl chloride may be explained by assuming a dicobalt octacarbonyl-based catalytic process. This may result in the reaction between $PhCH_2Co(CO)_4$ and $HOC(O)Co(CO)_4$, initiated by a radical fission[19b−d] of the former consuming a substantial fraction of the latter. The $Co_2(CO)_8$ formed in this manner is then transformed as indicated in Scheme 1.

It should be pointed out that the essential part of Scheme 1 together with our finding regarding the H_2 evolution can also be formulated as follows:

$$CO + 2OH^- + CO_3^{2-} + H_2$$

This formulation indicates that in biphasic or PTC $Co_2(CO)_8$/NaOH systems a kind of cobalt-assisted water gas shift reaction (WGSR)[19f−h] occurs. This point is now currently investigated in our laboratories.

Infrared spectroscopic studies of the reaction mixtures of *t*-AmOH and H_2O and (in a few cases) fusel oil/H_2O systems revealed the presence of dicobalt octacarbonyl (diminishing) and $[Co(CO)_4]^-$ (increasing) as the only cobalt carbonyls in the system in the absence of benzyl chloride.

The bands of dicobalt octacarbonyl disappeared after about 5−10 min. This was accompanied by the disappearance of the brown color. At this stage the distribution[20a] of the tetracarbonylcobaltate anion between the organic and aqueous phase showed marked differences depending on the presence or absence of the phase-transfer agent:

	aqueous phase	organic phase
t-AmOH	70%	30%
t-AmOH/PEG	0%	100%

This effect of PEG on the distribution of $[Co(CO)_4]^-$ in the *t*-AmOH/H_2O system and its influence on the yield clearly show that this anion “is needed” in the *organic phase* for the hydroxycarbonylation reaction. One can propose that the “organometallic part of the catalytic cycle” takes place exclusively in the organic phase.[20b] The fact that $[Co(CO)_4]^-$ is the only organocobalt species present before the benzyl halide is added supports the earlier supposition[2g,10e,g] that this anion is the entry point into the catalytic cycle.

Organocobalt Compounds in the Reaction Mixtures of Hydroxycarbonylation. The tetracarbonylcobaltate anion is known to react with benzyl halides in Et_2O when mixtures of (benzyl- and (phenylacetyl)-cobalt tetracarbonyls and (η^3-benzyl)cobalt tricarbonyls are formed.[3a,9a−d,10a] As intermediates of this reaction $[PhCH_2C(O)Co(CO)_3(X)]^-$ (X = Cl, Br, I) complexes were identified.[18f,21]

Several η^1-benzyl (**1**) and η^3-benzyl (**3**) as well as η^1-phenylacetyl (**2**) cobalt carbonyls were characterized by IR spectroscopy (unsubstituted, 4-Me, 3-Me, 2-Me,

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[17] The stoichiometry was originally established by Hieber et al.: (a) Hieber, W.; Schulten, H. *Z. Anorg. Allg. Chem.* **1937,** *232*, 18, 20. (b) Hieber, W.; Abeck, W.; Sedlmeier, J.; Abeck, W. *Chem. Ber.* **1953,** *86*, 700. (c) Wender, I.; Stenberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1952,** *74*, 1216.

[18] (a) Heck, R. F. *J. Organomet. Chem.* **1964,** *2*, 195. (b) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965,** *98*, 1744. (c) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982,** *104*, 6150. (d) Ungváry, F.; Markó, L. *Organometallics* **1983,** *2*, 1608. (e) Tasi, M.; Sisak, A.; Ungváry, F.; Pályi, G. *Monatsch. Chem.* **1985,** *116*, 1103. (f) Tasi, M.; Pályi, G. *Organometallics* **1985,** *4*, 1523. (g) Werner, H.; Hofmann, L.; Zolk, R. *Chem. Ber.* **1987,** *120*, 379. (h) Bartik, T.; Krümmling, T.; Markó, L.; Pályi, G. *Gazz. Chim. Ital.* **1989,** *119*, 307. (i) Bartik, T.; Krümmling, T.; Krüger, C.; Markó, L.; Boese, R.; Schmid, G.; Vivarelli, P.; Pályi, G. *J. Organomet. Chem.* **1991,** *421*, 323.

