Mechanistic Study of the Phase-Transfer-Catalyzed Reduction of Nitrobenzene to Aniline by Iron Carbonyl Complexes. Role of the Radical Anion $[Fe_3(CO)_{11}]^{\bullet-}$

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Contrary to what was earlier believed, the phase-transfer-catalyzed reaction of $Fe_3(CO)_{12}$ with OH^- affords the radical anion cluster $[Fe_3(CO)_{11}]^{\bullet-}$ and not $[HFe_3(CO)_{11}]^-$. When a nitro compound is also present, it is the radical anion that is mainly responsible for its reduction to aniline, not the hydride cluster, which is completely unreactive under the same experimental conditions.

Many different complexes have been reported to promote or to catalyze reduction and carbonylation of nitro compounds, with the most efficient metals being palladium, rhodium, and ruthenium.[1] Only limited attention has been given to the study of iron complexes as promoters for these reactions.[2−17] Several iron compounds are known to promote the stoichiometric reduction of nitro compounds, but few catalytic processes have been reported. Despite the apparent lower efficiency of iron-based catalysts, their use is of interest due to the comparative cost advantage of iron compared to the other metals commonly employed as catalysts for these reactions. Almost all of the reports on the use of iron carbonyl complexes in conjunction with a nitro compound concern the reduction of the nitro compound itself to amine. The starting iron complex may be $Fe_3(CO)_{12}$ (**1**),[2−9] $[HFe_3(CO)_{11}]^-$ (**2**),[9−11] $[HFe(CO)_4]^-$ (**3**),[12−15] or $Fe(CO)_5$ (**4**).[2,14,16,17] Whenever **1** is used as the iron compound, it needs to be activated by a base, which may be hydroxide ion under biphasic[2−4,7] or even triphasic[8] conditions, fluoride ion in the presence of water,[5] or basic alumina[6] (otherwise very high temperatures or hydrogen pressure are required[16]). In all of these cases, **2** was proposed to be formed by interaction of the base with **1**, eventually *via* $[Fe_3(CO)_{11}]^{2-}$ (**5**), and to be the species responsible for the reduction of the nitro compound. Several aspects of the reaction mechanism, including the finding that the hydrido-imido cluster $[HFe_3(\mu_3\text{-}NPh)(CO)_9]^-$ (**6**)[18] plays no role in the reaction, have been already analyzed by us in a work in collaboration with Geoffroy and his group.[19,20] However, the iron species responsible for the first step of the activation of nitroarenes in the biphasic process was not unequivocally identified, although it was suggested that **5** and **7** may also be involved as alternatives to or in competition with **2**.

In this paper, we report a study of this early stage of the phase-transfer-catalyzed reduction of nitrobenzene. This also required a reinvestigation of the products of the reactions of **1** under biphasic conditions and in the absence of nitrobenzene.

Results and Discussion

$Fe_3(CO)_{12}$ in the Presence of Hydroxide. The most efficient way of reducing nitroarenes with iron carbonyl complexes, at least as far as simple operations and mild experimental conditions are concerned, is the one employing $Fe_3(CO)_{12}$ (**1**) under phase-transfer-catalyzed conditions.[2−4] The reaction is conducted at room temperature for 0.75−2 h, employing benzene as the organic solvent and 1 M aqueous NaOH as a base, in the presence of a tetraalkylammonium halide or a crown ether as the phase-transfer catalyst (eq 1).[2−4] As earlier mentioned, $[HFe_3(CO)_{11}]^-$ (**2**) was proposed to be formed under the phase-transfer conditions and to

