Reaction of Potassium Tetracarbonylhydridoferrate with Aryl Halides: Mechanistic Study and Extension to the Catalytic Carbonylation of Iodobenzene by a Bimetallic $Fe(CO)_5–Co_2(CO)_8$ System

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Potassium tetracarbonylhydridoferrate, $KHFe(CO)_4$, reacts with aryl iodides in wet methanol to yield the corresponding arenes. This reaction is catalytic under carbon monoxide (1 atm) in the presence of an excess of base. Mechanistic investigations, both by IR analysis and by electrochemical experiments, show that the reaction involves an electron transfer from $HFe(CO)_4^-$ to the aryl halide to generate the corresponding radical anion. The resulting aryl radical either abstracts an hydrogen atom from potassium methoxide or combines with the $[HFe(CO)_4]^•$ radical species to form $ArFe(H)(CO)_4$, which yields ArH by reductive elimination. The catalytic carbonylation of iodobenzene to benzoic acid can be performed under very mild conditions by a bimetallic system, viz. $HFe(CO)_4^-–Co(CO)_4^-$. The observed synergetic effect is believed to involve first an electron transfer from $HFe(CO)_4^-$ to iodobenzene and generation of a phenyl radical, followed by reaction with $Co(CO)_4^-$, which acts as the actual carbonylation catalyst. In agreement with these hypotheses, the carbonylation of bromobenzene, which on its own is unreactive under these conditions, can be promoted by the presence of iodobenzene.

Introduction

In the last few years, we have been interested in studying the reactivity of tetracarbonylhydridoferrates, $[M^+][HFe(CO)_4^-]$, with the goal of developing new applications of these complexes in chemical synthesis. The main motivations lie in the fact that (i) they are easily accessible from the inexpensive iron pentacarbonyl and (ii) they appear, at least a priori, to be very versatile reagents.[1] Indeed, first, they exhibit a hydrogen–metal bond and are therefore expected to react with various unsaturated reactants. Second, the negative charge makes them potential nucleophiles or electron-transfer agents. Finally, the carbonyl ligands make them potential carbonylation reagents or catalysts.

We have recently reported new applications of $HFe(CO)_4^-$, both in organic synthesis and in coordination chemistry. For instance, the addition of the Fe–H bond to strained carbon–carbon bonds[2] or to α,β-unsaturated carboxylic acids[3] has been shown to be a valuable synthetic method. The catalytic, fully regioselective hydroxycarbonylation of acrylic acid to methylmalonic acid is particularly noteworthy.[4] The reaction of $KHFe(CO)_4$ with phosphines in protic media has been shown to be the best route to the neutral disubstituted $Fe(CO)_3(PR_3)_2$ complexes.[5,6] The reaction with phosphites is still more interesting, as it allows the easy, high-yield synthesis of the neutral dihydrides $H_2Fe(CO)_2[P(OR)_3]_2$,[7] the preparation of which was previously very tedious.[8]

We have also briefly reported that $KHFe(CO)_4$ allows the reduction of aryl iodides to the corresponding arenes and that this reaction is catalytic under very mild conditions (eq 1).[9]

$$ArI \xrightarrow[60°C,\ CO\ (1\ atm)]{Fe(CO)_5\ (cat.)/K_2CO_3/MeOH} ArH \tag{1}$$

Mechanistic speculations about this reaction led us to assume that an electron transfer was involved. This, in turn, led us to point out a bimetallic $Fe(CO)_5–Co_2(CO)_8$ system for the catalytic carbonylation of iodobenzene to benzoic acid.[10] The true mechanism, however, remained to be ascertained. We report here our study aimed at understanding the reactivity of $HFe(CO)_4^-$ toward aryl iodides and the iron–cobalt carbonyl synergetic effect observed for the catalytic carbonylation of iodobenzene to benzoic acid.

Results and Discussion

Reduction of Aryl Iodides. The conventional procedure for the preparation of $KHFe(CO)_4$ (**1**) is to allow $Fe(CO)_5$ to react with KOH in an alcohol, generally ethanol (eqs 2 and 3).[11]

$$Fe(CO)_5 + 2KOH \xrightarrow{EtOH} KHFe(CO)_4 + KHCO_3 \tag{2}$$

$$Fe(CO)_5 + 3KOH \xrightarrow{EtOH} KHFe(CO)_4 + K_2CO_3 + H_2O \tag{3}$$

In the present work, **1** was generated by reacting $Fe(CO)_5$ (3.66 mmol) with K_2CO_3 (42 mmol) in wet methanol (50 mL) (the water content, determined by a Karl Fischer titration, was in the range 20–30 mmol for 50 mL of methanol). Under these conditions (see Experimental Section), the IR spectrum of the methanolic solution was superposable (1700–2000-cm^{-1} region) with that of a solution prepared according to eq 2 or 3. According to McClean, the reaction first involves the formation of $[Fe(CO)_4(COOMe)]^-$ (eqs 4 and 5) (which we could detect

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Table I. Catalytic Reduction of Iodobenzene with $Fe(CO)_5$–K_2CO_3 in Methanol[a]

run no.	amt of C_6H_5I, mmol	atmosphere	amt of $Fe(CO)_5$, mmol	amt of K_2CO_3, mmol	C_6H_5I[b] conversn, %	amt of 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 GLC with decane as internal standard.