[19] (a) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1980,** *193*, 397. (b) Orchin, M. *Acc. Chem. Res.* **1981,** *14*, 59. (c) Galamb, V.; Pályi, G. *Atti Accad. Sci. Bologna, Cl. Sci. Fis.* **1982,** *270* (13/9), 157. (d) Pályi, G.; Ungváry, F.; Galamb, V.; Markó, L. *Coord. Chem. Rev.* **1984,** *53*, 37. (e) Murai, S.; Sonoda, N. *Angew. Chem.* **1979,** *91*, 896. (f) Roofer-De Poorter, C. K. *Chem. Rev.* **1981,** *81*, 447. (g) Ford, P. C. *Acc. Chem. Res.* **1981,** *14*, 31. (h) Henrici-Olivé, G.; Olivé, S. *The Chemistry of the Catalysed Hydrogenation of Carbon Monoxide*; Springer: Berlin, 1984.

[20] (a) Measured on the basis of the area of the ν(C−O) band. This assumes that the absorption coefficients were the same in different solvents. For this reason our data are only of qualitative character. (b) If anionic cobalt carbonyl species other than $[Co(CO)_4]^-$ would be formed in the catalytic cycle, these should also be concentrated in the organic phase.

[21] Analogous complexes were reported. $[XYCo(CO)_3]^-$ type: (a) Francalanci, F.; Gargano, A.; Abis, L.; Foà, M. *J. Organomet. Chem.* **1983,** *251*, C5. (b) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984,** *106*, 995. (c) Vlaic, G.; Bart, J. C. J.; Foà, M.; Francalanci, F.; Clement, R. *J. Organomet. Chem.* **1985,** *287*, 369. (d) See also refs 9d and 18e,f. (e) Röper, M.; Schieren, M.; Heaton, B. T. *J. Organomet. Chem.* **1986,** *299*, 131. (f) Galamb, V.; Pályi, G.; Boese, R.; Schmid, G. *Organometallics* **1987,** *6*, 861. (g) Röper, M.; Krüger, C. *J. Organomet. Chem.* **1988,** *339*, 159. (h) Fachinetti, G.; Funaioli, T.; Masi, D.; Mealli, C. *J. Organomet. Chem.* **1991,** *417*, C32. (η^3-benzyl)Co(CO)$_3$ type: (i) Ullah, S. S.; Molla, M. E.; Karim, M. M.; Begum, R. *Indian J. Chem.* **1985,** *24A*, 412. (j) Blecke, J. R.; Burch, R. R.; Caulman, C. R.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316.

4-MeO, 3,4-$(MeO)_2$, 4-Cl, 2,6-Cl_2)[9c,10a,21i] and the molecular structures of some similar complexes were determined by X-ray diffraction,[9bc,18c,21fj,22] but only a few compounds were studied by ^{1}H-NMR[9,21i] spectroscopy.

We summarize, in Tables 2−6, most of the ^{1}H- and ^{13}C-NMR data and the IR ν(C−O) spectra not studied earlier. These characteristics, considering the similarity to the spectra of compounds published earlier, and those also obtained by X-ray diffraction[9b,c,18c,21f,j,22] represent a reliable basis for the identity of **1**−**3**.

An infrared study of the organic and aqueous phase of the reaction mixtures in the hydroxycarbonylation experiments revealed the presence of these complexes but with characteristic variations of the relative concentrations. The alcoholic phase, without a PT agent, shows a high relative concentration of the (phenylacetyl)cobalt complex, a much lower concentration of the alkyl derivative, and very low quantities of the η^3-benzyl complex. (This can also be expected on basis of the polarity of the solvent, as will be demonstrated later.)

In these biphasic reactions, as hydroxycarbonylation proceeds, the relative amount of the η^3-benzyl complex increases. The end of the reaction is characterized by a change in color (see Experimental Section), disappearance of the benzyl chloride (GC), termination of CO absorption, and disappearance of the bands of all neutral cobalt carbonyls (including those of (η^3-benzyl)cobalt tricarbonyl).

The influence of the PT agent is convincingly demonstrated by the IR spectra. In the case of the *t*-AmOH/PEG/H_2O system, (η^3-benzyl)cobalt tricarbonyl is the *only* detectable neutral cobalt carbonyl during hydroxycarbonylation. If the reaction is run in a biphasic manner and PEG is added later, this change is observed immediately after the addition of the PT agent.

The intermediacy of the (η^3-benzyl)cobalt tricarbonyl complexes in the catalytic cycle(s) was demonstrated also by model experiments[23] (cf. Experimental Section). These experiments led to the following two important conclusions: (i) the (η^3-benzyl)cobalt tricarbonyl complexes show catalytic activity in the carbonylation of the corresponding benzyl halides; (ii) this catalytic activity increase in the presence of dicobalt octacarbonyl showing a typical synergetic effect.

