Me_2SO (0.2 cm^3, 2.8 mmol); after the solution was stirred for a few minutes, the suspension was cooled to −78 °C and hexamethyldialuminum (2.1 cm^3 of a 26.5% w/w solution in pentane, 5.0 mmol) was added dropwise. The suspension slowly turned yellow and after 30 min was allowed to warm to 20 °C. This solution was worked up as described above to give yellow crystals of **5b** (0.47 g, 80%). This complex could also be made from [$C_5Me_5IrCl_2(Me_2SO)$] if this was isolated from the reaction of Me_2SO with complex **1b**.

The rhodium complex **5a** as well as the complexes **4a**, **4b**, and **6** was all prepared by method A and are detailed in Table I. In addition complexes **4a**, **6**, and also **4b** were prepared by reaction of the Me_2SO complexes 5a and **5b**, respectively, with the appropriate ligand (method C).

Preparation of Complex 6. Method C. A solution of bis(diphenylphosphino)methane (0.11 g, 0.29 mmol) was added to a solution of complex **5a** (0.10 g, 0.29 mmol) in dry benzene (15 cm^3). The solution was refluxed (1 h), the solvent removed, and the residue extracted with wet pentane. On cooling, the pentane solution slowly gave yellow crystals of complex 6 (0.20 g, 75%).

Acknowledgment. We thank the S.E.R.C. for supporting this work, the Spanish Ministry of Education of the award of a scholarship (to A.V.deM.), Professor N. M. Atherton for ESR spectra, Ethyl Corp. for organoaluminum compounds, Dr. W. Schaefer (Chemischewerke Huels) for organic starting materials, and Johnson Matthey for the loan of iridium chloride.

Registry No. **1a**, 12354-85-7; **1b**, 12354-84-6; **3a**, 87174-69-4; **3b**, 87174-70-7; **4a**, 87174-71-8; **4b**, 87174-72-9; **5a**, 87183-26-4; **5b**, 87183-27-5; **6a**, 87174-73-0; Al_2Me_6, 15632-54-9; Ph_3P, 603-35-0; Me_2SO, 67-68-5; $Al_2Me_4Cl_2$, 14281-95-9; dppm, 2071-20-7; Al, 7429-90-5; Rh, 7440-16-6; Ir, 7439-88-5; acetone, 67-64-1.

Kinetics and Mechanism of the Phase-Transfer-Catalyzed Carbonylation of Benzyl Bromide by the Cobalt Tetracarbonyl Anion

Hervé des Abbayes,* Anne Buloup, and Guy Tanguy

Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

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The carbonylation of benzyl bromide with the cobalt carbonyl anion according to eq 1 and 2 was studied in a liquid–liquid two-phase system (H_2O/CH_2Cl_2, $H_2O/i\text{-}Pr_2O$, H_2O/C_6H_6). The disappearance of benzyl bromide was found to follow a second-order kinetic law under stoichiometric conditions. In these experiments, the concentration of the cobalt carbonyl anion in the organic phase remained constant throughout the reaction, owing to rapid pairing with the tetrabutylammonium cation used as a cationic carrier. Under catalytic conditions, the kinetics depended strongly on the stirring speed (which was not the case under stoichiometric conditions). A catalytic cycle is proposed for this liquid–liquid system, in which it is shown that the catalyst ($Bu_4N^+Co(CO)_4^-$) stays in the organic phase, and the product (the phenylacetate anion) is expelled into the aqueous phase. It is also shown that the rate-limiting reaction is not the nucleophilic displacement (1) (reaction of benzyl bromide with the cobalt carbonyl anion) but the cleavage of the acylcobalt carbonyl 4 by the ion pair $Bu_4N^+OH^-$ at the liquid–liquid interface. The presence of byproducts such as toluene and diphenylethane is accounted for in terms of the decomposition of a transient hydroxycarbonyl species **13** through loss of carbon dioxide.

One of the main challenges in the field of catalysis is to combine the advantages of heterogeneous and homogeneous catalysis. The former (mostly solid–gas) is very efficient, securing a good separation between the catalyst and the product, but lacks selectivity. The latter proceeds under mild conditions and is more selective, but catalyst and products are mixed in the same liquid phase. Several years ago, Bailar[1] suggested a liquid–liquid biphasic system which, in principle, should secure separation between the catalyst and the products by a proper choice of two immiscible liquids A and B. Useful combinations of catalyst, reagents, and products in such a liquid–liquid two-phase system are given in Scheme I.

Recent applications of phase-transfer catalysis[2] to organotransition-metal reactions[3] represent a step in this direction. Expected effects are as follows: (1) good separation between the catalyst and the product; (2) increased efficiency; (3) new selectivity due to the unusual conditions met within two-phase systems.

Scheme I

liquid A catalyst
liquid B reagents + products

liquid A catalyst + reagents
liquid B products

A number of experimental results have already been reviewed,[4] but, so far, no mechanistic investigation has been attempted. We report here a study of the catalytic carbonylation of benzyl bromide, run in a liquid–liquid phase-transfer system, with the cobalt carbonyl anion as

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[1] Bailar, J. C. *Catal. Rev.* **1974** *10*, 17.

[2] (a) Weber, W. P.; Gokel, G. W. "Phase Transfer-Catalysis in Organic Synthesis"; Springer Verlag: Berlin, Heidelberg, New York, 1977. (b) Starks, C. M.; Liotta, C. L. "Phase-Transfer Catalysis, Principles and Techniques"; Academic Press: New York, 1978. (c) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147–200.

[3] des Abbayes, H.; Alper, H. *J. Am. Chem. Soc.* **1977**, *99*, 98.

[4] (a) Cassar, L. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 208. (b) Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183.