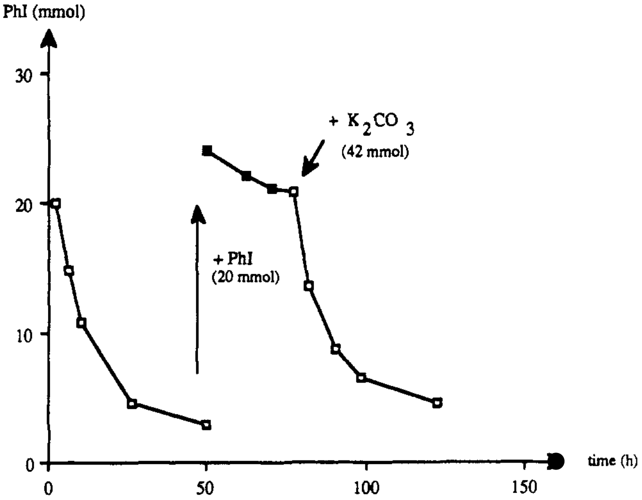

Figure 1. Reduction of iodobenzene under CO (1 atm).

by IR analysis in the early stage of the reaction at 20 °C), which rapidly evolves by reaction with water (eq 6) to yield 1 (IR bands at 2008 (w), 1920 (sh), and 1890 (s) cm^{-1}) and $MeOCO_2K$ (eq 7) (IR band at 1640 cm^{-1}).[12] The overall reaction is represented by eq 8.

$$MeOH + K_2CO_3 \rightleftarrows MeOK + KHCO_3 \qquad (4)$$

$$Fe(CO)_5 + MeOK \rightarrow [K^+][Fe(CO)_4(COOMe)^-] \qquad (5)$$

$$[K^+][Fe(CO)_4(COOMe)^-] + H_2O \rightarrow KHFe(CO)_4 + MeOCOOH \qquad (6)$$

$$MeOCOOH + K_2CO_3 \rightarrow MeOCOOK + KHCO_3 \qquad (7)$$

$$Fe(CO)_5 + MeOH + 2K_2CO_3 + H_2O \rightarrow KHFe(CO)_4 + MeOCOOK + 2KHCO_3 \qquad (8)$$

When iodobenzene (20 mmol) was reacted with the above $KHFe(CO)_4$ solution for 48 h at 60 °C under argon, 7 mmol of benzene was formed (i.e. a 190% yield with respect to 1), as indicated by GLC analysis with decane as internal standard (run 1, Table I). Control experiments showed that no reaction occurred whenever $Fe(CO)_5$ or K_2CO_3 was omitted.

When the same reaction was conducted under carbon monoxide (1 atm), a faster conversion was observed and 15.8 mmol of benzene (i.e. a 440% yield with respect to 1) was formed after 48 h at 60 °C (run 2, Table I).

IR analysis of the reaction medium after 48 h of reaction indicated the presence of small amounts of 1 together with large amounts of regenerated $Fe(CO)_5$. Further addition of iodobenzene (20 mmol) led to the consumption of the remaining 1 (IR analysis) along with formation of 2–3 mmol of benzene. The reaction then stopped (Figure 1).

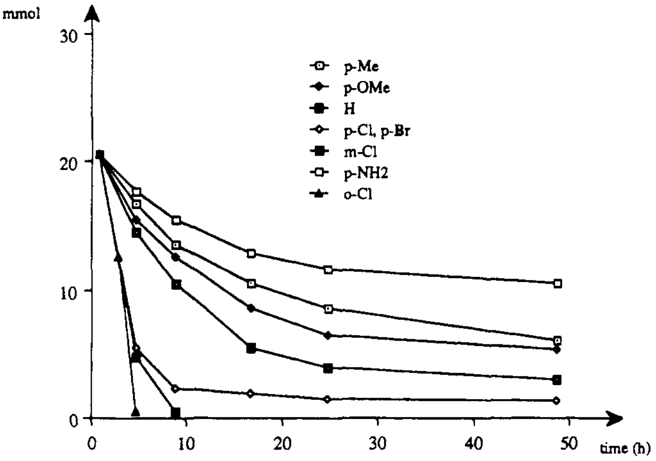

Figure 2. Reduction of substituted aryl iodides.

However, further addition of K_2CO_3 (42 mmol) to the reaction medium allowed transformation of the regenerated $Fe(CO)_5$ into $HFe(CO)_4^-$ and reduction recommenced, yielding, after stirring at 60 °C for a further 48 h, 35.5 mmol of benzene, i.e. nearly 10 turnovers. The overall carbon monoxide consumption was 38–40 mmol.

