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Carbonylative coupling of iodobenzene to benzophenone with [n-Bu$_4$N][HFe(CO)$_4$]

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Summary – The reaction of $Bu_4N^+[HFe(CO)_4]^-$ with iodobenzene in a biphasic medium (aqueous NaOH/benzene) under carbon monoxide (1 atm) affords benzophenone in 85% yield. Mechanistic investigations indicate that the reaction first involves an SET from $[HFe(CO)_4]^-$ to PhI. Evidence for the generation of phenyl radicals and $[(PhCO)Fe(CO)_4]^-$ species is presented. Separate experiments show that $[(PhCO)Fe(CO)_4]^-$ does not react with PhI, but does with phenyl radicals, generated from PhI and SmI_2, leading to benzophenone.

carbonylative coupling / iodobenzene / aryl iodide / benzophenone / pentacarbonyliron / tetracarbonylhydridoferrate / benzoyltetracarbonylferrate / radical process

Résumé – Couplage carbonylant de l'iodobenzène en benzophénone par [n-Bu$_4$N][HFe(CO)$_4$]. *La réaction de* $Bu_4N^+[HFe(CO)_4]^-$ *avec l'iodobenzène en milieu biphasique (NaOH aqueuse/benzène) sous monoxyde de carbone (1 atm) conduit à la benzophénone avec un rendement de 85%. L'étude mécanistique de cette réaction montre qu'elle met en jeu un transfert monoélectronique de* $[HFe(CO)_4]^-$ *sur PhI, conduisant ultérieurement à la formation de radicaux phényle et du complexe* $[(PhCO)Fe(CO)_4]^-$*. Il a été montré indépendamment que* $[(PhCO)Fe(CO)_4]^-$ *ne réagit pas avec PhI. Par contre,* $[(PhCO)Fe(CO)_4]^-$ *réagit avec des radicaux phényle, engendrés par action de* SmI_2 *sur PhI, pour conduire à la benzophénone.*

couplage carbonylant / iodobenzène / dérivé iodé aromatique / benzophénone / fer pentacarbonyle / tetracarbonyl hydruroferrate / benzoyltetracarbonyl ferrate / processus radicalaire

Introduction

Collman's reagent, $Na_2Fe(CO)_4$, is a supernucleophile that reacts with primary alkyl halides or tosylates via an S_N2 process to generate alkylferrate complexes $[RFe(CO)_4]Na$ [1-3]. In the presence of an additional ligand L (CO or PPh_3), a migratory insertion reaction occurs to give acylferrate complexes $[R(CO)Fe(CO)_3L]Na$ [1]. The latter are acyl anion equivalents, useful in organic synthesis, eg, for the synthesis of various aliphatic ketones by reaction with reactive alkyl halides.

However, $Na_2Fe(CO)_4$ does not react with aryl halides [1–4]. This is also the case for acylferrate complexes, which only react with iodobenzene in the presence of a catalytic system (($Pd(PPh_3)_3$, associated with $ZnCl_2$) which promotes the insertion into the aromatic carbon-iodine bond [5].

For several years, we have been studying the reactivity of hydridocarbonylferrates $M[HFe(CO)_4]$ with the goal of developing new applications of these reagents, which are simpler to prepare and handle than Collman's reagent [6, 7]. In particular, we found that in-situ-generated $KHFe(CO)_4$ reacts with aryl iodides ArI in a catalytic manner (up to 30 cycles), to afford the reduction product ArH (eq 1) [8].

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

We have investigated mechanism of this reaction [9], and proposed that it involves an SET transfer from $[HFe(CO)_4]^-$ to the aryl iodide, a process similar to the initiation step of $S_{RN}1$ substitution reactions of aryl halides. This conclusion has been exploited to design a catalytic process for the carbonylation of iodobenzene to benzoic acid using an in-situ-generated, bimetallic system $[HFe(CO)_4]^-/[Co(CO)_4]^-$ (eq 2) [10]. In this reaction, the carbonylcobaltate plays the role of a nucleophile, reacting with phenyl radicals generated from the radical anion of iodobenzene.

$$\mathrm{PhI} \xrightarrow[n\text{-}\mathrm{Bu_4NBr,\ CO\ (1\ atm),\ 65\ °C,\ 23\ h}]{\mathrm{Fe(CO)_5/Co_2(CO)_8,\ aqueous\ NaOH/C_6H_6/EtOH}} \xrightarrow{\mathrm{H_3O^+}} \mathrm{PhCO_2H} \qquad (2)$$

$PhI/Fe(CO)_5/Co_2(CO)_8=20{:}1.8{:}0.5$ Conversion: 73%
Yield: 68%.

During the study of the above reaction, it was observed that $[HFe(CO)_4]^-$ generated from $Fe(CO)_5$ in biphasic aqueous NaOH/benzene in the presence of a phase-transfer agent slowly reacts with PhI to yield,

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* Correspondence and reprints

Table I. Influence of the water/benzene ratio.