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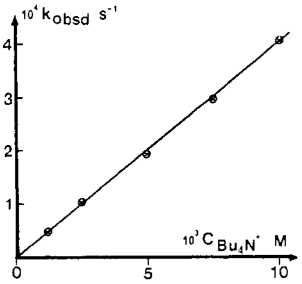

Figure 1. Dependence of the observed rate constant k_{obsd} on phase-transfer catalyst concentration (general conditions and 1100 rpm stirring in the H_2O/CH_2Cl_2 system) for stoichiometric carbonylation.

a catalyst. Two main steps, (1) and (2), are involved in this reaction.

$$\underset{1}{C_6H_5CH_2Br} + \underset{2}{Co(CO)_4^-} \xrightarrow[-Br^-]{} \underset{3}{C_6H_5CH_2Co(CO)_4} \overset{CO}{\rightleftharpoons} \underset{4}{C_6H_5CH_2COCo(CO)_4} \quad (1)$$

$$\underset{3}{C_6H_5CH_2Co(CO)_4} \overset{CO}{\rightleftharpoons} \underset{4}{C_6H_5CH_2COCo(CO)_4} \xrightarrow{OH^-} \underset{6}{C_6H_5CH_2CO_2H} + Co(CO)_4^- \quad (2)$$

Reaction 1 is the nucleophilic displacement of bromide by the cobalt carbonyl anion, followed by an equilibrium between the alkyl- and acylcobalt carbonyl species **3** and **4** under carbon monoxide atmosphere. This reaction was first studied under homogeneous conditions by Heck.[5] Reaction 2 is the cleavage of the organometallic species **4** (in equilibrium with **3**), by a base to give the acid and liberate the catalyst. Previous studies made by one of us[6] and others[7] have shown that high yields (>86%) of phenylacetic acid could be obtained under proper phase-transfer conditions. Our purpose here, rather than to get optimal yields, is to study how reactions 1 and 2 are involved in a two-phase system, under experimental conditions suitable for convenient kinetic and mechanistic investigations. As part of this effort, we have examined reaction 1 under stoichiometric conditions.[8]

Experimental Results

(1) Stoichiometric Reaction of the Cobalt Carbonyl Anion with Benzyl Bromide in a Two-Phase System. The following conditions were selected: 10 mL of the aqueous phase and 10 mL of an organic phase (benzene, diisopropyl ether, dichloromethane) at 20 ± 0.1 °C under 1 atm of carbon monoxide.

Magnetic stirring was electronically monitored. An excess (1 mmol) of sodium cobalt carbonylate was reacted with 0.5 mmol of benzyl bromide. For the extraction of the anionic reagent into the organic phase, tetrabutylammonium bromide was selected as a phase-transfer catalyst.[9] The kinetics of the reaction were followed by gas chromatographic (GC) analysis of benzyl bromide disappearance compared with an internal standard. Three runs were made for each experiment, and satisfactory pseudo-first-order plots were obtained, agreeing within ±4%. Above a stirring speed of 900 rpm, experimental kinetic constants k_{obsd} were independant of the stirring speed, whatever the organic solvent and the amount of cationic carrier up to 0.05 mmol. An example is given in Table I for the H_2O/CH_2Cl_2 system. Figure 1 shows the proportionality between k_{obsd} and concentration of tetrabutylammonium bromide. Table II gives essential kinetic data for reaction 1 in several two-phase systems.

Table I. k_{obsd} ($\times 10^5$ s^{-1}) **Variations vs. Stirring Speed for Stoichiometric Carbonylation**[a]

mmol of $Bu_4N^+Br^-$	stirring speed (rpm)			
	700	800	900	1100
0.025	7.7	8.7	9.9	9.9
0.05	12.4	15.5	19.5	19.6

[a] General conditions in the H_2O/CH_2Cl_2 system.

Table II. Kinetic Results for the Stoichiometric Reaction of Benzyl Bromide with the Cobalt Carbonyl Anion in a Two-Phase System[a]

two-phase system	H_2O/C_6H_6	$H_2O/i\text{-}Pr_2O$	H_2O/CH_2Cl_2	
10^3C_{org}(max) of Bu_4N^+, (calcd)	5	5	5	0
10^3C_{org}(max) of $Co(CO)_4^-$, (found)	5.1	1.6	4.9	0.42
10^5k_{obsd}, s^{-1}	6.9	11	20	0.97
10^2k_2, M^{-1} s^{-1}	1.38	6.9	4	2.3

[a] General conditions and 1100 rpm, 0.05 mmol of $Bu_4N^+Br^-$ was introduced, except for the last run. The maximal concentration of the ammonium cation in the organic phase (10 mL) should be $10^3C_{org}(max) = 5$ M.

An investigation of the quantity of cobalt carbonyl anion extracted into the organic layer was made by a colorimetric method according to the following sequence (3) in the absence of benzyl bromide. $(Bu_4N^+)_2Co(SCN)_4^{2-}$ was a blue complex extracted with chloroform (OD at 624 nm).

$$Co(CO)_4^- \xrightarrow{I_2} Co^{2+} \xrightarrow[SCN^-]{Bu_4N^+Cl^-} (Bu_4N^+)_2Co(SCN)_4^{2-} \quad (3)$$

The anion was fully oxidized by iodine to give the cation Co^{2+}[10] that was analyzed according to a standard colorimetric method.[11] As shown in Table II, the amount of cobalt carbonyl anion found in the organic phase and the quantity of tetrabutylammonium cation introduced agree well for benzene and dichloromethane as the organic phase, but not for diisopropyl ether. In the absence of the ammonium cation, extraction of the cobalt carbonyl anion in the organic phase is very limited (0.42×10^{-3} M in the H_2O/CH_2Cl_2 system). Consistent with these results is the very low aqueous solubility of the $Bu_4N^+Co(CO)_4^-$ salt found by the same method (7×10^{-5} M at 20 °C). The presence of a highly extractable competing anion such as iodide did not alter those results, since the selectivity coefficient $K_{Co(CO)_4^-/I^-}$ (defined in eq 4) showed a rather high value ($K_{Co(CO)_4^-/I^-} = 57$ in the water/dichloromethane system at 20 ± 0.1 °C).

$$K_{Co(CO)_4^-/I^-} = \frac{[I^-]_{aq}[Bu_4N^+Co(CO)_4^-]_{org}}{[Co(CO)_4^-]_{aq}[Bu_4N^+I^-]_{org}} \quad (4)$$

These results allow second-order rate calculations according to eq 5 and 6, which are given in Table II.

