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Preliminary communication

SYNTHESIS OF ACYLCOBALT CARBONYL COMPLEXES BY PHASE TRANSFER AND THREE PHASE CATALYSIS

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Summary

Some acylcobalt carbonyl compounds were prepared by reaction of RCH_2X ($X = Cl, Br, I$) with the cobalt carbonyl anion by phase transfer and three phase catalysis. A comparison between these two methods shows that the three phase system is twenty times less efficient than the two phase system.

Phase transfer catalysis, which is a much used technique in organic synthesis [1] was recently extended to organometallic chemistry [2]. In particular several applications were described of the "in situ" generation of the cobalt carbonyl anion in a two phase system consisting of benzene, water, $Co_2(CO)_8$, NaOH and $R_4N^+Cl^-$ [3a—d]. Since sodium hydroxide brings cleavage of complexes of type (II) [3c] they cannot be prepared in such a system, and we now describe an easy route to those complexes, which are valuable synthetic intermediates [3b,c], using the cobalt carbonyl anion free from NaOH* in a two phase or three phase [5] system (eq. 1).

$$\underset{\text{(I)}}{RCH_2X} \xrightarrow[\substack{NaCo(CO)_4\\ R_4N^+Cl^-\\ H_2O\\ CO\ (1\ atm.)\\ 1100\ r.p.m.\ 20^\circ C}]{CH_2Cl_2} \underset{\text{(II)}}{RCH_2COCo(CO)_4} \qquad (1)$$

($X = Cl, Br, I$)

$Bu_4N^+Cl^-$ is the catalyst in the two phase system. We found that the $Bu_4N^+Co(CO)_4^-$ ion pair is rather insoluble in water ($7 \cdot 10^{-5}$ M l^{-1} at 20°C), and that all the ammonium cation introduced in the system is present in the organic phase in

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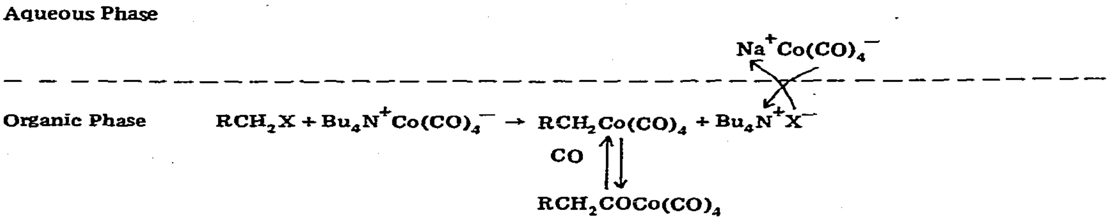
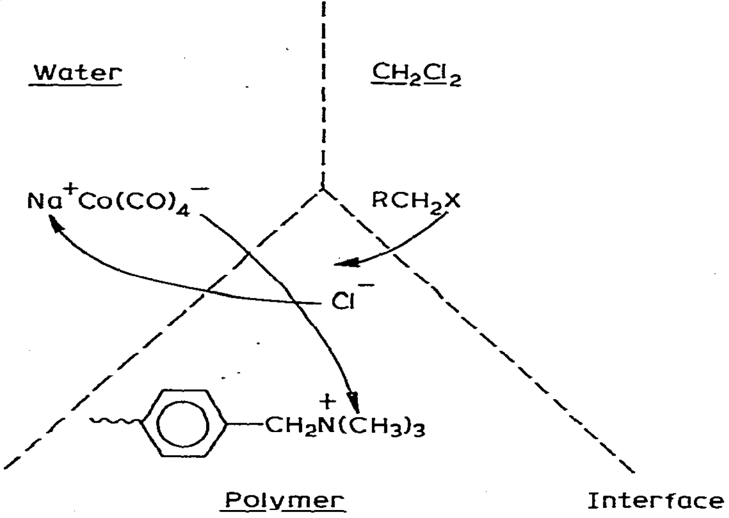
*$NaCo(CO)_4$ prepared according to ref. 4 contains no more than 0.2% of NaOH (as found by acid titration).

SCHEME 1

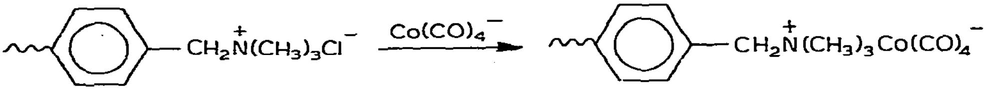


this ion pair [6]. So, the reaction probably proceeds by continuous migration of the ammonium cation between the two phases (Scheme 1). Catalysis by anionic exchange is involved in the three phase system represented in Scheme 2.

SCHEME 2



Here, the quaternary ammonium group is fixed to a crosslinked polystyrene matrix (commercial anionic exchange resin Lewatit Merck M 5080), and the following exchange is complete in a short time (eq. 2):



(2)

Without the quaternary ammonium catalyst, the reaction is extremely slow: for instance, with benzyl bromide only 10% of the starting material is consumed after three hours of stirring. Furthermore, the three phase system needs twenty times more ammonium sites than the two phase one for rates of the same order of magnitude [6].

The acylcobalt carbonyl complexes II cannot be isolated, but give the rather stable derivatives $RCH_2COCo(CO)_3P(C_6H_5)_3$ (III) with triphenyl phosphine [7]. Yields of the complexes III are given in Table 1 for some of the halides I. They are slightly lower for the three phase system.

TABLE 1

SYNTHESIS OF COMPLEXES $RCH_2COCo(CO)_3P(C_6H_5)_3$ (III)[a]

Starting halide I	Yield (%)[b]	
	two phase system	three phase system
$C_6H_5CH_2Br$	44	—
$BrC_6H_4CH_2Br$	42	36
$(CH_3)_3C_6H_2CH_2Cl$	38	—
$BrCH_2CO_2CH_3$	27	—
CH_3I	36	30
m-$CNC_6H_4CH_2Br$	57	48
β-Naphthyl CH_2Br	35	43
o-$CH_3C_6H_4CH_2Br$	51	44

[a] Experimental conditions. *Two phase system*: halide 2 mM, $NaCo(CO)_4$ 2 mM, $Bu_4N^+Cl^-$ 1/10 mM, H_2O 25 cm^3, CH_2Cl_2 25 cm^3; T 20°C; 1100 r.p.m. *Three phase system*: the same except 5 m eq. of anionic exchange resin instead of $Bu_4N^+Cl^-$. Time between a few hours and several days, depending on the technique and the halide. Complexes III were identified by comparison with published data [7,8] and by spectral methods [IR (CH_2Cl_2 (cm^{-1}): $\nu(C{=}O) \simeq 1680$w, $\nu(C{\equiv}O) \simeq 1790$vs, 1990vs, 2080s. ^1H NMR (CD_2Cl_2) δ $CH_2\underset{\overset{\|}{O}}{C} \simeq 4.5$ ppm (s).] [b] Of isolated complex after purification on silica gel.

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