Run	*% H_2O (vol)*	*% C_6H_6 (vol)*	*PhI conversion (%)^a*	*Ph(CO)Ph (%)^a*	*$PhCO_2H$ (%)^b*	*Ph-Ph (%)^a*	*Selectivity (%)^c*
1	25	75	20	5	5	4	25
2	37.5	62.5	38	12	14	6	31
3	50	50	38	15	9	4	40
4	62.5	27.5	48	22	13	6	46
5	75	25	51	28	15	2	55
6	87.5	12.5	84	55	7	4	66

Total solvent volume: 80 mL. $Fe(CO)_5$ = 1.8 mmol; PhI = 20 mmol; NaOH = 8 mol/L; $n\text{-}Bu_4NBr$ = 3 mmol; 70 °C; 750 rpm; 24 h; CO (1 atm). [a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column). [b] Isolated yield. [c] (Ph(CO)Ph %/PhI conversion) %.

Table II. Influence of the concentration of the sodium hydroxide solution.

Run	*NaOH (aq) (mol/L)*	*PhI conversion (%)^a*	*Ph(CO)Ph (%)^a*	*$PhCO_2H$ (%)^b*	*Ph-Ph (%)^a*	*PhH (%)^c*	*Selectivity (%)^d*
7	2	100	50	16	2	32	50
8	4	100	62	14	2	22	62
9	8	100	72	18	2	8	72

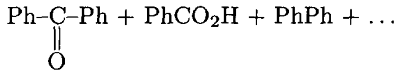
$Fe(CO)_5$ = 2.9 mmol; PhI = 10 mmol; H_2O = 60 mL; C_6H_6 = 20 mL; $n\text{-}Bu_4NBr$: 3 mmol; 70 °C; 750 rpm; CO (1 atm); 24 h. [a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column). [b] Isolated yield. [c] Calculated by difference. [d] (Ph(CO)Ph %/PhI conversion) %.

besides biphenyl (and probably benzene), a mixture of benzoic acid and benzophenone (eq 3) [11].

$$PhI \xrightarrow[n\text{-}Bu_4NBr,\ CO\ (1\ atm),\ 65\ ^\circ C]{Fe(CO)_5,\ aqueous\ NaOH/C_6H_6} \xrightarrow{H_3O^+}$$

$PhI/Fe(CO)_5$=10:0.9 23 h, conversion: 55%

H_2O/C_6H_6=20:20 mL 65 h, conversion: 80%

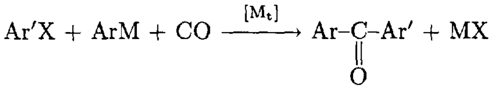


$$\underset{\underset{O}{\|}}{Ph\text{-}C\text{-}Ph} + PhCO_2H + PhPh + \ldots \quad (3)$$

20% 5% 13%

33% 18% 20%

There are very few examples of the formation of benzophenone by direct carbonylation of an aryl halide, as was shown in a recent review on the synthesis of diarylketones by carbonylative coupling [12]. In most cases, such reactions require the use of an arylmetal and a transition metal(0) catalyst (eq 4).



$$Ar'X + ArM + CO \xrightarrow{[M_t]} \underset{\underset{O}{\|}}{Ar\text{-}C\text{-}Ar'} + MX \quad (4)$$

It was thus of interest to study in more detail this newly discovered ability of $[HFe(CO)_4]^-$ to promote the direct carbonylation of iodobenzene to benzophenone [13].

Results

Our development of the reaction shown in eq 3 has included the study of the influence of the principal reaction parameters on the yield and towards the selective production of benzophenone. Some preliminary observations indicate that: i) the reaction is extremely slow at 25 °C and must be conducted at 70 °C to obtain reasonable conversions of iodobenzene within 24 h; ii) in the absence of the phase-tranfer agent, $n\text{-}Bu_4NBr$, practically no conversion of iodobenzene occurs; iii) the efficiency of stirring (modifiable by changing the speed of the magnetic stirrer) plays a significant role; the highest conversions of iodobenzene and the highest selectivity for benzophenone were obtained with a stirring speed of 750 rpm (at higher speeds, with the reaction vessel used, the results were not reproducible); and iv) in all cases, traces of benzaldehyde and benzil are formed (as detected by GC-MS analysis).

Among the other reaction parameters studied, two proved to have a strong influence on the progress of the reaction. One is the ratio of the volumes of solvents (water and benzene) used (table I). The results in table I show that the higher the water/benzene ratio, the higher the yield and the selectivity for benzophenone. Using still higher ratios than those shown leads to non-reproducible results. It should be noted that, under the optimal conditions (run 6), the reaction is catalytic with respect to iron carbonyl since 1.8 mmol of $Fe(CO)_5$ generate 6.9 mmol of carbonylation products (benzophenone and benzoic acid).

The second important parameter for the reaction in eq 3 is the concentration of NaOH. This parameter (table II) was studied using a $Fe(CO)_5$/PhI ratio of 2.9:10 (mmol) in order to assure a complete conversion of PhI within 24 h. As may be seen from table II, the best carbonylation yield and the best selectivity for benzophenone are obtained with a high concentration of aqueous NaOH. Using a lower concentration results in lower carbonylation yields and a relative increase in the reduction to benzene. With concentrations higher than 8 M, stirring of the reaction medium is less efficient and non-reproducible results are obtained.

Table III. Influence of atmosphere (CO or argon).