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[5] Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499.

[6] Alper, H.; des Abbayes, H. *J. Organomet. Chem.* **1977**, *134*, C11.

[7] Cassar, L.; Foa, M. *J. Organomet. Chem.* **1977**, *134*, C15.

[8] Preliminary accounts were published: des Abbayes, H.; Buloup, A. *J. Organomet. Chem.* **1980** *198*, C36. des Abbayes, H.; Buloup, A. *Tetrahedron Lett.* **1980**, *21*, 4343.

[9] This agent provided clean and quick separation between the two phases. Such was not the case with cetyltriethylammonium bromide (CTAB). Furthermore, it did not react with the catalyst (as does with benzyltriethylammonium chloride: Gambarotta, S.; Alper, H. *J. Organomet. Chem.* **1980**, *194*, C19.

[10] Sternberg, H. W.; Wender, I.; Orchin, M. *Anal. Chem.* **1952**, *24*, 174.

[11] Charlot, G. "Les méthodes de la chimie analytique"; Masson: Paris, 1966; p 714.

$$\text{rate} = k_{\text{obsd}}[C_6H_5CH_2Br]_{\text{org}} \qquad (5)$$

$$\text{rate} = k_2[Co(CO)_4^-]_{\text{org}}[C_6H_5CH_2Br]_{\text{org}} \qquad (6)$$

In the water/dichloromethane system, comparisons were possible between the reactivities of $Na^+Co(CO)_4^-$ and $Bu_4N^+Co(CO)_4^-$ ion pairs. The latter was shown to be slightly more reactive. This point is not of crucial importance in a catalytic system since reaction 1 is not necessarily rate determining (see below). For this reason, the influence of the state of hydration of the ion pair $Bu_4N^+Co(CO)_4^-$ on the reactivity has not been determined.[12]

The presence of the latter ion pair was demonstrated by IR analysis, showing a unique band near 1900 cm^{-1} consistent with a T_d symmetry for the cobalt carbonyl anion, which does not interact significantly with the tetrabutylammonium cation.[13]

Another band near 1720 cm^{-1} was ascribed to dibenzyl ketone (8) produced in situ as a byproduct and fully characterized by GC analysis and NMR. After complete reaction of benzyl bromide, the unstable acylcobalt 4 in equilibrium with the alkylcobalt carbonyl 3 was trapped as the triphenylphosphine derivative 5[14,15] in ≃45% yield after TLC purification (eq 7).

$$\underset{3}{C_6H_5CH_2Co(CO)_4} \overset{CO}{\rightleftharpoons} \underset{4}{C_6H_5CH_2COCo(CO)_4} \xrightarrow{(C_6H_5)_3P} \underset{5}{C_6H_5CH_2COCo(CO)_3P(C_6H_5)_3} + CO \qquad (7)$$

If sodium hydroxide was added instead of triphenylphosphine, then, after sufficient stirring, phenylacetic acid could be obtained in 30% yield. The same experiment under nitrogen atmosphere gave only poor yields of phenylacetic acid.

(2) Catalytic Carbonylation of Benzyl Bromide in a Two-Phase System. Production of phenylacetic acid from benzyl bromide becomes catalytic by combining steps (1) and (2) in the same liquid–liquid system. Due to the complexity of such a system, only an experimental kinetic approach was possible. Standard experimental conditions were the same as in section 1, except that the initial $[Co(CO)_4^-]/[C_6H_5CH_2Br]$ ratio was catalytic (1/20), and sodium hydroxide was introduced to give a 2 M aqueous phase. A typical kinetic curve is shown in Figure 2 for the water/dichloromethane system. Similar curves were obtained for the water/benzene system. It is seen that the initial rate of disappearance of benzyl bromide is the same as in stoichiometric conditions (AB part), but after a while, a slower good pseudo-first-order plot (BC part) is observed (eq 8). Since the first step of the catalytic cycle is reaction 1, which follows a second-order law (eq 6), we infer that during the BC interval, the concentration of the Bu_4N^+-$Co(CO)_4^-$ ion pair in the organic phase is stationary (eq 9).

$$\text{rate} = k'_{\text{obsd}}[C_6H_5CH_2Br] \qquad (8)$$

$$\text{rate} = k_2[Co(CO)_4^-]_s[C_6H_5CH_2Br] \qquad (9)$$

In eq 9, $[Co(CO)_4^-]_s$ is the stationary concentration of the catalyst $[Bu_4N^+Co(CO)_4^-]$ and $[C_6H_5CH_2Br]$ the concentration of benzyl bromide in the organic phase. If we define $[Co(CO)_4^-]_i$ as the initial concentration of Bu_4N^+-$Co(CO)_4^-$ ion pair, then

$$\text{rate} = k_2Q[Co(CO)_4^-]_i[C_6H_5CH_2Br] \qquad (10)$$

with $Q = [Co(CO)_4^-]_s/[Co(CO)_4^-]_i$ and then, in the BC part, the observed kinetic constant k'_{obsd} depends on Q according to eq 11.

$$k'_{\text{obsd}} = k_2Q[Co(CO)_4^-]_i \qquad (11)$$

Table III. Effect of the Amount of the Tetrabutylammonium Cation on the Observed Kinetic Constant k'_{obsd} for the Disappearance of Benzyl Bromide under Catalytic Conditions[a]

	mmol of Bu_4N^+				
	0.05	0.1	0.15	0.2	0.3
(a) Water/Dichloromethane System					
$10^4k'_{\text{obsd}}$, s^{-1}	0.57	1.08	1.56	2.02	3.02
Q(calcd)	0.28	0.27	0.39	0.50	0.76
Q(obsd)			0.31		
(b) Water/Benzene System					
$10^5k'_{\text{obsd}}$, s^{-1}		1.67		2.70	3.54
Q(calcd)		0.12		0.20	0.26
Q(obsd)		0.16			

[a] Experimental conditions: 10 mL of H_2O; 10 mL of organic solvent; 20 ± 1 °C; 1 atm of CO; 1100 rpm; 20 mmol of NaOH; 0.1 mmol of $NaCo(CO)_4$; 2 mmol of $C_6H_5CH_2Br$.