According to these observations, the reduction of 1 equiv of iodobenzene required 2 equiv of K_2CO_3 and 1 equiv of carbon monoxide. Thus, the reduction of iodobenzene can be written as in eq 9. However, the situation is probably more complex. Indeed, examination of the IR spectrum of the reaction medium at the end of the reaction indicates that a partial destruction of the iron carbonyl species has occurred.

$$C_6H_5I + MeOH + 2K_2CO_3 + H_2O + CO \xrightarrow{Fe(CO)_5} C_6H_6 + MeOCOOK + 2KHCO_3 + KI \qquad (9)$$

The above results were confirmed by reacting iodobenzene (40 mmol) with $Fe(CO)_5$ (1.84 mmol) in the presence of 84 mmol of K_2CO_3 (run 3, Table I). The turnover number reached 11.4 after 48 h and 17 after 72 h. Careful monitoring of the reaction by GLC analysis indicated that small amounts of methyl benzoate were formed and were then transformed in situ into potassium benzoate, which was isolated as benzoic acid (1–2 mmol). Traces of benzaldehyde and benzyl alcohol were also observed, but no trace of biphenyl, benzophenone, benzil, or methyl benzoylformate could be detected. Finally, the same reaction could be performed in wet ethanol, although with a slightly lower reaction rate.

Under the same conditions, bromobenzene, chlorobenzene, and 1-bromonaphthalene were not reduced and could be recovered quantitatively. The reactivity of 1 thus appeared to be specific to aryl iodides. Consequently, the influence of various substituents was briefly examined. The main results are summarized in Figure 2.

As may be seen, the highly electron-attracting substituents strongly accelerate the reaction, while electron-donating ones decrease the reaction rate (potassium 4-iodophenoxide was quite unreactive). Such an effect reflects a transition state with a marked increase in negative charge

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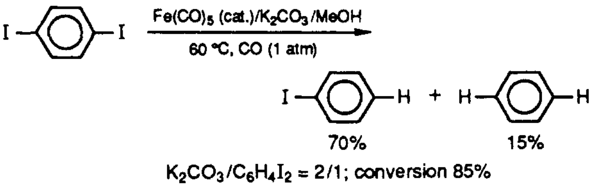
in the aromatic ring during the reaction. According to Kochi,[14] these observations are in accord with either a nucleophilic addition of $HFe(CO)_4^-$ or an electron transfer from $HFe(CO)_4^-$. The possible reaction mechanisms are discussed below.

The selective reduction of 1,4-diiodobenzene (eq 10) is noteworthy. The observed selectivity is accounted for by (i) the higher reactivity of 1,4-diiodobenzene, as compared to that of iodobenzene, and (ii) the fact that the reaction is controlled by the amount of base; i.e. 2 equiv of K_2CO_3 is necessary for the reduction of each carbon–iodine bond so that the reaction stopped at 85% conversion for lack of base.



(10)

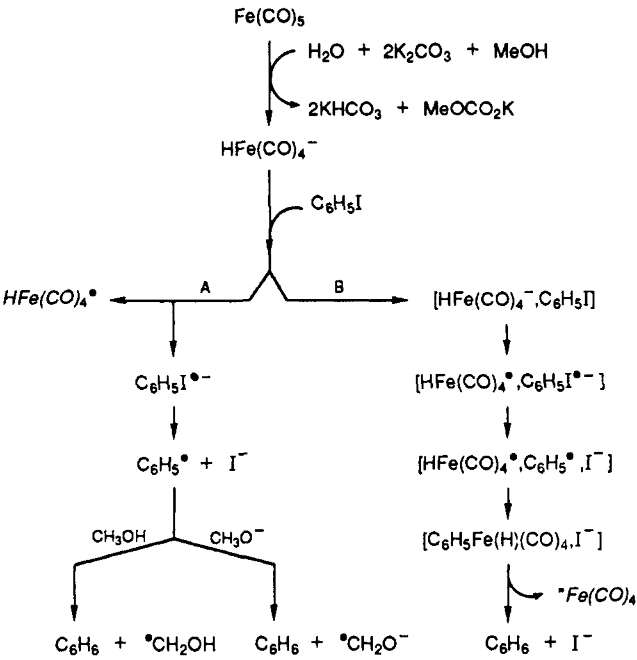
Finally, some further experiments were conducted to emphasize the chemoselectivity of **1** as a possible reducing agent in organic synthesis. For that purpose, we performed the reduction of 4-iodoanisole in the presence of some other reducible compounds. In each case, 4-iodoanisole was reduced to anisole, whereas the other reducible compound (cyclohexanone, benzonitrile, cyclooctene, and chlorocyclohexane) was recovered in more than 99% yield (GLC analysis). Comparison with literature data shows that **1** is one of the most attractive reagents for the chemoselective, catalytic reduction of aryl iodides.[13]

The reactivity of $HFe(CO)_4^-$ toward organic halides has been previously studied by several authors.[15-18] For example, Alper has shown that $NaHFe(CO)_4$ may be used, under very mild conditions, for the reduction of some activated alkyl halides such as α-halo ketones. In this case a S_N2 mechanism was evidenced.[17] Whitmire et al. recently reported a thorough study of the reaction of $HFe(CO)_4^-$ (as the Et_4N^+ salt) with methyl iodide. The main conclusion of their study was that $HFe(CO)_4^-$ reacted with methyl iodide via a S_N2 mechanism.[18]

Thus, to the best of our knowledge, this ability of $HFe(CO)_4^-$ to reduce aryl iodides is reported for the first time. Furthermore, this is the first example in which an organic halide is reduced with catalytic amounts of $HFe(CO)_4^-$. Consequently, it was very interesting to try to understand the mechanism of this reaction and how the regeneration of the catalytically active species is achieved.