Run	*Atmosphere*	*PhI conversion (%)*[a]	*Ph(CO)Ph (%)*[a]	*$PhCO_2H$ (%)*[b]	*Ph-Ph (%)*[a]	*PhH (%)*[c]	*Selectivity (%)*[d]
9	CO	100	72	18	2	4	75
10	Argon	100	64	24	2	6	67

$Fe(CO)_5$ = 2.9 mmol; PhI = 10 mmol; H_2O = 60 mL; C_6H_6 = 20 mL; n-Bu_4NBr: 3 mmol; 70 °C; 750 rpm; 24 h. [a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column). [b] Isolated yield. [c] Calculated by difference. [d] (Ph(CO)Ph %/PhI conversion) %.

Table IV. Carbonylative coupling of aryl iodides RC_6H_4I.

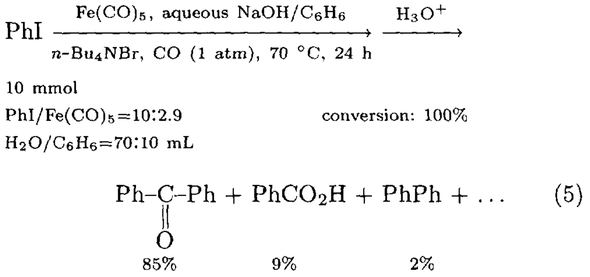
Run	*R*	*t (h)*	*Conversion (%)*[a]	*Ar(CO)Ar (%)*[c]	*$ArCO_2H$ (%)*[b]	*ArH (%)*[a]	*ArAr (%)*[a]	*ArCHO (%)*[a]	*ArCOCOAr (%)*[a]
11	H	24	100	85	9	2	2	Traces	Traces
12	*p*-MeO	48	100	62	17	8	4	3	2
13	*p*-Cl	52	98	50	20	16	6	4	Traces
14	*p*-Me	52	97	40	19	15	13	5	4
15	*m*-Cl	52	100	55	17	18	4	Traces	2
16	*m*-Me	52	95	44	31	12	3	2	Traces
17	*o*-Me	48	89	31	21	25	5	Traces	Traces
18	*o*-Cl	48	95	27	34	22	4	3	Traces

$Fe(CO)_5$ = 2.9 mmol; RC_6H_4I = 10 mmol; H_2O = 70 mL; C_6H_6 = 10 mL; n-Bu_4NBr: 3 mmol; 70 °C; 750 rpm; CO (1 atm). [a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column). [b] Isolated yield. [c] Isolated yield after column chromatography.

Two other observations are noteworthy. First, under the experimental conditions shown in table II ($Fe(CO)_5$/PhI ratio of 2.9:10), the reaction can be performed under an atmosphere of argon without a significant decrease in the carbonylation yield (table III). The data in table III shows that, although the yield of benzophenone is slightly decreased (64 vs 72%), the overall carbonylation yield is roughly the same with the use of argon (88 vs 90%). If we calculate the number of equivalents of CO introduced into the carbonylation products for the reaction carried out under argon (run 10) (3.2 mmol of benzophenone and 2.4 mmol for benzoic acid, ie, a total of 5.6 mmol), it is apparent that $[HFe(CO)_4]^-$ (prepared from 2.9 mmol $Fe(CO)_5$) is capable of transferring more than one equivalent carbon monoxide per iron equivalent [14].

The second observation concerns the reaction mechanism. When the organic solvent used is toluene instead of benzene, the reaction leads qualitatively to the same results. The carbonylation and benzophenone yields are lower because of an increase in the formation of benzene (20 vs 4%) and biphenyl (6 vs 2%). Most important, though, is the observation (GC-MS analysis) of the formation of two isomeric methylbiphenyls (3 to 4%). The exact position of the methyl groups in these two compounds has not been determined. Indeed, the fragmentation spectra of the three possible isomers are practically identical. Nevertheless, this observation indicates that phenyl radicals are generated by reacting PhI with $[HFe(CO)_4]^-$ [9].

This study of the influence of these main reaction parameters enabled us to design experimental conditions leading to an almost quantitative overall carbonylation yield (94%) and a very good selectivity for benzophenone (eq 5).



$$\mathrm{PhI} \xrightarrow[n\text{-}Bu_4NBr,\ CO\ (1\ atm),\ 70\ °C,\ 24\ h]{Fe(CO)_5,\ aqueous\ NaOH/C_6H_6} \xrightarrow{H_3O^+}$$

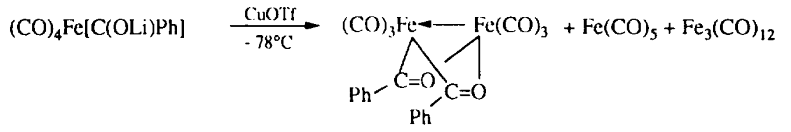
10 mmol
$PhI/Fe(CO)_5$=10:2.9 conversion: 100%
H_2O/C_6H_6=70:10 mL

$$\underset{85\%}{\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Ph}} + \underset{9\%}{PhCO_2H} + \underset{2\%}{PhPh} + \ldots \quad (5)$$

The above reaction, which is very easy to perform, thus increases the potential interest of carbonylferrates, which were previously considered inefficient for the functionalization of aryl halides. It is, however, limited to iodobenzenes (bromobenzene and bromonaphthalene do not react) and the presence of some substituents on the aromatic ring may have a detrimental effect on the diarylketone yield (table IV).