Table IV. Effect of Stirring on the Observed Kinetic Constants k'_{obsd} for Disappearance of Benzyl Bromide under Catalytic Conditions[a]

	rpm		
	700	900	1100
(a) Water/Dichloromethane System[a]			
$10^4k'_{\text{obsd}}$, s^{-1}	0.87	2.35	3.02
Q	0.22	0.59	0.76
(b) Water/Benzene System[b]			
$10^5k'_{\text{obsd}}$, s^{-1}	2.6	4.5	6.5
Q	0.09	0.16	0.23

[a] Same experimental conditions as in Table III, with 0.3 mmol of $Bu_4N^+Br^-$. [b] Same conditions as in Table III, except 0.2 mmol of $NaCo(CO)_4$ and 0.2 mmol of $Bu_4N^+Br^-$.

Table V. Product Ratios (% Yields Based on Benzyl Bromide Consumed) Resulting from Catalytic Carbonylation of Benzyl Bromide[a]

	two-phase system		
	H_2O/C_6H_6		H_2O/CH_2Cl_2
products	650 rpm (a)	1100 rpm (b)	1100 rpm (c)
6, $C_6H_5CH_2CO_2H$	34	36[b]	8
7, $C_6H_5CH_2CO_2CH_2C_6H_5$	11	8	3
8, $C_6H_5CH_2COCH_2C_6H_5$	15	14	12
9, $C_6H_5CH_3$	22	14	20
10, $C_6H_5CH_2CH_2C_6H_5$	17	21	50
11, CO_2	37	45	70

[a] Experimental conditions: 10 mL of H_2O; 10 mL of organic solvent; 20 ± 0.1 °C; 1 atm of CO; 20 mmol of NaOH; 2 mmol of $C_6H_5CH_2Br$; 0.1 mmol of $NaCo(CO)_4$; 0.1 mmol of $Bu_4N^+Br^-$. Method of analysis: **6**, gravimetric; **7**, **8**, and **10**, NMR; **9**, GC; CO_2, manometric. [b] An 85% yield was obtained under conditions which were not convenient for a kinetic analysis.[6]

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[12] (a) In the case of the iodide anion (which, in respect to electronegativity and polarizability[12b] presents close analogy with the cobalt tetracarbonyl anion) the state of hydration of the ion pair with the onium cation was found to be low and to have no significant effect on the reactivity.[2c] (b) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

[13] The interaction between the cobalt carbonyl anion and cations has been carefully studied: Edgell, W.; Chanjamsri, S. *J. Am. Chem. Soc.* **1980**, *102*, 148.

[14] Nagy-Magos, Z.; Bor, G.; Marko, L. *J. Organomet. Chem.* **1968**, 14, 205.

[15] des Abbayes, H.; Buloup, A. *J. Organomet. Chem.* **1979**, *179*, C21.

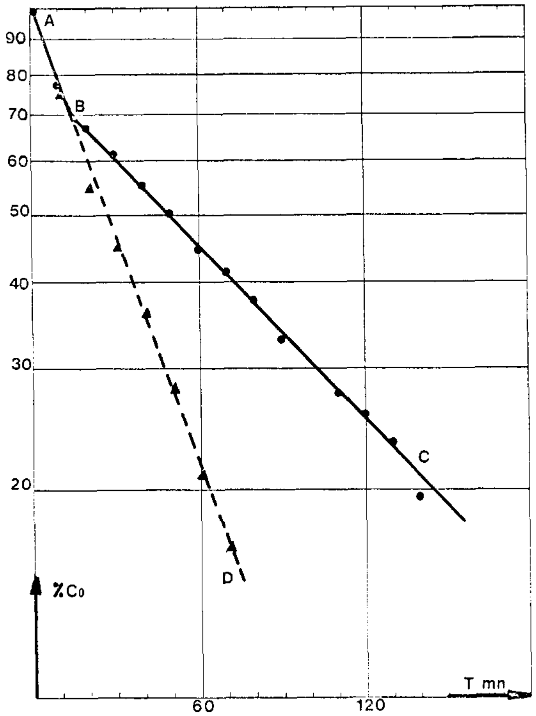


Figure 2. Kinetic curves obtained for the disappearance of benzyl bromide in the dichloromethane/water system. Stoichiometric conditions (- - -) 10 mL of H_2O; 10 mL of dichloromethane; 20 ± 0.1 °C, 1 atm of CO; 1100 rpm; 0.5 mmol of benzyl bromide; 0.1 mmol of tetrabutylammonium bromide; 1 mmol of sodium cobalt carbonylate. Catalytic conditions (–): 10 mL of H_2O; 10 mL of dichloromethane; 20 ± 0.1 °C; 1 atm of CO; 1100 rpm, 2 mmol of benzyl bromide; 0.15 mmol of tetrabutylammonium bromide; 0.1 mmol of sodium cobalt carbonylate; 20 mmol of NaOH. (Note that the initial concentration of $Co(CO)_4^-$ in the organic phase is the same under catalytic conditions as the permanent concentration of $Bu_4N^+Co(CO)_4^-$ in the organic phase under stoichiometric conditions.)

In some instances, values of Q were directly estimated from the absorbance at 1900 cm^{-1} which gives the exact amount of cobalt carbonyl anion present in the organic phase during the BC part of the kinetics. As shown in Table III, the observed values agree fairly well with the calculated ones obtained by using eq 11. As shown too in Table III, the observed kinetic constants k'_{obsd} are proportional to the amount of tetrabutylammonium cation introduced in both the water/dichloromethane and water/benzene systems.

Table IVa, shows that the variation of k'_{obsd} is linear with stirring speed in the 700–1100 rpm range.

