**Preliminary communication**

# Selective, iron pentacarbonyl catalyzed reduction of aryl iodides under mild conditions

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## Abstract

Potassium tetracarbonylhydridoferrate, generated in situ from $Fe(CO)_5/K_2CO_3$ in methanol has been found to bring about catalytic reduction (up to 18 cycles) of aryl iodides under 1 atm carbon monoxide pressure. This reagent is specific for iodoaromatics, and tolerates the presence of several functionnal groups.

## Introduction

Since the pioneering work of Hieber and coworkers on the reaction of $Fe(CO)_5$ with bases [1], there has been a great deal of interest in the use of tetra-carbonylhydridoferrates ($M^+$, $HFe(CO)_4^-$) in organic synthesis. The most convenient way of preparing this reagent is to treat $Fe(CO)_5$ with a base (alkali or alkaline earth metal hydroxide) in a hydroxylic solvent (generally an alcohol) either anhydrous or containing water [2].

Tetracarbonylhydridoferrates have been successfully used for numerous useful stoichiometric reactions that take place under mild conditions [2c,3]. However, none of these reactions has been made catalytic under atmospheric carbon monoxide pressure, and in fact, all the reactions reported to involve $HFe(CO)_4^-$ as a catalytic species needed high carbon monoxide pressure [4,5]. The most famous example is the Reppe modification of the hydroformylation reaction [5]. However, it has been shown by Pettit and coworkers [6] that under high carbon monoxide pressure the actual active species is $H_2Fe(CO)_4$ that is generated from $HFe(CO)_4^-$ when the pH of the reaction medium has been lowered by the reaction of carbon monoxide with the base. It thus appears that the involvement of $HFe(CO)_4^-$ as a catalytic species has never been clearly demonstrated. We report here that $HFe(CO)_4^-$, generated in situ from $Fe(CO)_5/K_2CO_3/MeOH$ mixtures, brings about reduction of aryl iodides and, most importantly, that the reactions are catalytic under 1 atm of carbon monoxide.

$$ArI \xrightarrow[\text{MeOH, 60°C}]{Fe(CO)_5(cat.)/K_2CO_3,\ CO\ (1\ atm)} ArH$$
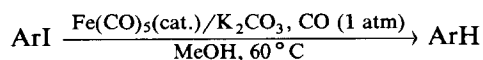
The stoichiometric reduction of aliphatic halides by $HFe(CO)_4^-$ has been reported by Alper [3i], and its mechanism studied recently by several authors [7,8]. However, the reaction of $HFe(CO)_4^-$ with aryl halides has not previously been reported.

*Results*

The reaction of $Fe(CO)_5/K_2CO_3/MeOH$ with iodobenzene was first investigated under argon. The reagent was prepared by treating $Fe(CO)_5$ (3.66 mmol) with $K_2CO_3$ (42 mmol) in 50 ml of dry, deoxygenated methanol under argon. After 1 h stirring at 60°C, the IR spectrum of the light pink reaction mixture was superposable on that of $KHFe(CO)_4$ prepared from $Fe(CO)_5$ and KOH [2], indicating complete transformation of $Fe(CO)_5$ to $KHFe(CO)_4$. Iodobenzene (20 mmol) then was added (together with decane as internal standard) in 30 ml of dry methanol. Monitoring of the reaction by GLC analysis of small aliquots indicated the formation of benzene up to 7 mmol after 48 h reaction at 60°C (no reduction was observed when either $Fe(CO)_5$ or $K_2CO_3$ was omitted). As the amount of benzene formed was greater than could come from stoichiometric action of $Fe(CO)_5$, we decided to examine the possibility of bringing about catalytic reduction of iodobenzene under carbon monoxide.

When the reaction was performed under 1 atm of carbon monoxide, catalytic reduction was observed (4.4 cycles, run 2, Table 1). Examination of the IR spectrum of the reaction mixture after 48 h reaction indicated that the main carbonyl complex present was $Fe(CO)_5$. Further addition of iodobenzene (20 mmol) resulted in a very sluggish reduction. However, addition of more $K_2CO_3$ (42 mmol) brought about further reduction to benzene, leading to an iron turnover of nearly 10. The overall consumption of carbon monoxide agreed well with the amount of iodobenzene reduced. It thus appears that the reduction of 1 mole iodobenzene consumed 1 mole of carbon monoxide and 2 equivalents of potassium carbonate.

Careful monitoring of the reaction by GC analysis indicated that small amounts of methylbenzoate were formed and were then transformed in situ into potassium benzoate, which was isolated as benzoic acid. This reaction involves an unusual type of $S_N2$ attack of potassium methoxide on the methyl group of methyl benzoate [9].

$$C_6H_5COOMe + MeOK \xrightarrow{MeOH} C_6H_5COOK + MeOMe$$
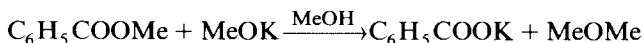
Traces of benzaldehyde and benzylalcohol were also observed, but no trace of biphenyl, benzophenone nor benzil could be detected.