Mechanistic investigations

In view of its novelty [12], we were interested in probing the possible reaction pathways involved in this carbonylative coupling of iodobenzene. The iron carbonyl reagent $[n\text{-}Bu_4N]^+[HFe(CO)_4]^-$ **1** was prepared under argon by adding $Fe(CO)_5$ to the biphasic medium of aqueous NaOH/benzene, which contained the ammonium salt Bu_4NBr. The reaction mixture was stirred for 15 min. Because it is insoluble in water, and only slightly soluble in benzene (or toluene), some of the complex **1** appeared as an insoluble orange solid at the interface of the two phases. At this point, the argon atmosphere could be flushed and replaced with carbon monoxide. Iodobenzene was then syringed in and the reaction vessel heated to 70 °C.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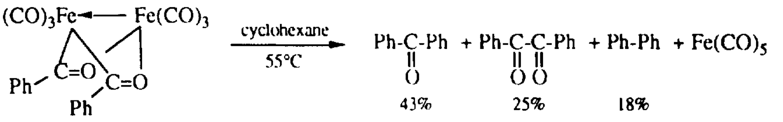

(7)

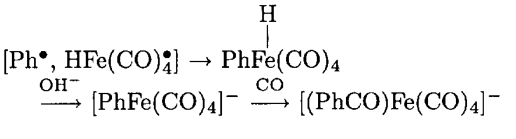
Detection of anionic iron carbonyl species

We first examined the fate of the iron carbonyl complexes during the reaction by IR analysis of the organic phase (toluene) in the range 1 500-2 000 $\mathrm{cm^{-1}}$. At the beginning of the reaction, the IR spectrum of the toluene phase exhibits only the absorptions characteristic of **1** (2 002 (w), 1 915 (sh) and 1 886, 1 876 (vs, br) $\mathrm{cm^{-1}}$). At the end of the reaction (complete conversion of PhI) the spectrum shows the juxtaposition of the above bands with those due to another iron carbonyl complex (2 012 and 1 899 $\mathrm{cm^{-1}}$). It also shows bands at 1 664 (s, benzophenone) and 1 683 $\mathrm{cm^{-1}}$ (w, benzil). The bands at 2 012 and 1 899 $\mathrm{cm^{-1}}$ (and other bands hindered by those of the starting complex) could correspond to those reported for the benzoylcarbonylferrate complex $[\mathrm{(PhCO)Fe(CO)_4}]^-[\mathrm{Me_4N}]^+$ (2 016 w, 1 912 m, 1 899 s and 1 883 $\mathrm{cm^{-1}}$ s(sh) in $\mathrm{CH_2Cl_2}$) [15]. ^{13}C NMR analysis of the organic phase (after evaporation of toluene and replacement by d_8-THF) confirmed this hypothesis. The ^{13}C NMR spectrum exhibits the same signals as an authentic sample of $[\mathrm{(PhCO)Fe(CO)_4}]^-[n\text{-}\mathrm{Bu_4N}]^+$ (see below), particularly the characteristic Ph*C*O signal at 265.4 ppm.

It has been reported that, in the presence of an oxidant, the lithium salt of this complex can be oxidized to a dinuclear complex (eq 6) which, when heated, affords a mixture of benzophenone, benzil and biphenyl (eq 7) by an intramolecular process [16].

The participation of $[\mathrm{(PhCO)Fe(CO_4)}]^-$ in our carbonylation reaction is certainly possible. Its formation could result from the following reaction pathways (eq 8 and 9), as previously suggested [9].

$$\mathrm{PhI} + [\mathrm{HFe(CO)_4}]^- \rightarrow [\mathrm{PhI}^{\dot{-}}, \mathrm{HFe(CO)_4^{\bullet}}] \xrightarrow{-\mathrm{I}^-} [\mathrm{Ph}^{\bullet}, \mathrm{HFe(CO)_4^{\bullet}}] \qquad (8)$$


$$[\mathrm{Ph}^{\bullet}, \mathrm{HFe(CO)_4^{\bullet}}] \rightarrow \mathrm{Ph}\overset{\mathrm{H}}{\overset{|}{\mathrm{Fe}}}\mathrm{(CO)_4} \xrightarrow{\mathrm{OH^-}} [\mathrm{PhFe(CO)_4}]^- \xrightarrow{\mathrm{CO}} [\mathrm{(PhCO)Fe(CO)_4}]^- \qquad (9)$$

We were thus interested in preparing this benzoyltetracarbonylferrate as its tetrabutylammonium salt, and studying its reactivity under our reaction conditions.

The complex $[\mathrm{(PhCO)Fe(CO)_4}]^-[n\text{-}\mathrm{Bu_4N}]^+$ **2** was prepared by the reaction of phenyllithium with $\mathrm{Fe(CO)_5}$, followed by metathesis with n-$\mathrm{Bu_4NBr}$ (eq 10) [15]. Its reactivity was then explored in a stepwise manner.

$$\mathrm{Fe(CO)_5} + \mathrm{PhLi} \xrightarrow[-60\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathrm{Fe(CO)_4[C(OLi)Ph]} \xrightarrow[\mathrm{H_2O}]{n\text{-}\mathrm{Bu_4NBr}} \downarrow [\mathrm{(PhCO)Fe(CO)_4}]^-[n\text{-}\mathrm{Bu_4N}]^+ \qquad (10)$$

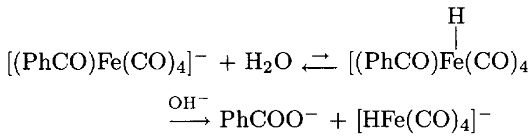
Stability of **2** *under our reaction conditions*

Heating **2** at 70 °C for 24 h in toluene under either carbon monoxide or argon caused no change to the complex, as determined by IR and GC analyses. This behavior differs from that of the corresponding nickel complexes $[\mathrm{(ArCO)Ni(CO)_3}]^-$, which give α-diketones upon heating to 50–60 °C [17].