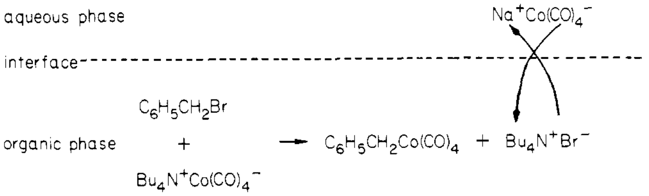
Finally, Table V shows the amounts of different products obtained under the same catalytic conditions after complete disappearance of benzyl bromide for differing organic phases and stirring speeds. It is shown that product ratios are not very dependent on the stirring speed between 650 and 1100 rpm but depend strongly on the nature of the organic phase.

Note the high production of neutral byproducts and carbon dioxide in the water/dichloromethane system. In every case, a small amount of benzyl ester 7 is found, resulting from a slow phase-transfer reaction of the phenylacetate anion with benzyl bromide.[2a]

Discussion

(1) Phase-Transfer Mechanisms in Reactions 1 and 2. Results concerning reaction 1 under stoichiometric conditions (Tables I and II) agree well with a theoretical study made by Gordon and Kutina[16] and with experimental data given by Starks[17] or Montanari[18] on nucleophilic displacements under phase-transfer conditions: extraction of the anionic reagent into the organic phase is rapid compared with the nucleophilic reaction and, consequently, kinetic results are independent of the stirring speed above a minimum level (Table I). Here, since the cobalt carbonyl anion and tetrabutylammonium cation do not coexist at significant concentration in aqueous phase, the extraction process works through simple anionic exchange at the interface without migration of the onium salt into the aqueous phase.[19] The concentration of the cobalt carbonyl anion (which is in excess in the aqueous phase) in the organic phase is kept constant throughout the reaction by rapid matching with the amount of tetrabutylammonium cation introduced (Table II) (except in the case of the water/diisopropyl ether system). Consequently, the disappearance of benzyl bromide follows a good pseudo-first-order kinetic law, proportional to the amount of tetrabutylammonium cation introduced (Figure 1 and eq 6). This mechanism is depicted in Scheme II.

Scheme II



Introduction of sodium hydroxide completes the catalytic cycle by combining reactions 1 and 2. Several anions compete for extraction into the organic phase as tetrabutylammonium salts. However, their ease of extraction varies considerably as shown in the following sequence, demonstrated for the water/dichloromethane system: $OH^- \ll Cl^- < C_6H_5CH_2CO_2^- < Br^- < I^-$[20] $< Co(CO)_4^-$. Extraction of the hydroxide anion was found to be so weak that its reality is questionable.[21] Here, owing to the presence of highly extractable anions such as the cobalt carbonyl anion (see above $K_{Co(CO)_4^-/I^-} = 57$ in the H_2O/CH_2Cl_2 system) and the lack of a "salting out" effect (in our experiments, the aqueous concentration of sodium hydroxide was only moderate: ≃8%), extraction of $Bu_4N^+OH^-$ into the organic phase is very unlikely, and this ion pair should exist at the liquid–liquid interface, on the aqueous side. This is consistent with the high dependence of the catalytic kinetics on stirring speed (Table IV),[22] in contrast to the behavior of the stoichiometric reaction (Table I).

The dependence of the kinetic constant k'_{obsd} on the amount of cationic carrier (Table III) supports the assistance of the tetrabutylammonium cation in reaction 2. This was further demonstrated in a separate experiment:

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[16] Gordon, J. E.; Kutina, R. E. *J. Am. Chem. Soc.* **1977**, *99* 3903.

[17] Starks, C. M.; Owens, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 3613.

[18] Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796.

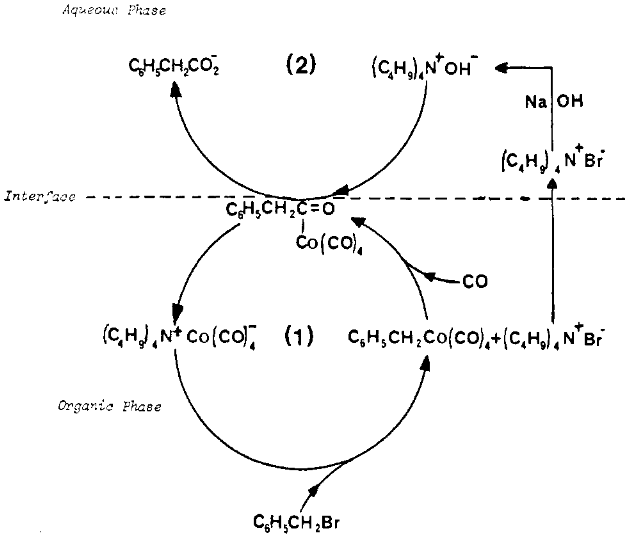
[19] Such a mechanism was proposed in a pure organic two-phase system: Landini, D.; Maia, A.; Montanari, F. *J. Chem. Soc., Chem. Commun.* **1977**, 112.

[20] Brandström, A. "Preparative Ion Pair Extraction"; Apotekarsocietaten Häsale Lakemedel: Stockholm, 1974.

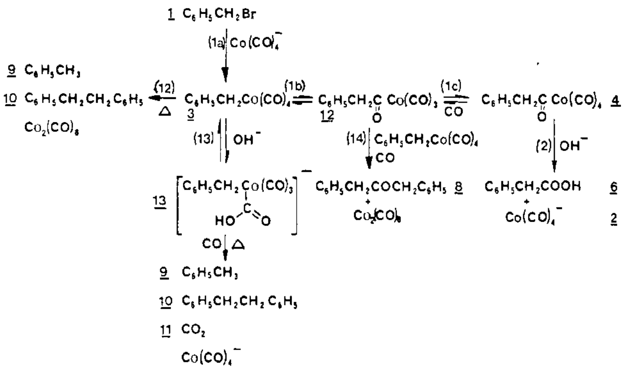
[21] See a discussion in ref 2c.