These observations allow the following conclusions. (i) If the final step of hydroxycarbonylation is accelerated, (η^3-benzyl)cobalt tricarbonyl type complexes are accumulated in the reaction mixture (this effect becomes more important when the η^3-benzyl complex is more stable, as in the case of the naphthyl derivatives). (ii) In order to explain this phenomenon we have to assume that the (η^3-benzyl)cobalt tricarbonyl complexes are the true intermediates of the catalytic cycle, not only representing a "cobalt reservoir" which is present because of the equilibrium between the η^1- and η^3-benzyl species. We suggest therefore that the η^3-benzyl complexes may be formed from $[PhCH_2C(O)Co(CO)_3X]^-$ *via* decarbonylation to $[PhCH_2Co(CO)_3X]^-$, followed by loss of halide. This pathway thus constitutes an additional loop of the mechanism proposed by des Abbayes.[2g] (iii) The effect of the PT agent can be interpreted either in terms of the des Abbayes hypothesis,[2g] supposing that the presence of PEG decreases the interfacial term of the activation energy for nucleophilic attack of the OH^- ion on the acylcobalt complex at the interface or, alternatively, that PEG increases the concentration of NaOH in the organic phase. The first possibility should be regarded as being more probable since our experiments showed no characteristic change in the partition of NaOH upon addition of PEG.

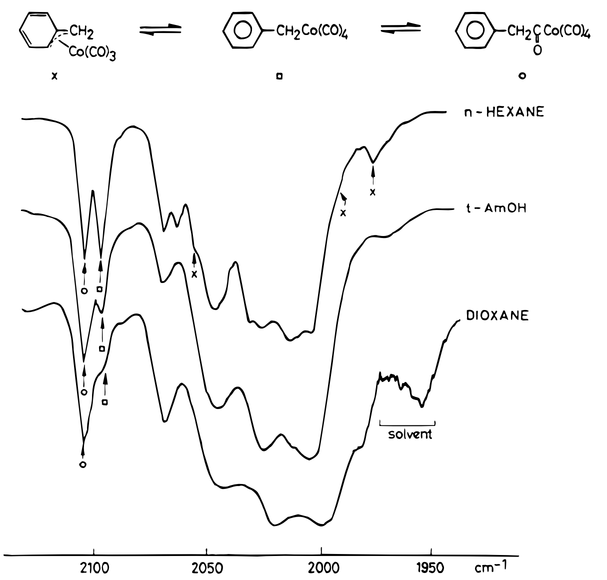

Figure 1. Infrared ν(CO) spectra of equilibrium mixtures of (η^1-phenylacetyl)$Co(CO)_4$, (η^1-benzyl)$Co(CO)_4$, and (η^3-benzyl)$Co(CO)_3$ in different solvents.

Perhaps the most important conclusion of the infrared investigations of the hydroxycarbonylation reaction mixtures is that the role of the PT agent is not only to change the partition of the $[Co(CO)_4]^-$ anion[10e] between the two phases but also to promote a subsequent step of the catalytic cycle: the cleavage of the acyl complex by hydroxide ion (most probably by increasing the reactivity of OH^- through coordinating to the Na^+ cation[20a,d]). It remains to be demonstrated whether the reaction pathway found for *t*-AmOH/PEG/H_2O can be generalized to other $Co_2(CO)_8$−PTC systems.

Solvent and Substituent Effects. The kinetics of the reaction between benzyl chloride and $Na[Co(CO)_4]$ in various solvents has been investigated by Moro et al.[10d] These authors found that the rate of this reaction decreases in the order anisole > *i*-Pr_2O > n-Pr_2O > THF > AN > DMF. This means that increasing polarity of the solvent disfavors the activation step of the catalytic cycle.

Since the polarity of the (η^1-benzyl-, (η^3-benzyl-, and (η^1-phenylacetyl)cobalt complexes is presumed to be different, a marked solvent effect is also expected on the equilibria between these compounds.

In fact it was found that increasing the polarity of the solvent favors the formation of the acyl complex (Figure 1). Since this complex is believed to be the immediate precursor of the end product, more polar solvents should be preferred. We observed, however, that solvents of high polarity like DMF or DMSO gave undesirable side reactions (a kind of "base reaction" leading to Co(II) and $[Co(CO)_4]^-$) with the neutral

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(22) Pályi, G.; Zucchi, C.; Bartik, T.; Herbrich, T.; Kriebel, C.; Boese, R.; Sorkau, A.; Fráter, G. *Atti Accad. Sci. Bologna, Rend. Cl. Sci. Fis.* **1992/93**, *281* (14/10), 159.