When placed in a water/toluene medium for 65 h at 70 °C under argon, **2** gave only trace amounts of benzene, benzaldehyde and benzoic acid. Traces of complex **1** were also observed (by IR) for this reaction mixture.

When the same reaction was performed in an aqueous NaOH/toluene biphasic medium, a larger amount of **1** was formed (IR) and benzoic acid could be isolated in 10% yield. No trace of either benzophenone or biphenyl was detected. Unexpectedly, this reaction is slower when conducted under a carbon monoxide atmosphere.

In our opinion, the above reaction is best represented by eq 11 rather than by the direct nucleophilic attack of hydroxide ions on the anionic benzoyltetracarbonylferrate.


$$[\mathrm{(PhCO)Fe(CO)_4}]^- + \mathrm{H_2O} \rightleftharpoons [\mathrm{(PhCO)}\overset{\mathrm{H}}{\overset{|}{\mathrm{Fe}}}\mathrm{(CO)_4}] \xrightarrow{\mathrm{OH^-}} \mathrm{PhCOO^-} + [\mathrm{HFe(CO)_4}]^- \qquad (11)$$

Our results also suggest that $[\mathrm{HFe(CO)_4}]^-$ does not react rapidly with $[\mathrm{(PhCO)Fe(CO)_4}]^-$. This conclusion was confirmed by combining complexes **1** and **2**. After 65 h at 70 °C in a water/toluene biphasic medium, GC analysis of this reaction mixture indicated the formation of benzene (5%) and only 10% benzaldehyde. The latter is probably formed via the binuclear mechanism previously described by Barborak and Cann [18].

Reactivity of **2** *towards iodobenzene*

No reaction occurs between **2** and PhI in 24 h at 70 °C in toluene (carbon monoxide or argon atmosphere) as determined by IR and GC analyses. This result rules out the possibility that PhI plays the role of oxidant in a transformation of the type represented in eq 6 (see above).

Table V. Reaction of PhI with $[n\text{-}Bu_4N][(PhCO)Fe(CO)_4]$ and $[n\text{-}Bu_4N][HFe(CO)_4]$ in neutral water/toluene medium.

Run	*$[Fe(CO)_4COPh]^-$ (mmol)*	*$[HFe(CO)_4]^-$ (mmol)*	*PhI conversion (%)[a]*	*PhCOPh (%)[a]*	*$PhCO_2H$ (%)[b]*	*PhCHO (%)[a]*	*$(PhCO)_2$ (%)[a]*	*Ph-Ph (%)[a]*	*PhH (%)[a]*	*Ph-tol (%)[a]*
19	–	1.5	16	–	–	Traces	–	Traces	9	Traces
20	1.5	–	25	5	4	4	Traces	Traces	10	Traces
21	1.5	1.5	46	9	4	6	3	5	16	Traces

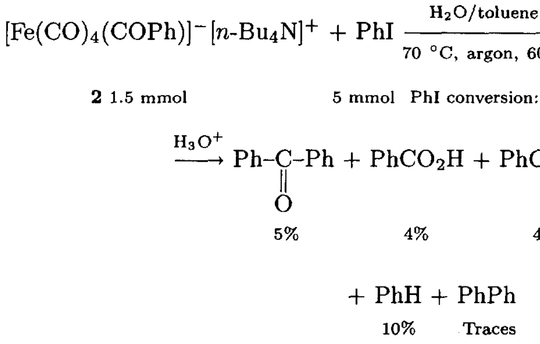
PhI = 5 mmol; H_2O = 30 mL; toluene = 10 mL; 70 °C; 750 rpm; 65 h; argon. [a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column). [b] Isolated yield.

Table VI. Reaction of PhI with $[n\text{-}Bu_4N][(PhCO)Fe(CO)_4]$ and $[n\text{-}Bu_4N][HFe(CO)_4]$ in basic aqueous NaOH/toluene medium.

Run	*$[Fe(CO)_4COPh]^-$ (mmol)*	*$[HFe(CO)_4]^-$ (mmol)*	*Atmosphere (1 atm)*	*PhI conversion (%)[a]*	*PhCOPh (%)[a]*	*$PhCO_2H$ (%)[b]*	*$(PhCO)_2$ (%)[a]*	*Ph-Ph (%)[a]*	*PhH (%)[a]*	*Ph-tol (%)[a]*
22	1.5	–	CO	100	37	20	2	8	24	4
23	1.5	–	Argon	100	42	24	1	10	17	5
24	–	1.5	CO	100	62	7	Traces	6	17	3
25	–	1.5	Argon	100	50	13	–	6	18	3

PhI = 5 mmol; H_2O = 30 mL; NaOH 8 M; toluene = 10 mL; 70 °C; 750 rpm; 24 h. [a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column). [b] Isolated yield.