Considering first the three usual mechanisms through which nucleophiles may react with aryl halides,[19] the S_NAr and aryne mechanisms could be ruled out. Indeed, S_NAr reactions are only facile in the presence of highly electron-attracting substituents, and the nature of the leaving halogen affects the ease of nucleophilic addition in the order F > Cl > Br, I. None of these effects are observed in the reduction of aryl halides with $HFe(CO)_4^-$. The aryne mechanism can also be ruled out because of insufficiently basic conditions. In contrast, an electron transfer from $HFe(CO)_4^-$ to the aryl iodide, as proposed for the initiation step of $S_{RN}1$ reactions, appeared quite possible.[20] The possibility of an electron transfer from $HFe(CO)_4^-$ has been previously proposed both for the reduction of nitro aromatics[21] and for the reduction of polycondensed aromatics[22] such as anthracene, although under much more drastic conditions in the latter case. Another possibility could be an oxidative addition of the aryl iodide to a coordinatively unsaturated iron carbonyl species such as $HFe(CO)_3^-$. The intervention of such a species has been previously proposed for the addition of $HFe(CO)_4^-$ to ethyl acrylate in THF. However, both Takegami[23] and Collman[24] observed that such a reaction was severely inhibited (by at least 100-fold) under carbon monoxide (1 atm). Since the reaction of $KHFe(CO)_4$ with iodobenzene was not slowed down by a carbon monoxide atmosphere in its early stages, we concluded that such a mechanism was unlikely to be involved. Therefore, it appears that the most plausible mechanism starts by an electron transfer from $HFe(CO)_4^-$ to the aryl iodide. As previously noted, the dramatic effect of electron-withdrawing substituents (Figure 2) is in agreement with such an hypothesis.[14]

Scheme I



Within this hypothesis, at least two reaction pathways can be proposed to account for the formation of benzene (Scheme I). In the first one (pathway A), an electron is transferred to C_6H_5I to generate the radical anion $[C_6H_5I^{\bullet -}]$. This species splits off to give a phenyl radical, which can abstract a hydrogen atom either from the solvent or, more probably, from potassium methoxide, as proposed earlier by Bunnett et al.[25] In the second pathway (pathway B), the electron transfer occurs within a

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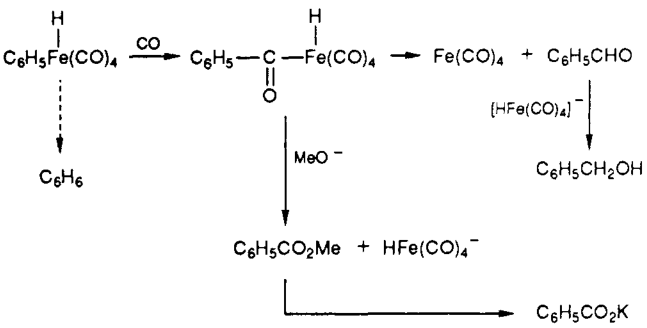
Scheme II



solvent cage, thus leading to radical species that can combine to give $C_6H_5Fe(H)(CO)_4$. Reductive elimination would then give benzene.

We lack the data to discern between these two pathways. It must be noted, however, that the formation of carbonylation products (vide supra) during reactions under carbon monoxide is a strong argument to consider that the reaction occurs, at least in part, through $C_6H_5Fe(H)(CO)_4$ or similar arylcarbonyliron species. The proposed pathway for the formation of the observed carbonylation products is outlined in Scheme II.

Another very important question was how the active reducing species could be regenerated under the reaction conditions. In order to try to answer this question, the reaction of $KHFe(CO)_4$ with iodobenzene, under both argon and carbon monoxide, was carefully monitored by IR spectroscopy with the hope of detecting some intermediate iron carbonyl species.

When the reaction was conducted under argon, the absorption bands of $HFe(CO)_4^-$ slowly disappeared to give new bands at 1930 cm^{-1} (attributed to $HFe_2(CO)_8^-$) and 1960 cm^{-1}. The former then decreased to give a large band at 1960 cm^{-1}. According to literature data,[26] this band can be attributed to the tetranuclear species $Fe_4(CO)_{13}^{2-}$. This was checked by showing that, in the presence of a base (K_2CO_3 in MeOH), $[PPN^+][HFe_4(CO)_{13}^-]$ gave rise to that 1960-cm^{-1} band.