(23) The concept of these experiments was suggested by one of the reviewers of this paper. The authors acknowledge gratefully this suggestion.

intermediates. Dioxane and THF were found to favor pyruvic acid formation in a similar system.[3aa] Thus a compromise had to be found and it turned out that *t*-AmOH (or components of fusel oil or the branched ketone used by us) represents just such an advantageous intermediate case of being not too reactive yet sufficiently polar. A further practical advantage of these alcoholic systems is that the chemoselectivity is quantitative: the formation of the corresponding esters was never observed.

One can speculate whether the (η^3-benzyl)cobalt tricarbonyls in (even "hard") donor-type solvents are present as true η^3-benzyl complexes or as (η^1-benzyl)cobalt tricarbonyl solvent $PhCH_2Co(CO)_3(S)$ adducts,[24-26] since the IR band pattern (A_1 + E—the latter broadened) would be the same for both, and the observed band positions are between those of (η^3-benzyl)cobalt tricarbonyl (in an apolar solvent) and (η^1-benzyl)cobalt tricarbonyl triphenylphosphine adducts. However attempts to isolate such a solvent adduct failed, but the smooth and almost quantitative formation of η^1-$Ph_RCH_2Co(CO)_3PPh_3$ complexes from the corresponding η^3-$Ph_RCH_2Co(CO)_3$ derivatives and PPh_3 (cf. ref 9c) supports this view.

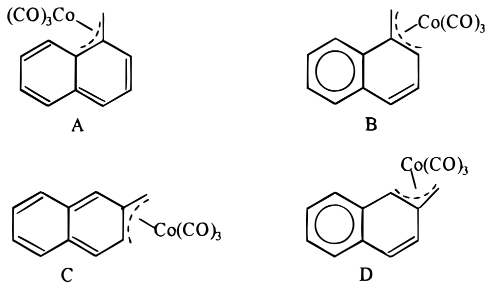
It is evident that a considerable substituent effect has to be expected in the hydroxycarbonylation reaction. Kinetic studies of the substituent effects in related systems were performed on the rates of activation of benzyl chloride[10d] and bromide[10g] by the $[Co(CO)_4]^-$ anion. Only a very slight substituent effect was detected in the former case, which was interpreted in terms of interesting mechanistic speculations which will be discussed later. Our results (Table 1) showed that the benzyl halides containing electron acceptor substituents (F, Cl) provided relatively low yields of the hydroxycarboxylated product.

The negative slope of the K vs σ_p plot of the alkyl/acyl equilibrium[9b] provides independent support for the presently accepted mechanism of CO insertion according to which "insertion" should be regarded as an intramolecular nucleophilic attack of the alkyl group at one of the coordinated carbonyl groups.[9b,10a,24] On the other hand, the positive slope of the equilibrium constant of the η^1-alkyl $\rightleftharpoons$ η^3-benzyl equilibrium[9b] indicates that (η^3-benzyl)cobalt tricarbonyl is an electrophilic center susceptible to nucleophilic attack by CO.[25] One can also rationalize these findings in terms of the acceptor substituent on the ring destabilizing η^3-coordination and thus facilitating attack (addition) of the "fourth" CO.

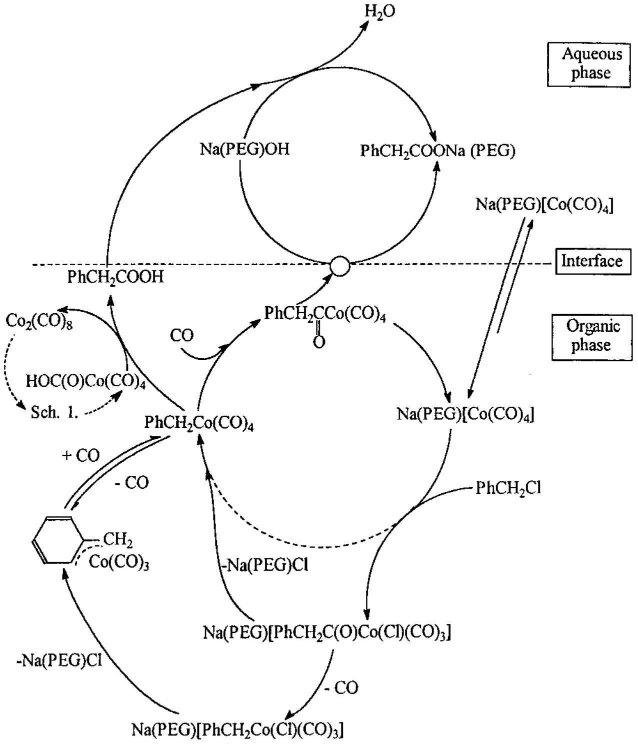
The opposite sense of the two subsituent effects explains, in part, the preparative problems encountered[9] in efforts to enrich reaction mixtures in some individual complexes of these equilibrium mixtures (for preparative purposes) and also the compromises which have to be worked out frequently in carbonylation studies.

