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Preliminary communication

Bimetallic catalysis. A new method for carbonylation of aryl iodides under mild conditions

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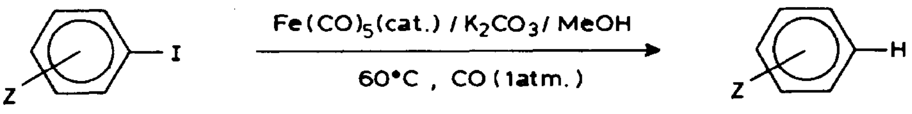
Abstract

Catalytic carbonylation of iodobenzene to give benzoic acid can be performed under mild conditions (60 °C, 1 atmosphere pressure of CO) with a bimetallic $Fe(CO)_5/Co_2(CO)_8$ catalyst system under phase transfer conditions (NBu_4Br, aq. $NaOH/C_6H_6/EtOH$). Carbonylation of bromobenzene (which on its own is unreactive under these conditions) can be brought about in the presence of iodobenzene.

Introduction

As part of our study aimed at developing the use of $HFe(CO)_4^-$ in organic synthesis and catalysis, we recently showed that this complex ion acts as a catalytic species for the selective reduction of aryl iodides under mild conditions [1].



(Z = H , p-Me , p-MeO , o-Cl , m-Cl , p-Cl , p-Br , p-I)

Although the mechanism of these reactions has not yet been fully elucidated, preliminary investigations [2] led us to suspect the intervention of radical anions $(ArI)^{\dot{-}}$ formed by an electron transfer process, essentially identical to that proposed for the initiation step of $S_{RN}1$ reactions [3]. We thought that it should be possible to intercept the resulting aryl radicals with nucleophiles, thus providing a novel way of promoting $S_{RN}1$ reactions. Since carbonylations of aryl halides are the subject of current interest [4], we decided to use $Co(CO)_4^-$ as the first nucleophile. This anionic complex is known to act as an effective nucleophile in photostimulated, $S_{RN}1$ type, reactions, thus allowing the catalytic carbonylation of aryl halides [5].

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We thus investigated the reactivity of $Fe(CO)_5/Co_2(CO)_8$ bimetallic systems towards iodobenzene in the presence of sodium hydroxide under phase transfer conditions and under carbon monoxide (1 atm).

Results

Dicobalt octacarbonyl is known to react with sodium hydroxide in a two-phase liquid–liquid (C_6H_6/H_2O) medium in the presence of NBu_4Br to yield the benzene soluble NBu_4^+, $Co(CO)_4^-$ salt [6]. Iron pentacarbonyl also reacts with aqueous sodium hydroxide under the above conditions to afford NBu_4^+, $HFe(CO)_4^-$ [7], but this salt is insoluble both in water and in benzene. However, we found that, under the conditions used (vide infra), the presence of ethanol enables the extraction of this salt almost quantitatively into the organic layer. Moreover, qualitative control experiments (IR analysis) showed that, under the biphasic conditions used (50 ml aqueous NaOH/20 ml benzene), the presence of ethanol (10 ml) increases the solubility of NBu_4^+, $Co(CO)_4^-$ in the organic upper layer.

The procedure was as follows [8*]. To a two-phase system consisting of 50 ml of 8*M* aqueous sodium hydroxide, 20 ml of benzene and 10 ml of ethanol, NBu_4Br (3 mmol) and $Fe(CO)_5$ (1.8 mmol) were added, under argon. After 0.5 h stirring (750 rpm) at room temperature, $Co_2(CO)_8$ (0.5 or 0.25 mmol) was introduced. After a further 0.5 h stirring, the reaction flask was purged with carbon monoxide and connected to a gas buret filled with carbon monoxide (1atm). Iodobenzene (20 mmol) was then introduced, together with decane as internal standard, and the temperature was raised to 60 °C in a preheated oil bath. After 23 h the layers were separated. The organic layer was analysed by GLC. The aqueous layer was acidified, to give benzoic acid, which was isolated by classical procedures [9*]. The main results are summarized in Table 1.

$$C_6H_5I \xrightarrow[\text{NBu}_4\text{Br, CO (1 atm.), 60}^\circ\text{C, 23 h.}]{\text{(1) Fe(CO)}_5\text{(cat.)/Co}_2\text{(CO)}_8\text{(cat.), aq. NaOH/C}_6\text{H}_6\text{/EtOH}} C_6H_5COOH$$

$$\text{(2) } H_3O^+$$

As can be seen, control experiments unexpectedly [10] showed that $Co(CO)_4^-$ alone does react with iodobenzene. However, the yield of benzoic acid is low (run 1).