When the reaction was performed under carbon monoxide (1 atm), the same species as above were transiently observed (bands at 1930 and 1960 cm^{-1}) but slowly disappeared to give $HFe(CO)_4^-$ and $Fe(CO)_5$.

Thus, two species, namely $HFe_2(CO)_8^-$ and $Fe_4(CO)_{13}^{2-}$, could be detected during the reaction of $HFe(CO)_4^-$ with iodobenzene, under either argon or carbon monoxide.

Considering the postulated mechanisms (Scheme I), the possible intermediate iron carbonyl species are $Fe(CO)_4$ and $HFe(CO)_4^{\bullet}$. On the basis of literature data,[23] the recombination reactions depicted in eqs 11–13 can be proposed.

$$\mathrm{Fe(CO)_4 + CO \rightarrow Fe(CO)_5} \qquad (11)$$

$$\mathrm{Fe(CO)_4 + HFe(CO)_4^- \rightarrow HFe_2(CO)_8^-} \qquad (12)$$

$$\mathrm{2HFe(CO)_4^{\bullet} \rightarrow H_2Fe_2(CO)_8 \xrightarrow{base} HFe_2(CO)_8^-} \qquad (13)$$

Equations 12 and 13 account for the generation of $HFe_2(CO)_8^-$ in the reaction medium. Interestingly, it has been shown by Collman et al. that $HFe_2(CO)_8^-$ rapidly reacts with carbon monoxide (1 atm) to form $HFe(CO)_4^-$ and $Fe(CO)_5$ (eq 14).[23]

$$\mathrm{HFe_2(CO)_8^- + CO \rightarrow HFe(CO)_4^- + Fe(CO)_5} \qquad (14)$$

Therefore, eqs 11–14 serve to explain the catalytic character of the reaction of $HFe(CO)_4^-$ with iodobenzene under a carbon monoxide atmosphere in the presence of excess K_2CO_3. However, the formation of $Fe_4(CO)_{13}^{2-}$ was somewhat unexpected. This species seems to be formed at the expense of $HFe_2(CO)_8^-$ (IR analysis), suggesting again an electron transfer from $HFe_2(CO)_8^-$ to iodobenzene (eq 15) and recombination of the resulting iron carbonyl radicals to give a tetranuclear species (eq 16).

$$\mathrm{HFe_2(CO)_8^- + C_6H_5I \rightarrow HFe_2(CO)_8^{\bullet} + [C_6H_5I^{\bullet -}]} \qquad (15)$$

$$\mathrm{2HFe_2(CO)_8^{\bullet} \xrightarrow[-3CO]{} H_2Fe_4(CO)_{13} \xrightarrow{base} Fe_4(CO)_{13}^{2-}} \qquad (16)$$

To the best of our knowledge, the reactivity of this dianionic cluster has been little studied.[26] However, we have shown qualitatively (IR analysis) that, under the reaction conditions (60 °C, K_2CO_3 in MeOH), $Fe_4(CO)_{13}^{2-}$ (generated from $[PPN^+][HFe_4(CO)_{13}^-]$) reacts with carbon monoxide (1 atm) to give $HFe(CO)_4^-$ (eq 17).

$$\mathrm{Fe_4(CO)_{13}^{2-} \xrightarrow[60\ ^{\circ}C]{MeOH,\ K_2CO_3,\ CO\ (1\ atm)} HFe(CO)_4^-} \qquad (17)$$

The above facts allow us to explain the catalytic reduction of aryl iodides under carbon monoxide. The reaction involves an electron transfer from $HFe(CO)_4^-$ and, at least in part, from $HFe_2(CO)_8^-$ to the aryl iodide. Furthermore, the intervention of $HFe_2(CO)_8^-$ as an electron-donor species, a possibility that has been previously considered by Collman et al.,[24] explains the fact that the reaction of $HFe(CO)_4^-$ with iodobenzene *under argon* yields benzene in amounts greater than could come from a stoichiometric reaction of $HFe(CO)_4^-$ (vide supra). In addition, it rationalizes the formation of $Fe_4(CO)_{13}^{2-}$ during the reaction.

Thus, it appears that the main feature of these reactions is that they involve an oxidation of hydridocarbonylferrates by aryl iodides. In order to verify our hypothesis, the electrochemical oxidation of a methanolic $KHFe(CO)_4$ solution, prepared as above, was performed (see Experimental Section) and the course of the reaction was monitored by IR analysis.

As expected, the oxidation (−0.1 V) of $KHFe(CO)_4$, under either argon or carbon monoxide, gave rise to the same transient species as those observed during the reaction with iodobenzene. Under argon, the reaction rapidly stopped at the $Fe_4(CO)_{13}^{2-}$ stage, whereas, under carbon monoxide, a mixture of $HFe(CO)_4^-$ and $Fe(CO)_5$ resulted. In the latter case, prolonged electrolysis at −0.1 V resulted in partial loss of iron carbonyl species, exactly as observed in the catalytic reduction of iodobenzene. Thus, these electrochemical experiments, which allowed us to mimic the evolution of iron carbonyl species observed during the reduction of iodobenzene, support the proposed mechanism.