In the presence of **2**, in water/toluene, PhI was partially converted (25% in 65 h at 70 °C under argon) into a mixture of products (eq 12) of the same nature as those formed in our reaction (eq 5). At the end of the reaction, IR analysis of the organic phase indicated that the main iron carbonyl species present was $Fe(CO)_5$, accompanied by traces of $[HFe_3(CO)_{11}]^-$. Similar results were obtained when the reaction was conducted under carbon monoxide.



$$\underset{\mathbf{2}\ 1.5\ mmol}{[Fe(CO)_4(COPh)]^-[n\text{-}Bu_4N]^+} + \underset{5\ mmol}{PhI} \xrightarrow[70\ ^\circ C,\ argon,\ 60\ h]{H_2O/toluene} \text{PhI conversion: 25\%}$$

$$\xrightarrow{H_3O^+} \underset{5\%}{Ph\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}Ph} + \underset{4\%}{PhCO_2H} + \underset{4\%}{PhCHO} + \underset{10\%}{PhH} + \underset{Traces}{PhPh} \quad (12)$$

By contrast, under the same conditions, the reaction of **1** with PhI gave only reduction to benzene while no traces of benzophenone or benzoic acid were detected (tables V, run 19). It is interesting to note that the conversion of PhI was higher for the reaction with **2** (run 20) than for the reaction with **1** (run 19). This observation suggests that, in the presence of **2**, a species is formed (probably the radical anion of $[(PhCO)PhFe(CO)_4]$) which reacts efficiently with PhI (via a radical chain mechanism).

The same reaction performed in a basic medium (aqueous NaOH/toluene) led to complete conversion of PhI in 24 h at 70 °C (runs 22 and 23, table VI). The relative ratios of the reaction products were slightly different depending on whether the reaction was performed under carbon monoxide or under argon. For comparison, the reaction of PhI with **1** was performed under the same conditions (runs 24 and 25).

Table VI shows that roughly the same results are obtained by reacting PhI with either **1** or **2**. Nevertheless, these results do not conclusively indicate the intervention of **2** in the reaction of PhI with **1**. While we know that in the presence of aqueous NaOH, **2** generates **1** (eq 11), it should be noted that this reaction is very slow and that after 24 h the amount of **1** formed was far from 1.5 mmol. This suggests that in runs 22 and 23, the complex **2** is both a precursor of **1** and a source of phenyl groups for the formation of benzophenone.

Comparison of the results of run 19 (table V) and 25 (table VI) also highlights the dramatic role of hydroxide ions in the reaction of PhI with **1**. NaOH is essential for the formation of carbonylation products in this system (the benzophenone yield increases with increasing NaOH concentration, see table II). The results concerning the role of **2** suggest that hydroxide ions are necessary for the formation of this complex from PhI and **1**. A likely hypothesis is that the reaction of PhI with **1** generates $PhFe(H)(CO)_4$ by an $S_{RN}1$-type mechanism (see below) [9]. In the absence of base, $PhFe(H)(CO)_4$ gave benzene by reductive elimination. In contrast, in strongly basic medium, $PhFe(H)(CO)_4$ was deprotonated to give the phenylferrate $[PhFe(CO)_4]^-$ which, in the presence of an additional ligand L, generated $[(PhCO)Fe(CO)_3L]^-$ (L = CO or solvent).

Reaction of **2** *with iodoanisole*

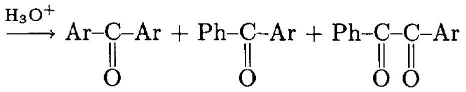
In order to evidence the participation of the phenyl group of **2** in the carbonylation process, **2** was reacted with 4-iodoanisole in basic medium. This reaction (eq 13) leads to a mixture of ketones consisting of 4,4′-dimethoxybenzophenone, 4-methoxybenzophenone and 4-methoxybenzil (no traces of benzophenone). Similar results were obtained by reacting **2** with

2-iodothiophene (2-benzoylthiophene yield: 20%, no benzophenone).

$$[(PhCO)Fe(CO)_4]^- \, [n\text{-}Bu_4N]^+ + ArI \xrightarrow[70\ ^\circ C,\ CO,\ 52\ h]{NaOH\ aqueous/toluene}$$

2 3 mmol 10 mmol

Ar = 4-MeO-C$_6$H$_4$ ArI conversion: 98%



$$\xrightarrow{H_3O^+} Ar\text{–}\underset{\underset{O}{\|}}{C}\text{–}Ar + Ph\text{–}\underset{\underset{O}{\|}}{C}\text{–}Ar + Ph\text{–}\underset{\underset{O}{\|}}{C}\text{–}\underset{\underset{O}{\|}}{C}\text{–}Ar$$

0.7 mmol 1.6 mmol 0.4 mmol

$$+ ArCO_2H + PhCO_2H + ArH + Ar\text{-}C_6H_4Me$$

1.3 mmol 0.4 mmol 2.5 mmol 1 mmol (two isomers)

$$+ Ar\text{–}Ar \qquad (13)$$

Traces

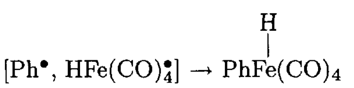
The formation of 4-methoxybenzophenone (53%/**2**) and 4-methoxybenzil (13%/**2**) clearly demonstrates that **2** has reacted with a species generated from the reaction of 4-iodoanisole with **1** (in situ generated from **2**, see eq 11). The formation of anisyltoluenes (eq 13) suggests that this species may be a radical (ie, the radical anion of iodoanisole or the anisyl radical).