Table 1

Catalytic reduction of iodobenzene with $Fe(CO)_5$-$K_2CO_3$ in methanol [a]

| Run | $C_6H_5I$ (mmol) | Atmosphere | $Fe(CO)_5$ (mmol) | $K_2CO_3$ (mmol) | $C_6H_5I$ (conv.%) | $C_6H_6$ [b] mmol | Iron turnover |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 1 | 20 | Argon | 3.66 | 42 | 42.5 | 7.0 | 1.9 |
| 2 | 20 | CO(1 atm) | 3.61 | 42 | 88.0 | 15.8 | 4.4 |
| 3 | 40 | CO(1 atm) | 1.84 | 84 | 67.0 | 21.0 | 11.4 |

[a] Reactions in 80 ml of methanol at 60°C for 48 h. [b] Determined by GC analysis with decane as internal standard.

Table 2

Catalytic reduction of aryl iodides under 1 atm of carbon monoxide [a]

| Run | Aryl halide (20 mmol) | Fe(CO)$_5$ (mmol) | Reaction time (h) | Aryl halide (conv. %) | Reduction products (mmol) [b] |
|---|---|---|---|---|---|
| 1 | 4-BrC$_6$H$_4$I | 3.57 | 48 | 98 | C$_6$H$_5$Br(19) |
| 2 | 4-ClC$_6$H$_4$I | 3.67 | 48 | 95 | C$_6$H$_5$Cl(18.5) |
| 3 | 4-ClC$_6$H$_4$I [c] | 0.93 | 48 | 42 | C$_6$H$_5$Cl(17) |
| 4 | 4-IC$_6$H$_4$I | 3.63 | 48 | 90 | C$_6$H$_5$I(14)+C$_6$H$_6$(3) |
| 5 | 3-ClC$_6$H$_4$I | 3.58 | 8 | 100 | C$_6$H$_5$Cl(19.5) |
| 6 | 2-ClC$_6$H$_4$I | 3.63 | 2 | 100 | C$_6$H$_5$Cl(19) |
| 7 | 4-CH$_3$C$_6$H$_4$I | 3.62 | 48 | 72 | C$_6$H$_5$CH$_3$(12.5) |
| 8 | 4-CH$_3$OC$_6$H$_4$I | 3.64 | 48 | 75 | C$_6$H$_5$OCH$_3$(14) |
| 9 | 4-NH$_2$C$_6$H$_4$I | 3.63 | 48 | 50 | C$_6$H$_5$NH$_2$(10) |
| 10 | 4-HOC$_6$H$_4$I | 3.68 | 48 | 25 | C$_6$H$_5$OH(3.5) |

[a] Reactions in 80 ml of methanol at 60°C; K$_2$CO$_3$: 42 mmol. [b] Determined by GC analysis with appropriate internal standards. [c] Experiment conducted on 40 mmol ClC$_6$H$_4$I with 87 mmol K$_2$CO$_3$; iron turnover: 18.

The above catalytic system was tried with several aryl halides (Table 2). The reagent appears to be specific for the reduction of iodoaromatics; chlorobenzene, bromobenzene, and 1-bromonaphthalene were not reduced under the conditions used, and could be quantitatively recovered.

This feature was utilized to bring about selective catalytic reduction of bromo-, chloro-iodobenzenes to bromo- or chloro-benzene without any trace of further reduction to benzene (run 1–6, Table 2). The presence of electron-withdrawing substituents on the aromatic nucleus of aryl iodides, especially in the *ortho* position, was found to increase the rate of reduction. This feature was utilized to carry out the selective reduction of 1,4-diodobenzene to iodobenzene in 70% yield (run 4, Table 2) (The reagent was found to be unreactive towards 1,4 dibromobenzene). In contrast, 4-iodoaniline was slowly reduced, and the reduction of 4-iodophenol rapidly stopped owing to the in situ formation of the corresponding 4-iodophenoxide which is not reduced under the conditions used. Finally, we found that iron turnovers in the range 18–20 could be obtained (run 3, Table 2) but not significantly exceeded. A loss of iron carbonyl species was observed by IR spectroscopic analysis.

The selectivity of the reducing system was further exemplified by showing that the catalytic reduction of aryl iodides could be performed in the presence of other reducible compounds such as cyclohexanone, chlorocyclohexane, benzonitrile, or cyclooctene without reduction ( < 1%) or modification of any of them. (It should be noted, however, that, as previously reported [3a], the reagent isomerises linear olefins, such as 1-octene, to a mixture of isomeric internal alkenes.)

These preliminary results show that HFe(CO)$_4^-$ can act as a catalytic species under mild conditions. This very cheap and easy-to-handle catalytic system appears of interest in comparison with more conventional reagents which do reduce aryl iodides but exhibit lower chemoselectivities.

Studies are in progress on the mechanism of the reduction and on the regeneration of the catalytically active species.

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