Carbonylation of Iodobenzene. All the experiments described above are consistent with a mechanism that involves an electron transfer from $HFe(CO)_4^-$ to C_6H_5I to generate the corresponding radical anion. As previously noted, this electron transfer corresponds to the initiation step of $S_{RN}1$ reactions.[20] Therefore, the reaction with $HFe(CO)_4^-$ appeared to be an original way to promote such reactions, provided that an adequate nucleophile is present in the reaction medium.

It has previously been shown that $Co(CO)_4^-$ is a good nucleophile for the catalytic carbonylation of bromobenzene in the presence of the electron-donor "NaH–RONa" association in THF.[27] For this reaction, a $S_{RN}1$

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Table II. Carbonylation of Iodobenzene under Carbon Monoxide (1 atm)[a]

run no.	amt of $Fe(CO)_5$, mmol	amt of $Co_2(CO)_8$, mmol	amt of Bu_4NBr, mmol	C_6H_5I[b] conversn, %	$C_6H_5CO_2H$ yield, %[c]	$(C_6H_5)_2CO$ yield, %[b]	$(C_6H_5)_2$ yield, %[b]
1	1.8		3	55	2	2	15
2		0.5	3	20	15		
3	1.8	0.5	3	73	65	4.5	2.5

[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 with internal standards. [c] Isolated yields based on the amount of iodobenzene initially introduced.

mechanism has been determined.[27] Thus, we decided to attempt the carbonylation of iodobenzene ($HFe(CO)_4^-$ does not react with bromobenzene) by a bimetallic $HFe(CO)_4^-$–$Co(CO)_4^-$ system.

One of the easiest ways to generate $Co(CO)_4^-$ is to allow $Co_2(CO)_8$ to react with a biphasic aqueous $NaOH$–C_6H_6 medium in the presence of a phase-transfer agent such as Bu_4NBr.[28] Under these conditions, the benzene-soluble $[Bu_4N^+][Co(CO)_4^-]$ is formed in nearly quantitative yield. Under similar conditions, $Fe(CO)_5$ does react with NaOH to yield $[Bu_4N^+][HFe(CO)_4^-]$, but this complex is almost insoluble in benzene (it is also insoluble in water).[29] Therefore, we designed a biphasic system consisting of an aqueous NaOH solution and an upper C_6H_6–EtOH layer. Under the basic conditions used (see Experimental Section), both $Co(CO)_4^-$ and $HFe(CO)_4^-$, as Bu_4N^+ salts, were soluble in the organic phase. Moreover, qualitative control experiments (IR analysis) showed that, under the conditions used (50 mL of aqueous NaOH–20 mL of benzene), the presence of ethanol (10 mL) notably increased the solubility of $[Bu_4N^+][Co(CO)_4^-]$ in the organic layer. Thus, this biphasic reaction medium appeared well-suited to test our hypothesis. The main results are summarized in Table II.

First, control experiments showed that the reaction of $[Bu_4N^+][HFe(CO)_4^-]$ alone with iodobenzene led, as expected, to only traces of benzoic acid (run 1, Table II). However, it should be noted that some amounts of biphenyl were also formed (together with some traces of benzophenone), in agreement with our hypothesis of a radical mechanism. In the absence of iron species, $[Bu_4N^+][Co(CO)_4^-]$ reacts with iodobenzene (run 2, Table II) to give benzoic acid. This result with quite unexpected, since it had been reported that $Co(CO)_4^-$ does not react with aryl halides.[30] This experiment was repeated several times with use of $Co_2(CO)_8$ from different batches and from different sources. In each case, benzoic acid could be isolated in 10–15% yield. However, when both iron and cobalt carbonyl species were present, a catalytic carbonylation of iodobenzene to benzoic acid reproducibly occurred in fair yields and with a high selectivity (run 3, Table II). Comparison of run 1 and run 3 (Table II) clearly shows that benzoic acid is formed at the expense of biphenyl and benzene, as expected from our hypothesis. Further experiments, which are not reported here, have shown that the reaction could be conducted with even smaller amounts of cobalt carbonyl (C_6H_5COOH–$Co_2(CO)_8$ = 40/1).[10] Finally, the stirring speed was found not to have a significant influence in the range 500–1000 rpm, thus indicating, as expected for a relatively slow reaction, that the transfer of carbon monoxide at the gas–liquid interface is not limiting.