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$$Fe_3(CO)_{12} + ArNO_2 \xrightarrow[\text{1 M NaOH in } H_2O\text{, 0.75−2 h, room temp}]{\text{benzene, } [PhCH_2NEt_3][Cl]} ArNH_2 \quad (1)$$

be the active species. However, this is surprising, since the direct reaction between **2** and nitrobenzene has been reported to require refluxing in THF for 18 h to reach completion and other reduction reactions of nitroarenes to anilines employing **2** as reagent under homogeneous conditions (the use of alumina-supported **2** will be discussed later) all require heating.[9,10] To test if the unusual biphasic conditions were responsible for the much higher rate of reduction in the phase-tranfer-catalyzed process, we reacted preformed [Et_4N]**2** with nitrobenzene under the same conditions reported in ref 2, but in the absence of additional alkylammonium salts (we used toluene instead of benzene for toxicity reasons, but this does not alter the general reactivity, as independently tested by us; *vide infra*). No reaction at all was observed even after 1 day. On the other hand, a parallel reaction run employing **1** and a 1:1 molar amount of [Et_4N][Cl], in place of [Et_4N]**2**, gave an approximately 80% conversion in 3 h, with the rest of the nitrobenzene then being more slowly converted upon stirring overnight. The reason for the remarkable slowing down of the reaction after some time is to be ascribed to the fact that, after 3 h, no more **1** was present in solution or as a solid and the only observable organometallic species in the organic phase was $Fe(CO)_5$ (**3**), formed by decomposition of **1** (*vide infra*). $Fe(CO)_5$ has also been reported to promote the reduction of nitroarenes to anilines under biphasic conditions, but at least under our conditions, this process was slower than the reaction of **1**.[21] These results clearly show that, contrary to what is commonly accepted, **2** plays no role in the phase-transfer-catalyzed reduction of nitroarenes by **1**.

In order to identify the metal species responsible for the initial activation of the nitroarene, we started an investigation of the reactions of **1** under biphasic conditions, both in the presence and in the absence of [Et_4N][Cl], using either toluene or THF as the organic phase. The use of THF was prompted by the observation that several anionic complexes are insoluble in toluene and water and they precipitated out of the reaction mixture when these solvents were used, whereas clear solutions were always observed in the case of THF/H_2O.

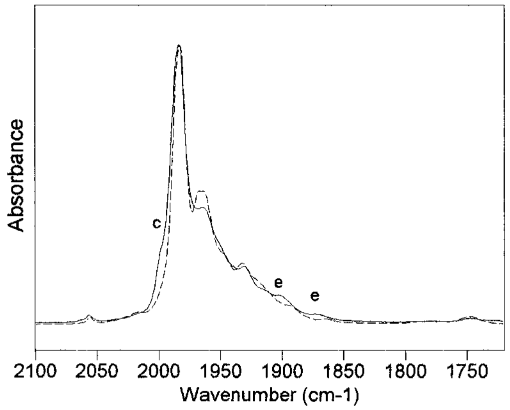

Figure 1. IR spectra of the precipitate of reaction 2 extracted in THF (solid line) and of an authentic sample of [PPN][$Fe_3(CO)_{11}$] in the same solvent (dashed line): (c) [$HFe_3(CO)_{11}$]$^-$; (e) [$HFe(CO)_4$]$^-$; (f) [$Fe_3(CO)_9(\mu_3\text{-}O)$]$^{2-}$.

When a suspension of **1** in toluene (under the concentration conditions reported in ref 2, **1** is only partially soluble in the toluene solvent and it accumulates as a solid on the walls of the flask and at the water-toluene interface) was stirred with a 1 M aqueous NaOH solution, in the presence of a 1:1 molar amount of [Et_4N][Cl], a slow reaction was observed, requiring several hours to reach completion. Monitoring by IR of the toluene layer during the reaction showed the gradual disappearance of the IR absorptions due to **1** and the appearance of the band of **4** as the only observable products in solution.[22] The solid dark green **1** gradually dissolved, while a brick orange precipitate formed. The solid was treated with THF, affording a red solution and an orange residue. The red solution showed the presence of the radical anion [$Fe_3(CO)_{11}$]$^{\bullet-}$ [19] (**7**) as the almost exclusive product, accompanied by only trace amounts of **2** and **3** (Figure 1). The residue was treated with CH_3CN, affording an orange solution of [$Fe_3(CO)_9(\mu_3\text{-}O)$]$^{2-}$ (**8**),[23] as evidenced by comparison of the IR bands with those of an authentic sample. This last product may be derived from the reaction of **7** with trace amounts of oxygen, as this is also the way it was first obtained,[23] but is more probably derived from another pathway (*vide infra*). An insoluble residue still remained, which showed no IR absorption in the carbonyl region and was identified as α-FeOOH (goethite) by X-ray powder diffraction (eq 2).