[22] This criterion is extensively discussed in: (a) Hanson, C. "Recent Advances in Liquid-Liquid Extraction"; Pergamon Press: Oxford, 1971; chapter 12. (b) Jonczyk, A.; Kwast, A.; Makosza, M. *Tetrahedron Lett.* **1979**, *6*, 541. (c) Menger, F. M. *Pure Appl. Chem.* **1979**, *51*, 999. (d) Solaro, R. S.; D'Antoine, S.; Chiellini, E. *J. Org. Chem.* **1980**, *45*, 4179. (e, Othani, N.; Besse, J. J.; Regen, S. L. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 607.

Scheme III



Scheme IV



in its absence, the concentration of benzyl bromide remained constant.

If we consider now the experimental kinetic law (10), the following conclusions can be drawn: If $Q = 1$, the rate-limiting step is reaction 1. This case is approached for the water/dichloromethane system at high stirring speeds and high concentration of cationic carrier (Table IVa, 1100 rpm).

If $Q \ll 1$, the rate-limiting step is reaction 2. Such is the case for the water/benzene system at low stirring speed and low concentration of cationic carrier (Table IVb, 700 rpm).

Scheme III summarizes these results and shows how reactions 1 and 2 work in a two-phase system.

Reaction 1 occurs entirely in the organic phase and follows the second-order kinetic law given in eq 10. Reaction 2 occurs at the liquid–liquid interface, so it depends strongly on the stirring speed. According to this scheme, catalyst $Bu_4N^+Co(CO)_4^-$ and product $C_6H_5CH_2CO_2^-$ are separated in two different phases, and this was one of the expected effects of liquid–liquid catalytic systems.

(2) Organometallic Mechanisms Involved in Reactions 1 and 2 under Phase-Transfer Conditions. Scheme III does not account for all the products shown in Table V. A more complete description is given in Scheme IV. The presence of ketone **8** is well explained by addition of benzylcobalt carbonyl **3** to the unsaturated species **12**, followed by reductive elimination and production of dicobalt octacarbonyl (reaction 14).[23] Several explanations can be proposed for presence of toluene (**9**) and diphenyl ethane (**10**):

(a) Reaction 1, instead of going according to an S_N2 mechanism, could occur via single electron transfer (reaction 15).

$$C_6H_5CH_2Br + Co(CO)_4^- \rightarrow C_6H_5CH_2Br^{-\cdot} + Co(CO)_4\cdot \rightarrow C_6H_5CH_2\cdot + Br^- + Co(CO)_4\cdot \rightarrow C_6H_5CH_2Co(CO)_4 + \underset{9}{C_6H_5CH_3} + \underset{10}{C_6H_5CH_2CH_2C_6H_5} + Co_2(CO)_8 \quad (15)$$

Abstraction of hydrogen from the solvent by the benzyl radical would give toluene, and coupling would give the hydrocarbon **10**. Along with these products, dicobalt octacarbonyl would be produced by coupling of the cobalt tetracarbonyl radical. Despite growing interest in single electron-transfer mechanism of metal carbonyl anions on halides[24] no convincing experimental proof is available so far to assert pathway 15. A spin trap experiment with galvinoxyl was not conclusive since we observed a reaction of galvinoxyl with the cobalt carbonyl anion. Our kinetic law (6) (which also held under homogeneous conditions[25]) although consistent with a S_N2 mechanism is far from being sufficient to prove it, and the question is still open.

(b) Despite the lack of reliable data on the metal–carbon bond dissociation energies for compounds such as **3**, there is no doubt that these are low (<30 kcal/mol).[26] Consequently, a thermal homolytic cleavage of this species, followed by recombination, should be considered (eq 12).

$$C_6H_5CH_2Co(CO)_4 \rightleftarrows C_6H_5CH_2\cdot + Co(CO)_4\cdot \rightarrow C_6H_5CH_3 + C_6H_5CH_2CH_2C_6H_5 + Co_2(CO)_8 \quad (12)$$

Whatever the mechanism for production of **8**, **9**, and **10**, a maximum of 0.5 mol of dicobalt octacarbonyl should be produced for 1 mol of benzyl bromide disappearing as **8**, **9**, or **10** (see reactions 12, 14, 15). Recycling of this metal carbonyl as the cobalt carbonyl anion would occur according to Hieber's reaction (16).[27]

$$Co_2(CO)_8 + CO + 4OH^- \rightarrow 2Co(CO)_4^- + CO_3^{2-} + 2H_2O \quad (16)$$

Consequently, for 1 mol of benzyl bromide disappearing according to reactions 12 or 14 and 15, 0.5 mol of carbonate anion should be produced. So, considering the amounts of **8**, **9**, and **10** (in % of benzyl bromide consumed) given in Table V, maximum production of carbon dioxide should be 27%, 24%, and 41%, respectively, for columns a, b, c, which disagrees strongly with experimental results (37%, 45%, and 70%). We checked that in the absence of benzyl bromide, and for the same reaction time, no significant amount of CO_2 was produced.

Therefore, we suggest that a new reaction scheme operates for production of **9** and **10**. Attention is now drawn to the reactivity and labilization of metal carbonyls by attack of hydroxide anion, giving a transient hydroxycarbonyl species.[28] In some instances, such a species has been fully characterized.[29] Thus we propose (Scheme IV, reaction 13) that the same reaction occurs on the alkylcobalt carbonyl **3** giving the unstable hydroxycarbonyl anion **13** by attack of $Bu_4N^+OH^-$ at the interface according to the phase-transfer mechanism described above.

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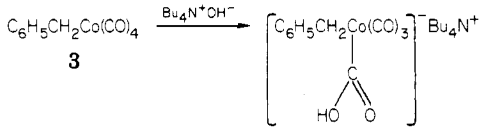

(13)

13

Decomposition of species **13** would give products such as toluene (**9**), diphenylethane (**10**), and carbone dioxide (**11**) and would recycle the catalyst $Co(CO)_4^-$. An important feature of this scheme is that for 1 mol of benzyl bromide disappearing 1 mol of carbon dioxide should be produced. The calculated amounts of CO_2 produced according to sequence (13) and (14) + (16) are 46%, 42%, and 76% for columns a, b, and c of Table V, which agree fairly well with the experimental results.