It is also interesting to note that traces of the homocoupling product Ar-Ar are detected in these reactions, whereas no trace of the cross-coupled product Ar-Ph could be detected. This observation suggests that the formation of biphenyl in the reaction of PhI with **1** (eq 5) results from the recombination of phenyl radicals rather than from its reductive elimination from an iron complex.

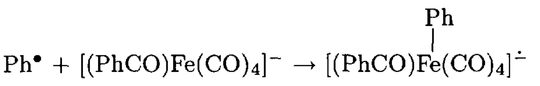
Reaction of 2 *with phenyl radicals*

The hypotheses that result from the analysis of the above experiments can be summarized by the following equations (eq 14–17).

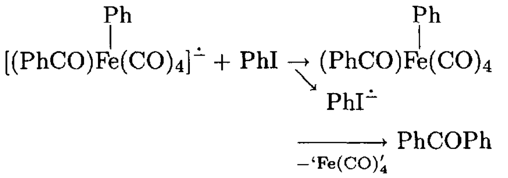
$$PhI + [HFe(CO)_4]^- \rightarrow [PhI^{\bullet-}, HFe(CO)_4^\bullet] \xrightarrow{-I^-} [Ph^\bullet, HFe(CO)_4^\bullet] \rightleftarrows Ph^\bullet + HFe(CO)_4^\bullet \qquad (14)$$



$$[Ph^\bullet, HFe(CO)_4^\bullet] \rightarrow Ph\overset{\overset{H}{|}}{Fe}(CO)_4 \xrightarrow{OH^-} [PhFe(CO)_4]^- \xrightarrow{CO} [(PhCO)Fe(CO)_4]^- \qquad (15)$$



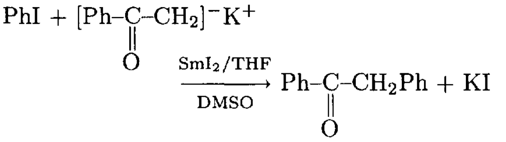
$$Ph^\bullet + [(PhCO)Fe(CO)_4]^- \rightarrow [(PhCO)\overset{\overset{Ph}{|}}{Fe}(CO)_4]^{\bullet-} \qquad (16)$$



$$[(PhCO)\overset{\overset{Ph}{|}}{Fe}(CO)_4]^{\bullet-} + PhI \rightarrow (PhCO)\overset{\overset{Ph}{|}}{Fe}(CO)_4 \searrow PhI^{\bullet-} \xrightarrow[-\text{'}Fe(CO)_4^{\text{'}}]{} PhCOPh \qquad (17)$$

Eq 14 represents an SET yielding two radicals in a solvent cage. These radicals can either recombine directly, forming the neutral complex PhFe(H)(CO)$_4$ (eq 15) or escape from the solvent cage to give further reactions (formation of Ph-Ph and H$_2$Fe$_2$(CO)$_8$) [19], including that in eq 16.

In an attempt to verify the hypothetical eq 16, we reacted **2** with PhI in the presence of SmI$_2$. This reagent is known [20] to react with PhI by generating phenyl radicals [21]. This property has recently been used to promote S$_{RN}$1 substitutions on iodobenzene (eq 18) [22].



$$PhI + [Ph\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_2]^-K^+ \xrightarrow[DMSO]{SmI_2/THF} Ph\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_2Ph + KI \qquad (18)$$

The reaction of PhI with **2** in the presence of 1 equiv of SmI$_2$ led (carbonyl reaction products) to a mixture of benzophenone and benzil (eq 19).

$$[n\text{-}Bu_4N]^+[(PhCO)Fe(CO)_4]^- + PhI$$

2

$$\xrightarrow[25\ ^\circ C,\ 24\ h]{SmI_2,\ THF} PhCOPh + PhCOCOPh + \ldots \qquad (19)$$

Conversion PhI: 55% 6% 10%

In the absence of PhI, the reaction of SmI$_2$ with **2** does not give any of either benzophenone or benzil. Since **2** does not react with PhI alone (see above and [5]), the formation of benzophenone (and benzil) in eq 19 results from the reaction of **2** with the phenyl radical generated by the reaction of SmI$_2$ with PhI. It thus appears that [(PhCO)Fe(CO)$_4$]$^-$ can play the role of nucleophile in an S$_{RN}$1 reaction with PhI, confirming our hypothesis (eq 16).

Reaction of 2 *with PhCOCl*

The formation of traces of benzil in the reaction of PhI with **1** in basic medium (eq 5) suggests the intermediate formation of a dibenzoylcarbonyliron complex of the type [(PhCO)$_2$Fe(CO)$_n$L]. This complex could be expected to give reductive elimination both with and without loss of carbon monoxide. Other researchers have shown that the reaction of Li$^+$[(PhCO)Fe(CO)$_4$]$^-$ with PhCOCl in ether at −40 °C affords a mixture of benzophenone (40%) and benzil (10%) [23]. In order to confirm this result under conditions more similar to our reaction conditions, we have reacted **2** with benzoyl chloride in toluene at 70 °C (eq 20).