$$\begin{aligned} Fe_3(CO)_{12} \xrightarrow[\text{1 M NaOH in } H_2O\text{, room temp}]{\text{toluene, } [Et_4N][Cl]} &\underset{\mathbf{7}}{[Fe_3(CO)_{11}]^-} + \\ &\underset{\mathbf{4}}{Fe(CO)_5} + \underset{\mathbf{8}}{[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}} + \\ &\underset{\mathbf{3}}{[HFe(CO)_4]^-}\text{ (trace)} + \\ &\underset{\mathbf{2}}{[HFe_3(CO)_{11}]^-}\text{ (trace)} + \alpha\text{-FeOOH} \quad (2) \end{aligned}$$

When the same reaction was performed in the absence of [Et_4N][Cl], it proceeded only very slowly and a small amount of unreacted $Fe_3(CO)_{12}$ was still present after stirring for 3 days. Very little **4** was formed, and no precipitate was observed, but the aqueous phase was red and contained a mixture of organometallic complexes, of which the most predominant was [$Fe_4(CO)_{13}$]$^{2-}$ (**9**).[24] No **2** was detectable. The formation of **9** is not surprising, since decomposition of **7** in solution is known to afford this product.[19]

As the long reaction times required when toluene is used as solvent may lead to the decomposition of reactive compounds such as **7** and the precipitation of

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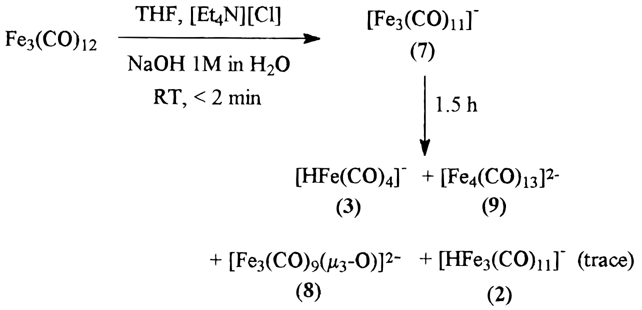
(21) (a) The efficiency of the reaction was somewhat inferior to that of the reaction reported in ref 2, but this is likely mainly due to the lower solubility of water in toluene with respect to that in benzene,[21b] although the use of [Et_4N][Cl] as the phase-transfer catalyst instead of [Et_3NCH_2Ph][Cl], or different stirring speed may also play a role. (b) Stephen, H., Stephen, T., Eds. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1963; Vol. 1.

(22) As the solution is initially saturated with **1**, the intensities of its bands do not vary detectably during the first part of the reaction, until all of the solid **1** has dissolved, after which a steady decrease is observed.

(23) Ceriotti, A.; Resconi, L.; Demartin, F.; Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1983**, *249*, C35.

Scheme 1



several products makes it difficult to follow the development of the reaction, we repeated the same reactions using THF as the organic solvent.

When an aqueous 1 M NaOH solution, also containing $[Et_4N][Cl]$ in a 1:1 molar amount with respect to **1**, was added to a THF solution of **1**, an immediate reaction took place, leading to the complete disappearance of **1** in less than 2 min. An IR spectrum of the red THF solution at this point showed the presence of **7** *as the almost exclusive carbonyl species* (as shown by comparison with the IR spectrum of an authentic sample of [PPN]**7**[20] under the same conditions; a trace amount of **3** was also present). The radical anion **7** is not stable in solution under these conditions, and after 10 min, formation of some **3**, **9**, and **8** could be observed by IR. Only a trace amount of **2** was present at this stage. The reaction then continued likewise. Complete disappearance of **7** required about 1.5 h (Scheme 1):