These results seem to be in agreement with our initial hypothesis. In order to gain more information, the nature of the carbonyl species formed during the preparation of the bimetallic system (i.e. before addition of iodobenzene) was investigated by IR analysis. Examination of the IR spectrum of the organic phase (proportions of carbonyl metals as in run 3, Table II) showed a weak band near 2000 cm^{-1} (attributed to $HFe(CO)_4^-$), a broad band near 1880 cm^{-1}, which is the result of the superposition of the bands of $HFe(CO)_4^-$ and $Co(CO)_4^-$ (as shown by separate experiments with each metal carbonyl complex alone), and a weak shoulder at 1950 cm^{-1}. When this reaction medium was stirred for 10 min at 60 °C under carbon monoxide (1 atm), the IR spectrum was not changed, expect that the weak shoulder at 1950 cm^{-1} disappeared. 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 heterobinuclear species during the course of the reaction cannot be precluded. Indeed, 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 $Fe(CO)_4$ is generated) to give $FeCo(CO)_8^-$.[31] Since the generation of $Fe(CO)_4$ could result from the reaction of $HFe(CO)_4^-$ with iodobenzene (vide supra, Scheme I), the participation of $FeCo(CO)_8^-$ could not be precluded. Monitoring the carbonylation reaction by IR analysis of the organic phase at regular intervals showed the formation of a species that exhibited an absorption band near 1950 cm^{-1}. However, $FeCo(CO)_8^-$ is known to exhibit two main absorption bands at 1945 (s) and 1776 (m) cm^{-1}.[30] Since no band could be detected near 1780 cm^{-1}, it was concluded that $FeCo(CO)_8^-$ is unlikely to be formed in the reaction medium and that the observed band at 1950 cm^{-1} can be attributed to $Fe_4(CO)_{13}^{2-}$. In agreement with what had been observed during the reduction of iodobenzene by $HFe(CO)_4^-$ under carbon monoxide, the intensity of the 1950-cm^{-1} band first increased with time and then slowly decreased.

A simplified reaction mechanism for the carbonylation of iodobenzene by the bimetallic $Fe(CO)_5$–$Co_2(CO)_8$ system is depicted in Scheme III (the possibility of electron transfer from $HFe_2(CO)_8^-$ to iodobenzene has been omitted for clarity).

As expected from our results about the reactivity of $HFe(CO)_4^-$ toward aryl halides and from literature data about the reactivity of $Co(CO)_4^-$,[27] the above bimetallic system is inactive toward bromobenzene. However, the carbonylation of bromobenzene by $Co(CO)_4^-$ in the presence of the powerful electron source "NaH-*t*-AmONa" in THF[32] has been shown to occur via a $S_{RN}1$ mechanism in which a $[C_6H_5Co(CO)_4^{\bullet -}]$ radical anion is believed to transfer an electron to bromobenzene, thus allowing the propagation steps.[27] Since the same radical anion is postulated (Scheme III) for the carbonylation of iodobenzene, with the bimetallic iron–cobalt carbonyl system, we reasoned that the carbonylation of bromobenzene could be promoted by the presence of iodobenzene. Experiments conducted in this way proved our hypothesis to be correct. Indeed, starting from different C_6H_5I–C_6H_5Br mixtures

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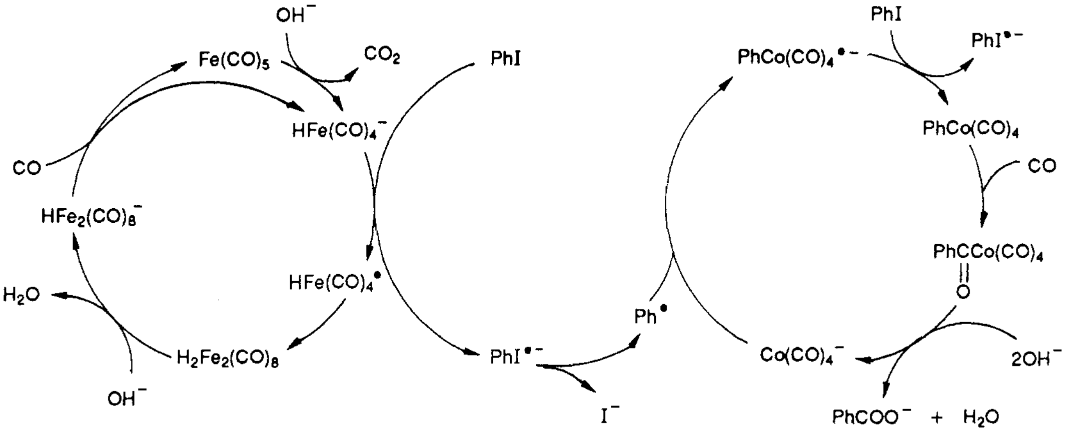
Scheme III



always led to conversion of bromobenzene with simultaneous formation of carbonylation products (mainly benzoic acid) in sufficient amount to be sure that some bromobenzene had been carbonylated. For example, under the conditions of run 3 (Table II), a mixture of iodobenzene–bromobenzene (5/15 mmol) gave 7 mmol of isolated benzoic acid together with 0.2 mmol of benzophenone (GLC analysis), (C_6H_5I conversion 100%; C_6H_5Br conversion 40%).

Last, it must be noted that, under slightly different experimental conditions, $HFe(CO)_4^-$ alone and, better, the $HFe(CO)_4^-$–$Co(CO)_4^-$ combination have been shown to promote the carbonylation of iodobenzene to give benzophenone as the major product.[33] This is the first example of a catalytic, direct conversion of an aryl halide into benzophenone. Developments and mechanistic studies of this new, very promising reaction are actively underway.