According to this scheme, the main pathway for production of **9** and **10** would be a simple S_N2 reaction for step 1 followed by transient production of the unstable hydroxycarbonyl anion **13** (Scheme IV).

To account for the production of phenylacetic acid, we invoke the well-known route of alkyl migration to coordinated CO (reaction 1b) followed by attack of the hydroxide anion on the acylcarbonyl group of the organometallic **4**.[30] If the equilibrium between **4** and **3** is well established,[5,14] the only sure experimental result of reaction 2 is that, under CO, **4** and **3** in equilibrium give the phenylacetate anion in the presence of a base. Thus, while attack of OH^- on the acyl group of species **4** is reasonable, it is by no means proved. Therefore, alternative pathways such as decomposition of the hydroxycarbonyl **13** could account for production of phenylacetic acid as well.[31] At the moment, we favor the classical Scheme (2) since, under stoichiometric conditions under nitrogen, cleavage by sodium hydroxide of the organometallic **3** (then weakly equilibrated with **12**)[14] gave only poor yields of phenylacetic acid.

A consequence of Scheme IV is that an increase in CO pressure should shift equilibria 1b and 1c from **3** to **4** and thus lower the extent of side reactions (12)–(14). In fact, the situation becomes more complicated since, at 60 atm of CO, a new reaction takes place: besides the expected phenylacetic acid (**6**), a new acid is produced (phenylpyruvic acid (**14**) resulting from a formal double CO insertion (reaction 17) (**14**/**6** ratio = 2). We have already observed this double carbonylation in a two-phase system at atmospheric pressure with benzyl halides activated by donor groups.[32] This important reaction will be discussed on in a future paper.

$$\underset{\mathbf{1}}{C_6H_5CH_2Br} \xrightarrow[\text{NaOH, } Bu_4N^+Co(CO)_4^-\text{, 60 atm of CO}]{\text{two-phase system}} \underset{\mathbf{6}}{C_6H_5CH_2CO_2H} + \underset{\mathbf{14}}{C_6H_5CH_2COCO_2H} \quad (17)$$

Experimental Section

NMR spectra were recorded with a Varian EM 360 spectrometer. Infrared spectra were recorded with a Philips Unicam SP 1100 spectrometer. Colorimetric analyses were recorded with a Beckman DB UV visible spectrophotometer. GC analyses were carried out with an Intersmat ICG 12 gas chromatograph equiped with a 1-m column of Apiezon (on Chromosorb HMDS) and fitted with a 3390 A Hewlett-Packard integrator.

Materials and Solvents. Benzyl bromide and GC internal standards (naphthalene, *p*-xylene, biphenyl, dibenzyl distilled were used as provided by Aldrich Co., after NMR and GC purity checks.

Water was distilled twice under nitrogen. Organic solvents of analytical quality (benzene, diisopropyl ether, dichloromethane) were distillated under nitrogen. Sodium cobalt carbonylate was prepared from dicobalt octacarbonyl (Strem Co) according to Edgell's procedure.[33] Aqueous solutions of sodium cobalt carbonylate, stored under carbon monoxide, were checked before use by a manometric method;[10] aqueous solutions of tetrabutylammonium bromide (from Aldrich Co.) were titrated potentiometrically (Br^-); aqueous sodium hydroxide was titrated by acidimetric analysis.

Reaction Apparatus. A round-bottom Schlenk tube (diameter 40 mm) surrounded by a thermostated jacket (circulation LAUDA thermostat, ±0.1 °C) equipped a with a rubber septum capped side arm was connected to a vacuum–carbon monoxide line. Stable stirring was secured by introducing a "Baroval" magnetic bar fitting the round bottom, driven by an electronically monitored Combimag stirring plate (±50 rpm maximum drift). Stroboscopic examination verified the stability and accuracy of the stirring speed.

Kinetic Measurements. The following procedure was typical. The thermostated cell (20 ± 0.1 °C) was first purged by several vacuum–carbon monoxide filling cycles and then filled with carbon monoxide at atmospheric pressure. The desired amounts of sodium cobalt carbonylate, sodium hydroxide, and tetrabutylammonium bromide were introduced by syringe injection of suitable volumes of titrated aqueous solutions through the rubber septum, and the aqueous phase was adjusted to 10 mL. The organic phase (10 mL) containing the internal standard (1 mmol of naphthalene for 1 mmol of benzyl bromide used) was injected. After the mixture was stirred for several minutes to obtain thermal equilibrium, the correct volume of benzyl bromide was quickly injected. Samples of the organic phase ($\simeq 5\ \mu L$) were withdrawn every 10 min after stopping the stirring for 30 s (sufficient for a good separation of the two phases) and quickly injected in the GC apparatus. GC analysis required less than 5 min. Every run was followed up to at least 80% consumption of benzyl bromide. At least three runs were made for one experiment. Analytical data were satisfactorily plotted on semilog paper and pseudo-first-order constants k_{obsd} calculated according to the half-life of benzyl bromide ($k_{obsd} = 0.69/t_{1/2}$). Scatter between duplicate runs was found to be less than 4%.

Colorimetric Analysis of the Cobalt Carbonyl Anion. The principle is given in eq 3. Colorimetric absorptions were compared with a standard curve drawn from results given with a titrated solution of cobalt chloride.

This standard 10^{-2} M solution (A) was prepared from analytically pure $CoCl_2{\cdot}6H_2O$ and checked by potentiometric analysis of the chloride anion. Also used were the following: iodine, 12.6 g/L in CCl_4 (B); KSCN, 50% in water (C); $Bu_4N^+Cl^-$, 2% in water (D); $Na_2S_2O_3$, M/10 in water (E); HCl, M/100 in water (F).

