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Preliminary communication

GENERATION OF THE COBALT TETRACARBONYL ANION BY PHASE TRANSFER CATALYSIS, APPLICATIONS TO THE SYNTHESIS OF π-ALLYL AND CLUSTER COMPLEXES

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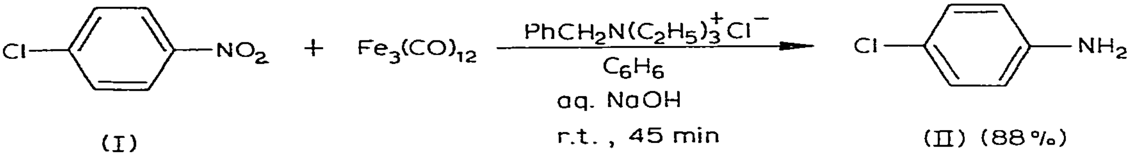
Summary

Phase transfer catalysis provides a simple, convenient, and rapid means for preparing π-allylcobalt carbonyl and alkylidynetricobalt nonacarbonyl complexes.

Many organic reactions involving anionic species can be effectively catalyzed using an aqueous-organic two-phase system [1]. Several facile phase transfer catalyzed organometallic reactions (e.g. I → II) have recently been observed [2, 3]. We now wish to report that phase transfer catalysis is an excellent method for synthesizing π-allyl and cluster complexes.



π-Allylcobalt tricarbonyl complexes (IV) were obtained in 70—80% yields by reaction of a benzene solution of an allyl bromide (III) with dicobalt octacarbonyl, 5*N* NaOH, and benzyltriethylammonium chloride as the catalyst. The reactions were complete in 15-60 min at room temperature. The π-allyl complexes were characterized either as IV or as the triphenylphosphine substituted derivatives (V). The yields are given in Table 1.

The phase transfer catalyzed preparation of IV is superior to other syntheses of these complexes in terms of yield, speed, mildness, and simplicity. Pressure conditions are required for the preparation of IV in modest yields from $HCo(CO)_4$ and 1,3-dienes [4, 5], while variable amounts of IV result from reaction of III

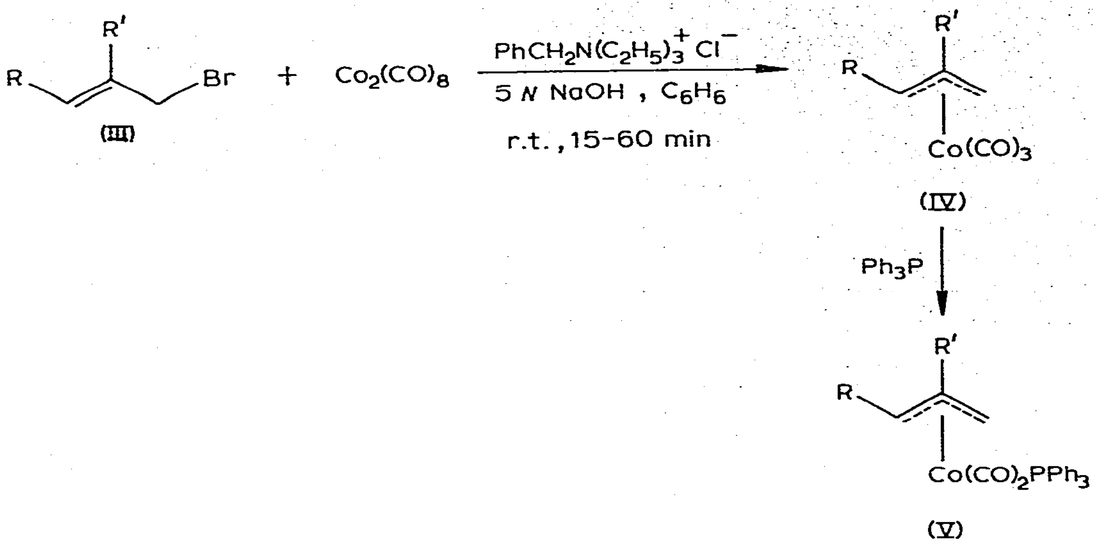


TABLE 1

YIELDS OF π-ALLYL COMPLEXES[a]