A special kind of substituent effect was observed with 1-chloro- and 2-(bromomethyl)naphthalene. The reactions of these compounds with $Na[Co(CO)_4]$ provide the usual acyl/alkyl/η^3-benzyl mixture, but here the equilibrium lies so much on the η^3-benzyl side that in an argon atmosphere the cobalt tetracarbonyl complexes almost disappear and under 1 bar CO the η^3-benzyl-type complex still predominates.

Chart 1



Scheme 2



The high relative stability of the (η^3-methylenenaphthalene)cobalt tricarbonyls has some interesting consequences: (i) The lower yield in hydroxycarbonylation of 1-(chloromethyl)naphthalene may principally be due to the stability of the η^3-complex. (ii) The preferential formation of these compounds is apparently a consequence of the more facile dearomatization of the substituted ring in naphthalene as compared to the corresponding benzene or thiophene derivatives.[27,28] (iii) The structures of these complexes[29] show that the process

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[24] We cite here only some early key papers on this point: (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961,** *83*, 4024. (b) Markó, L. *Chem. Ind. (London)* **1962**, 260. (c) Nitschmann, E. R. *Chem. Ber.* **1964,** *97*, 2098. Two excellent, recent spectroscopic studies provide independent experimental support for the existence of $RCo(CO)_3$ and $RC(O)$-$Co(CO)_3$: (d) Roe, D. C. *Organometallics* **1987,** *6*, 942. (e) Sweany, R. L. *Organometallics* **1989**, *8*, 175.

[25] (a) Calderazzo, F. *Angew. Chem.* **1977,** *89*, 305. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980,** *33*, 195. (c) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978,** *100*, 7224.

[26] In agreement with the supposition of an (η^3-benzyl)$Co(CO)_3$ $\rightleftharpoons$ (η^1-benzyl)$Co(CO)_3$ equilibrium; cf. also ref 23.

[27] (a) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966,** *88*, 709. (b) King, R. B.; Kapoor, R. N. *Inorg. Chem.* **1969,** *8*, 2535. (c) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969,** *91*, 1339. (d) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1977,** *99*, 2509. (f) Blecke, J. R.; Burch, R. R.; Caulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981,** *20*, 1316.

[28] See for example: Coulson, C. A.; O'Leary, B.; Mallison, R. B. *Hückel Theory for Organic Chemistry*; Academic Press: London, 1978; pp 44, 151−155.

[29] See the Experimental Section of this work and: Sámpár-Szerencsés, E.; Thiele, K. H.; Pályi, G. Unpublished results.

is regiospecific (Chart 1B,D); isomers involving the loss of the aromatic character of *both rings* (Chart 1A,C) are obviously less favored.

Concluding Remarks on the Mechanism. This study accounts for most details of the *t*-AmOH/PEG/H_2O system. It can reasonably be assumed that most of the conclusions can be generalized to all biphasic or PTC carbonylations of benzyl halide type substrates. The main mechanistic features, summarized in Scheme 2, lead to the following conclusions:

(i) The role of PEG is not simply to transport $[Co(CO)_4]^-$ from the aqueous to the organic phase (similarly as the "quats" were found to act in earlier studies[2g,4e,g]) but also to accelerate the hydrolysis of the acylcobalt tetracarbonyl complex.

(ii) We demonstrated experimentally the presence of the acyl-, alkyl- and (η^3-benzyl)cobalt complexes in the hydroxycarbonylation reaction mixtures. The acyl and alkyl complexes have been known[2,10,30] for some time, but the presence of (η^3-benzyl)cobalt-type complexes (which undergo dramatic kinetic enrichment in certain cases) and their role as intermediates in phase-transfer reactions was not previously observed.

Acknowledgment. The authors acknowledge helpful discussions with Drs. T. U. Kállay (Budapest), F. Kovács (Várpalota), and M. Musulin (Veszprém), communication of unpublished experimental data by Prof. R. L. Sweany (New Orleans, LA), and help in obtaining the GC and IR measurements by Drs. I. Ötvös and K. Nagy-Perge. The University of Ottawa scientists are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work. A fellowship (to C.Z.) is acknowledged from the Hungarian Academy of Sciences (Budapest).

Supporting Information Available: Tables of X-ray data, positional and thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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[30] Braterman, P. S.; Walker, B. S.; Robertson, T. H. *J. Chem. Soc., Chem. Commun.* **1977**, 651.