$$[n\text{-}Bu_4N]^+ \, [(PhCO)Fe(CO)_4]^- + PhCOCl$$

2

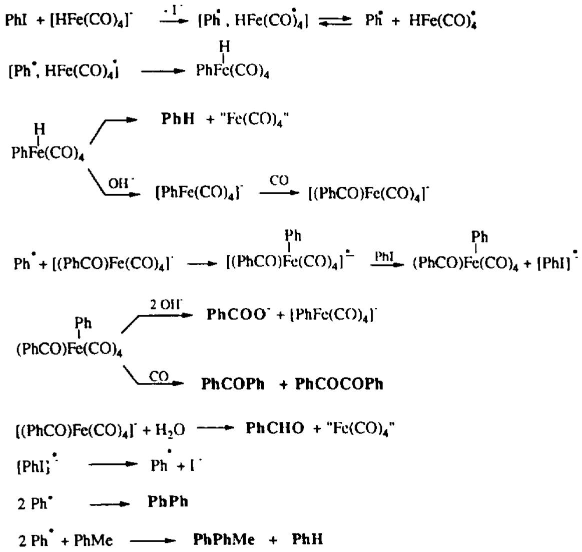
$$\xrightarrow[argon,\ 70\ ^\circ C]{toluene} PhCOPh + PhCOCOPh + \ldots \qquad (20)$$

10% Traces

This reaction yields benzophenone and only traces (1–2%) of benzil (GC-MS analysis). A similar result was obtained when the reaction was conducted under carbon monoxide (1 atm). It thus appears that [(PhCO)$_2$Fe(CO)$_4$], which was assumed to be the first complex formed during the reaction in eq 20, primarily decarbonylates before reductive elimination to give benzophenone [24].

Mechanistic proposal

The formation of benzophenone and all the secondary products in the reaction of iodobenzene with **1** in basic medium can thus be rationalized by the simplified set of equations in scheme 1.



Scheme 1

Conclusion

We have thus discovered that the direct carbonylative coupling of iodobenzene to benzophenone (85% yield) can be effected by semi-catalytic amounts (30%) of $[HFe(CO)_4]^-$ under 1 atm of carbon monoxide. Although the reaction has been optimized, extension to substituted iodobenzenes gave yields lower than 50% in some cases. Mechanistic investigations suggest a multistep reaction sequence involving an SET transfer from $[HFe(CO)_4]^-$ to iodobenzene and the generation of phenyl radicals and $[(PhCO)Fe(CO)_4]^-$ species. The latter have been shown to react with phenyl radicals, affording benzophenone. Application of these findings to new functionalizations of aryl iodides using carbonylferrates is underway.

Experimental section

General

All experiments were conducted under a well-ventilated hood. Manipulations of air-sensitive iron 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), toluene (SDS) methanol (Prolabo) were used as received and degassed before use. Iron pentacarbonyl (Fluka), sodium hydroxide (Prolabo), tetrabutylammonium bromide (Fluka), phenyllithium (Aldrich) and samarium(II) iodide (THF solution) (Aldrich) were used without further purification. All aryl halides were purified before use by distillation or recrystallization.

IR spectra were recorded on a Perkin-Elmer FTIR 1725 spectrophotometer using CaF_2 (0.05 mm) windows. ^1H and ^{13}C NMR spectra were recorded on Bruker (WM 250 or AC 200) instruments. Reactions were monitored by GC analysis on a Hewlett-Packard 5890 gas chromatograph (FID) fitted with a 50 m capillary column (OV1) using linear alkanes as internal calibration standards. Peak areas were determined with a Spectra-Physics SP4290 computing integrator. GC-MS (EI) analyses were carried out on a Hewlett-Packard 5890 gas chromatograph coupled to a 5970 Hewlett-Packard mass-selective detector. CHN elemental analyses were performed on a Perkin-Elmer 2400 serie II instrument.

Preparation of iron carbonyl complexes

- *Preparation of* $[HFe(CO)_4]^-[n\text{-}Bu_4N]^+$

This complex was prepared according to the procedure previously described [25].

- *Preparation of* $[(PhCO)Fe(CO)_4]^-[n\text{-}Bu_4N]^+$

The title complex was prepared (80% yield) according to Fischer et al [15] by reaction of phenyllithium with $Fe(CO)_5$, giving $[(PhCOLi)Fe(CO)_4]$, followed by metathesis with $n\text{-}Bu_4NBr$. The following ^{13}C NMR data were obtained:

$[(PhCOLi)Fe(CO)_4]$: (d_8-THF) δ (ppm) 127.6, 128.8, 130.4 and 157 (aromatic carbons), 221.2 ($C{\equiv}O$), 288.4 (C–OLi).

$[(PhCO)Fe(CO)_4]^-[n\text{-}Bu_4N]^+$ (iron carbonyl part only): (d_8-THF) δ (ppm) 128.6, 128.9, 129.8 and 154.4 (aromatic carbons), 222.4 ($C{\equiv}O$), 265.4 (acyl).

General procedure for the carbonylative coupling of iodobenzenes

Tetrabutylammonium bromide (3 mmol) was added to a biphasic medium consisting of 70 mL of 8 M aqueous NaOH and 10 mL benzene. The mixture was stirred (magnetic bar) and degassed by bubbling argon through a needle for 15 min. Iron pentacarbonyl (2.9 mmol) was syringed into the flask under argon and the mixture was stirred for 30 min at room temperature. The argon atmosphere was then flushed and replaced by carbon monoxide. Finally, iodobenzene (10 mmol) and the internal standard (dodecane, 10 mmol) were added and the reaction mixture heated to 70 °C with stirring (750 rpm).

Acknowledgments

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