R, R' (IV)	Reaction time (min)	Yield (%)
H, H	15	80
H, CH_3	40	73
CH_3, H	15	80
Ph, H	60	72

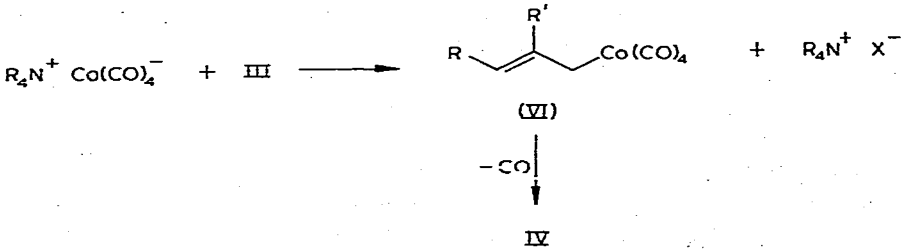
[a] The structures of the products were determined by comparison of physical properties with those reported in the literature [4—6].

with $NaCo(CO)_4$ in ether at 25°C for 2—20 h, followed by heating at 80°C for 1—3 h [6].

The initial step in the reaction is likely conversion of the ammonium halide to the hydroxide in the aqueous phase. The ammonium hydroxide is then transferred to the organic phase as an ion-pair, where it readily attacks $Co_2(CO)_8$ forming the cobalt tetracarbonyl anion [7]. The latter then reacts with III to give IV

$$R_4N^+ X^- + OH^- \longrightarrow R_4N^+OH^- + X^-$$

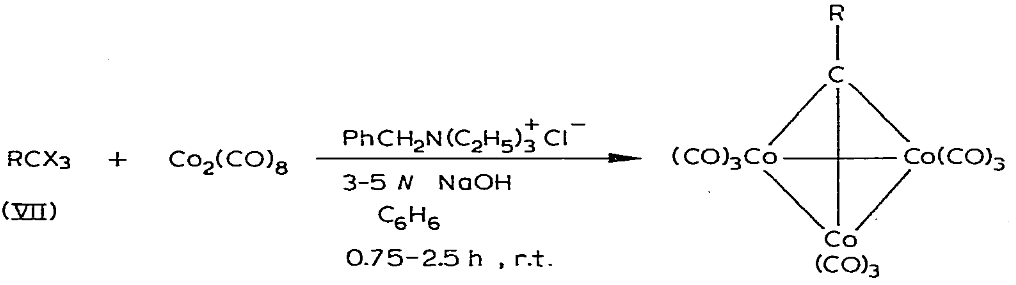
$$32\,R_4N^+ OH^- + 11\,Co_2(CO)_8 \longrightarrow 20\,R_4N^+ Co(CO)_4^- + 6[R_4N]_2CO_3 + 2\,CoCO_3 + 16\,H_2O$$



(via VI) and the ammonium halide, which migrates to the aqueous phase. When $Co_2(CO)_8$ was treated for 2 h with NaOH (two-phase system) in the absence of III and the catalyst, the metal carbonyl was recovered in 85% yield. With added catalyst, complete conversion of $Co_2(CO)_8$ to the $Co(CO)_4^-$ ion occuned within 15 min.

Splendid work has been carried out by Seyferth and coworkers [8] on the use of alkylidynetricobalt nonacarbonyls $[RCCo_3(CO)_9]$ in organic and organometallic synthesis. A general method for preparing these complexes is by reaction of di- or tri-halomethyl compounds with dicobalt octacarbonyl for 3—72 h at 25—50°C, depending on the organic reactant [9]. Since the $Co(CO)_4^-$ ion is a probable intermediate in the formation of alkylidynetricobalt nonacarbonyls [8], this reaction seemed ideally suited to phase transfer catalysis techniques.