Table 1

Carbonylation of iodobenzene under carbon monoxide (1 atm.) [a]

Run	$Fe(CO)_5$ (mmol)	$Co_2(CO)_8$ (mmol)	NBu_4Br (mmol)	unreacted C_6H_5I (% [b])	C_6H_5COOH (yield% [c])	$(C_6H_5)_2C{=}O$ (% [b])	C_6H_5-C_6H_5 (% [b])
1	–	0.5	3	80	15	–	–
2	1.8	–	3	45	2	2	15
3	1.8	0.5	3	27	65	4.5	2.5
4 [d]	1.8	0.25	3	35	50	2	6
5	1.8	0.5	–	75	8	traces	traces

[a] Reaction conditions: iodobenzene (20 mmol); benzene (20 ml); water (50 ml); EtOH (10 ml); NaOH (400 mmol); temperature: 60 °C; reaction time: 23 h. [b] Determined by GLC analysis with internal standards. [c] Isolated yields (see ref. 9), based on amount of iodobenzene initially introduced. [d] Reaction time 48 h.

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* Reference numbers with asterisks indicate notes in the list of references.

In the absence of the cobalt complex (run 2), use of $HFe(CO)_4^-$ leads to only traces of carbonylation products (the main reaction is probably reduction to benzene). However, it should be noted that a little biphenyl and a little benzophenone are formed, whereas no traces of these products were detected in reactions of $KHFe(CO)_4$ with iodobenzene in methanol [1]. In contrast, when both cobalt and iron carbonyl species are present, catalytic carbonylation to sodium benzoate occurs in fair yield (run 3). Moreover, although the reaction conditions have not yet been optimized, the result of run 4 shows that the reaction can be conducted with even smaller amounts of cobalt carbonyl ($C_6H_5COOH/Co_2(CO)_8 = 40$). We finally note that only very low yields of benzoic acid are obtained in the absence of the ammonium salt (run 5).

As expected from our previous results on the reactivity of $HFe(CO)_4^-$ towards aryl halides [1] and from literature data [5], bromobenzene does not react with the above bimetallic system. However, we found that the carbonylation of bromobenzene is promoted by the presence of iodobenzene. Thus, under the conditions of run 3, a mixture of iodobenzene and bromobenzene (5/15 mmol) gave 7 mmol of isolated benzoic acid together with 0.2 mmol of benzophenone and 0.4 mmol of biphenyl (GLC analysis), C_6H_5I conversion: 100%, C_6H_5Br conversion: 40%).

These preliminary results seem to be in agreement with our initial hypothesis. However, further work is needed to gain insight into the reaction mechanism.

The nature of the carbonyl species formed during the preparation of the reaction medium (i.e. before addition of aryl halide) was investigated by IR analysis. Examination of the IR spectrum of the organic phase (proportions of carbonyl metals as in run 3) showed a weak band near 2000 cm^{-1} (attributed to traces of $HFe_3(CO)_{11}^-$) and a broad, strong band near 1880 cm^{-1}, which is the result of superposition of the bands of $HFe(CO)_4^-$ and $Co(CO)_4^-$, as shown by separate experiments with each metal carbonyl under the same conditions. The IR spectrum is not changed when the reaction medium is kept for 1 h at 60 °C under carbon monoxide (1 atm). These observations suggest that, at least at the beginning of the reaction, the only carbonyl species are $HFe(CO)_4^-$ and $Co(CO)_4^-$. However, the formation of binuclear species during the course of the reaction cannot be excluded. It is known that $Co(CO)_4^-$ does not react thermally with $Fe(CO)_5$, but does so upon irradiation (i.e. conditions under which $Fe(CO)_4$ species are generated) to give $FeCo(CO)_8^-$ [11]. As the formation of $Fe(CO)_4$ species could result from reaction of $HFe(CO)_4^-$ with iodobenzene, the participation of $FeCo(CO)_8^-$ cannot be ruled out. The nature of the reactions of such species with aryl halides are at present unknown.

Work is in progress to elucidate the nature of catalytically active species and to determine the scope and limitations of bimetallic systems based on iron carbonyl.

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