The UV–visible spectrophotometer was stardardized at 624 nm according to the following procedure: from standard solution A were withdrawn x μL, to which was added 2 mL of solution C and 0.3 mL of solution D. The blue complex was extracted three times with chloroform and the solution adjusted to 5 mL. The OD at 624 nm was linear with respect to the number (n) of μmol of Co^{2+} first introduced: OD = $0.385n$. A typical analysis was conducted as follows: a biphasic system was made of 1 mmol of $NaCo(CO)_4$, 0.1 mmol of $Bu_4N^+Br^-$, 10 mL of H_2O, and 10 mL of CH_2Cl_2. After 3 h of stirring at 20 °C under CO atmosphere and 1 h of decantation, 50 μL of the organic solution was withdrawn, oxidized with 100 μL of solution B, evaporated, and washed with solution E, the pH was adjusted to $\simeq 5$ with solution F, and then the mixture was treated as above. Co (0.52 mmol) was found in the sample, i.e., 1.04×10^{-2} M. Three analyses were done for each experiment.

The solubility of $Bu_4N^+Co(CO)_4^-$ in the aqueous phase was measured according to a similar procedure: after saturation of water with this salt and filtration, 7 mL of this colorless solution was treated as above, except that cobalt was oxidized by an aqueous solution of iodine and potassium iodide. The same

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technique was used to titrate freshly prepared aqueous solutions of sodium cobalt carbonylate. In this latter case, manometric analysis was also used.[10]

The coefficient of selectivity $K_{\mathrm{Co(CO)_4^-/I^-}}$ defined in eq 4 was similarly obtained: into a two-phase system (10 mL of H_2O, 10 mL of CH_2Cl_2) at 20 °C were introduced 10 mmol of NaI, 0.1 mmol of $Bu_4N^+Br^-$, and 0.25 mmol of $NaCo(CO)_4$. After sufficient stirring, the amount of cobalt in the organic phase was determined as above and found to be 0.0053 M. Considering that all the introduced ammonium cation is present as a $Bu_4N^+Co(CO)_4^-$ or $Bu_4N^+I^-$ ion pair in the organic phase, due to the low aqueous solubility of these salts, $K_{\mathrm{Co(CO)_4^-/I^-}}$ is directly available from formula 4. Selective analysis of the $Co(CO)_4^-$ anion in organic phase, during catalytic experiments, was made by IR analysis ($\nu_{C\equiv O}$ = 1900 cm^{-1}) after standardizing the IR spectrophotometer with a titrated solution of $Bu_4N^+Co(CO)_4^-$.

Quantitative Analysis of Products 6-11 (Table V). Phenylacetic acid (6): directly extracted, after acidification, from aqueous phase and weighted after evaporation of solvent.

Ester 7, ketone 8, and hydrocarbon 10: NMR ($\delta(CH_2)$) on the crude mixture resulting from evaporation of the organic phase, after destruction of any remaining cobalt carbonyl catalyst with iodine.

Toluene (9): GC analysis of the organic phase after introducing *p*-xylene as an internal standard.

Carbon dioxide (11): manometric measurement after prior destruction of the cobaltcarbonyl catalyst, followed by acidification of the aqueous phase with hydrochloric acid.

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Binuclear Isocyanide Complexes of Platinum(I). Facile N-Protonation and Alkylation of Bridging Isocyanide Ligands To Yield Bridging Aminocarbyne Complexes

Kevin R. Grundy* and Katherine N. Robertson

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3 Canada

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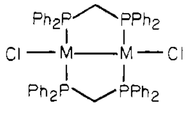
The platinum(I) dimers $Pt_2X_2(\mu\text{-dppm})_2$ (X = Cl, I) react with *p*-tolyl isocyanide (CNR) under various conditions to give $Pt_2X_2(\mu\text{-CNR})(\mu\text{-dppm})_2$, $[Pt_2X(CNR)(\mu\text{-dppm})_2]^+$, $[Pt_2(CNR)_2(\mu\text{-dppm})_2]^{2+}$, and $[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2]^{2+}$. The complexes with bridging isocyanides undergo facile N-protonation and alkylation to yield the series of complexes $[Pt_2L_2(\mu\text{-CNRR}')(\mu\text{-dppm})_2]^{n+}$ (L = X, R′ = H, Me, n = 1; L = CNR, R′ = H, Me, n = 3). All structural assignments are made on the basis of vibrational, ^1H NMR, and ^{31}P NMR spectroscopy.

Introduction

Over recent years, the chemistry of dinuclear complexes of Pd(I) and Pt(I), and the A-frame type complexes of Rh(I) and Ir(I), has been the subject of increasing attention. Much of the interest in this chemistry has focussed upon the ability of these complexes to coordinate small molecules (sometimes reversibly) and their ability to act as catalysts for certain processes[1,2] or serve as models for proposed intermediates in catalytic cycles.[3] The platinum(I) and palladium(I) bis(diphenylphosphino)methane (dppm) bridged dimers, $M_2Cl_2(\mu\text{-dppm})_2$, I, have an especially rich chemistry with regard to their ability to coordinate molecules via addition across the metal–metal bond, resulting in complexes of the type $[M_2Cl_2(\mu\text{-X})(\mu\text{-dppm})_2]^{n+}$, II. To date, examples with X = CO,[3,4] CNR,[4] CH_2,[3,4] H^+,[3] N_2R^+,[4] SO_2,[3,4] S,[3,4] Se,[5] C_2R_2,[3,4] and CS_2[6] have been isolated, although not necessarily with both metals. Unlike their rhodium analogues, however, these A-frame complexes of platinum and palladium have shown no tendency to coordinate small molecules or atoms to the face of the complex opposite the bridging ligand.



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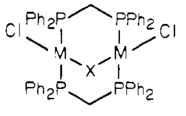

II

Our interest in the chemistry of such binuclear complexes centers principally upon the chemistry of the bridging ligand.[7] In particular, we are interested in the effect that binuclear activation can have upon the chemistry of the bridging group itself and also in the effect that varying the bridghead ligand has upon the chemistry of the complex as a whole. The complex $Pt_2Cl_2(\mu\text{-dppm})_2$ appears as an ideal starting point for investigating the chemistry of the bridging groups in dinuclear complexes for two reasons: (i) the great reactivity of the Pt–Pt bond gives access to a wide variety of bridging groups and (ii) investigating the chemistry of the bridging group is not hampered by competing reactions occurring on the other face of the dimer. When this project was initiated, dimeric,

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