Experimental Section

All experiments were conducted under a well-ventilated hood. Manipulations of air-sensitive iron and cobalt carbonyl complexes were performed with use of standard Schlenk tube techniques. Argon U (L'Air Liquide), and carbon monoxide N20 (L'Air Liquide) were used. Thiophene-free benzene (Aldrich), methanol (Prolabo, 98%), and absolute ethanol (Prolabo, Normapur) were used as received and degassed under argon just before use. Water was treated with anion- and cation-exchange resins and degassed before use. Potassium carbonate (Prolabo, 98%, Normapur), sodium hydroxide (Prolabo), and tetrabutylammonium bromide (Fluka) were used without further purification. All aryl halides were purified before use, either by distillation or by recrystallization.

Determination of the water content in the reagents was achieved with a Mettler DL18 Karl Fischer titrator. IR spectra were recorded on Perkin-Elmer 597 and 983 spectrophotometers, using CaF_2 (0.05 mm) windows. Reactions were monitored by GLC analysis on a Delsi 330 and an Intersmat IGC 121 gas chromatograph (flame ionization detectors) fitted with a 50-m capillary column (OV1) and a 3-m SE30 (10%) column, respectively, using linear alkanes C_{10}–C_{20} as internal calibration standards. In each case, peak areas were determined with a Spectra-Physics SP4290 computing integrator. Electrochemical measurements were carried out with a homemade potentiostat controlled by an Apple II microcomputer. This apparatus allows an automatic *iR* drop correction. The electrochemical cell was a conventional one with three electrodes: reference electrode Ag/AgCl, KCl (10^{-1} M), H_2O; working electrode carbon gauze; auxiliary electrode Pt wire.

Preparation of a Methanolic $KHFe(CO)_4$ Solution. Potassium carbonate (42 mmol) was added to methanol (50 mL) in a 250-mL Schlenk tube, and the mixture was degassed for 20 min by bubbling argon. Iron pentacarbonyl (3.66 mmol) was then added with a syringe and the reaction flask heated to 60 °C with a preheated oil bath. $KHFe(CO)_4$ was formed within 30 min (pale pink color), as shown by IR analysis of a small aliquot.

Reduction of Aryl Iodides: General Procedure. The aryl halide (20 mmol) and the corresponding internal standard (10 mmol) in degassed methanol (30 mL) were added with a syringe to the above $KHFe(CO)_4$ solution at 60 °C. When the reaction was conducted under a carbon monoxide atmosphere, the Schlenk tube was then immediately purged with carbon monoxide and connected to a gas buret filled with carbon monoxide (1 atm). Reactions were monitored by analysis of small aliquots (as is for IR analyses; after acidification with dilute HCl and extraction with diethyl ether for GLC analyses).

Electrolysis of Methanolic $KHFe(CO)_4$ Solutions. Electrochemical oxidations were carried out under argon or carbon monoxide at atmospheric pressure. The $KHFe(CO)_4$ solution was prepared, at room temperature for 1 h, directly in the electrochemical cell, from K_2CO_3 (42 mmol), MeOH (50 mL), and $Fe(CO)_5$ (3.66 mmol). Potassium carbonate (0.84 M) acted as a supporting electrolyte. Small aliquots were periodically removed with a syringe and analyzed by IR spectroscopy.

Preparation of the $HFe(CO)_4^-$–$Co(CO)_4^-$ System. Aqueous 8 M NaOH (50 mL), benzene (20 mL), ethanol (10 mL), and Bu_4NBr (3 mmol) were placed in a 250-mL three-necked, round-bottomed flask and the mixture was degassed by bubbling argon for 20 min. Iron pentacarbonyl (1.8 mmol) was then added with a syringe and the mixture stirred for 30 min at room temperature (IR analysis of the organic layer showed that all the $Fe(CO)_5$ had been converted to $[Bu_4N^+][HFe(CO)_4^-]$). Dicobalt octacarbonyl (0.5 mmol) was then added under argon and the reaction mixture stirred for 30 min at room temperature (IR analysis of the organic layer showed that all the dicobalt octacarbonyl had been converted to $[Bu_4N^+][Co(CO)_4^-]$).

Carbonylation of Iodobenzene. The reaction flask was then purged with carbon monoxide and connected to a gas buret filled with carbon monoxide (1 atm). Iodobenzene (20 mmol) was then introduced, together with decane as internal standard, and the reaction temperature was raised to 60 °C with a preheated oil bath. After 23 h of stirring (750 rpm) at 60 °C, the reaction flask was cooled to room temperature and the layers were separated. The organic layer was washed with dilute HCl and analysed by GLC. The aqueous layer was acidified with dilute HCl and extracted with diethyl ether. The ethereal solution was then washed several times with a 5% sodium thiosulfate solution until clear. Conventional workup gave pure benzoic acid (mp, IR, and ^1H NMR data).

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