Treatment of a trihalomethyl compound VII with $Co_2(CO)_8$ (3 : 1 mole ratio of $Co_2(CO)_8$: VII), using benzyltriethylammonium chloride as the catalyst, and 3—5 *N* NaOH in benzene for 0.75—2.5 h at room temperature affords the cluster VIII. The reaction conditions used, and the yields of VIII are given in Table 2.



(VIII)

TABLE 2

YIELDS OF CLUSTER COMPOUNDS[a]

Reactant halide	R (VIII)	NaOH conc. (*N*)	Reaction time (h)	Yield (%)
CCl_4	Cl	5	2.0	42
CBr_4	Br	5	0.75	11
$PhCCl_3$	Ph	3	2.5	53
$CCl_3COOC(CH_3)_3$	$COOC(CH_3)_3$	3	2.5	30
CCl_3CH_2OH	CH_2OH	3	2.5	trace

[a] The structures of the products were determined by comparison of physical properties (e.g., IR, NMR) with those reported in the literature [9, 10].

Except for VIII (R = Br), the yields of alkylidynetricobalt nonacarbonyls are comparable with (R = Cl, CH_2OH), or superior to (R = Ph, $COOC(CH_3)_3$), those reported in the literature [8, 9]. It is noteworthy that VIII (R = $COOC(CH_3)_3$), was formed in reasonable yield without hydrolysis of the ester function. In addition, the reaction is effected under mild conditions, and is simple to work-up.

The only attempt at yield optimization involved variation of the concentration of sodium hydroxide. Better yields of halosubstituted clusters (VIII, R = Cl, Br) were realized using 5 *N* rather than 3 *N* NaOH.

The following general procedures were used (N_2 atmosphere: Note: $Co_2(CO)_8$ is toxic; $Co_2(CO)_8$ and the π-allyl complexes are air-sensitive):

(a) π-allyl complexes

Into a 50 ml filtering flask was placed 0.11 g (0.5 mmol) of $PhCH_2N(C_2H_5)_3{}^+Cl^-$, 5 *N* NaOH (10 ml), and benzene (6—10 ml) in which was dissolved $Co_2(CO)_8$ (0.5 mmol) and III (1.0 mmol). After stirring for 15—60 min, the layers were separated and the benzene layer showed only π-allyl complex (NMR). Complex IV was isolated by evaporation or as the more stable triphenylphosphine complex V [6], formed by addition of an equimolar amount of PPh_3 to the organic phase.

(b) Cluster complexes

To a mixture of VII (1—3 mmol), 3 equivalents of $Co_2(CO)_8$, and $PhCH_2N(C_2H_5)_3{}^-Cl^-$ (0.4—0.6 equivalents relative to VII — except for $CCl_3COOC(CH_3)_3$ where 0.8 equivalents were used) in benzene (20—35 ml) was added 15—20 ml of NaOH (3—5 *N*) [N_2 atmosphere]. The resulting mixture was vigorously stirred at room temperature for 0.75—2.5 h. The layers were separated (centrifuge), and hexane (40—80 ml) was added to the organic layer. The hexane/benzene solution was washed with water, dried, and evaporated to give VIII. Further purification, if necessary, was effected by sublimation or by column chromatography.

We are currently investigating the application of phase transfer catalysis to the synthesis of other π-allyl complexes (e.g. Mn), and to reactions where $Co_2(CO)_8$ functions as a catalyst (e.g. hydroformylation).

Acknowledgments

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Note added in proof. Use of CH_2Cl_2 instead of C_6H_6 as the solvent in the cluster synthesis gives higher yields of VIII in some cases, e.g. R = Ph, 74%.