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Preliminary communication

APPLICATION OF PHASE-TRANSFER CATALYSIS IN ONE STEP SYNTHESIS OF SOME ALKYLIDYNECOBALT NONACARBONYL COMPLEXES

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Summary

Cobalt cluster carbonyl complexes $XCCo_3(CO)_9$ (X = Cl, Br, H) can be synthesised from $Co(NO_3)_2 \cdot 6H_2O$ in a one step process and under atmospheric pressure of CO by using a phase-transfer catalyst.

Alkylidynetricobalt nonacarbonyl complexes of the general formula $XCCo_3(CO)_9$ (I) show varied and interesting behaviour involving the apical carbon atom [1]. Most such complexes are usually prepared from one of the more easily obtainable analogues where X is either hydrogen or bromine or chlorine. For X = H, Br, or Cl the routes reported involve reaction of $Co_2(CO)_8$ with $CHBr_3$, CBr_4, or CCl_4 respectively [2]. Dicobaltoctacarbonyl is air-sensitive and pyrophoric, and could be synthesised only by high pressure carbonylation. We wanted to devise a single step synthesis of I (X = H, Br, or Cl) starting from simple cobalt salts and avoiding the specialized apparatus necessary for high pressure reactions. In this communication we describe the use of phase-transfer catalysis for effecting such a reaction. Uses of phase-transfer catalysis in isotopic enrichment of some metal carbonyls and in water gas shift reactions have been recently reported [3], but to our knowledge ours is the first example of application of phase-transfer catalysis to the synthesis of a carbonyl cluster.

It has been suggested that the formation of I proceeds through the participation of mononuclear intermediate $[Co(CO)_4]^-$. In water this anion is stable and remains in solution with $[Co(H_2O)_6]^{2+}$ as the counter ion.

A phase-transfer catalyst could therefore be used to transfer $[Co(CO)_4]^-$ ions from the aqueous phase to the organic phase containing the other reactant such as CCl_4, $CHCl_3$, $CHBr_3$ or CBr_4. There is a reported procedure

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TABLE 1

Product	Reaction time [b] (h)	Yield (%) [a]
$ClCCo_3(CO)_9$	1.5	42
	3.5	None
$BrCCo_3(CO)_9$	0.75	36
$HCCo_3(CO)_9$	0.75	30

[a] Based on $Co(NO_3)_2 \cdot 6H_2O$. [b] After addition of the organic phase with the organic reactant and the phase transfer catalyst.

starting from $Co(NO_3)_2 \cdot 6H_2O$ and using dithionite as a reducing agent to generate $[Co(CO)_4]^-$ in aqueous ammoniacal solution under one atmosphere pressure of CO [4].

Thus for the single-step synthesis of I (X = Cl, Br or H) the following representative procedure is followed. $Co(NO_3)_2 \cdot 6H_2O$ (8.7 g) in aqueous ammoniacal solution (200 cm^3, 12%) is reduced with sodium dithionite under an atmosphere of carbon monoxide as described by Hieber and Fischer [4]. A benzene (100 cm^3) solution of carbon tetrachloride (3 cm^3) (X = Cl) and catalytic amount of cetyltrimethylammonium bromide (0.25 g) is added to the aqueous solution and the mixture is stirred vigorously. The benzene layer becomes dark purplein about 2 h, and, it is then separated, dried and taken to dryness to give crude $ClCCo_3(CO)_9$ (2 g) which can be purified by passage through a short silica gel column with n-hexane as eluant. The IR spectrum of the pure material is identical with that of an authentic sample.

A similar procedure is followed for reactions involving $CHBr_3$ or CBr_4. It is important to note that in the absence of the phase-transfer catalyst, there is no reaction in all cases. For these reactions it was observed that there are optimum reaction times after which the yields of carbonyl cluster decrease. With prolonged reaction time colouration followed by gradual decolourisation of the organic phase is observed, and no carbonyl cluster can be isolated. Table 1 lists the optimum reaction times and the yields of the carbonyl clusters.

$XCCo_3(CO)_9$ clusters are known to decompose on treatment with base [1]. It seems likely that upon prolonged reaction the phase-transfer catalyst catalyses the transfer of OH^- ions from the aqueous phase to the organic phase, eventually leading to the total decomposition of the carbonyl cluster. In accord with the explanation, the total yields of I (X = H, Cl or Br) are always somewhat below the expected values. We are currently exploring the potential of this reaction for the synthesis of other cluster carbonyls.

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