On a longer time scale, (overnight), **9** disappeared, the amount of **3** increased, and a small but significant amount of **2** was formed. After 3 days, **3** is the principal product in solution (Figure 2). An orange-brown residue was also formed, which contained some **8** and some α-FeOOH. When the reaction was performed in the absence of $[Et_4N][Cl]$, an identical outcome was observed. On the other hand, when the same reaction was performed with an aqueous solution of $[Et_4N][Cl]$ not containing NaOH, the reaction proceeded much more slowly and it needed about 3 h to reach completion.[25] A large amount of **4** was also produced together with **7**. The relative intensities of the bands of **7** and **4** during the reaction are essentially constant, indicating that they are both produced at the same time and **4** is not a decomposition product of **7**. Accordingly, the solution after the end of the reaction is stable for at least several hours and no decomposition of the products was observed (compare with the instability of **7** in the presence of NaOH).

The outcome of these last three reactions clearly shows that, at least when THF is the solvent, the reaction proceeds almost completely through the interaction of hydroxide anion, and not of chloride, with **1**.

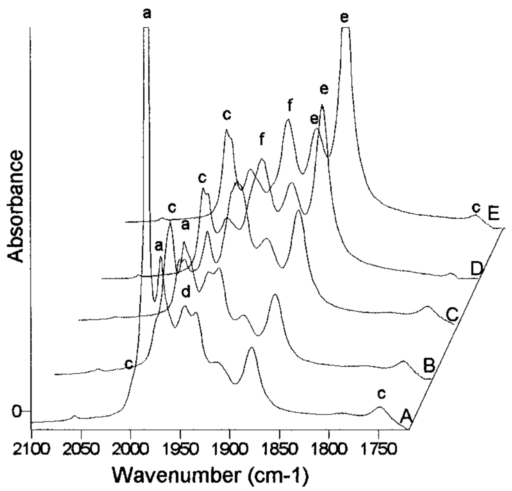


Figure 2. IR spectra in the absorbance mode of the evolution of the reaction between $Fe_3(CO)_{12}$ and NaOH in THF/H_2O: (A) after 10 min; (B) after 30 min; (C) after 1.5 h; (D) after 18 h; (E) after 3 days; (a) $[Fe_3(CO)_{11}]^{\bullet -}$; (b) $Fe(CO)_5$; (c) $[HFe_3(CO)_{11}]^-$; (d) $[Fe_4(CO)_{13}]^{2-}$; (e) $[HFe(CO)_4]^-$; (f) $[Fe_3(CO)_9(O)]^{2-}$.

We have already reported that halide anions promote the disproportionation of **1** to **7** and iron(II) halides, with **4** being the main byproduct.[19,20] The surprising finding is that **7** not only is stable in the presence of large amounts of water but can also be generated by the action of hydroxide anion. As already mentioned, formation of **8** during the base-promoted decomposition of **7** may be partially derived from trace amounts of oxygen. However, the fact that no **8** at all was observed when the reaction was performed in the absence of NaOH suggests that it is derived from a direct reaction of OH^- with **7**, leading to a disproportionation affording **8**, **3**, and iron oxides.

The previously described reactions indicate that **2** is not a product of the phase-transfer-catalyzed reaction of **1** with OH^-, not even in THF. However, to be sure that this product did not form and then decompose quickly, we subjected pure $[Et_4N]$**2** to standard reaction conditions (including a catalytic amount of $[Et_3NCH_2Ph][Cl]$). No reaction was observed, even when the concentration of the NaOH solution was increased to 5 M. Thus, under the standard reaction conditions, **2** has no tendency to be deprotonated to afford **5**, which may then be involved in further reactions.[26]

We can now wonder which is the mechanism by which **7** is formed from **1** and hydroxide anion. The formation of variable amounts of $Fe(CO)_5$ (**4**) in all reactions involving chloride as the active reagent,[19] but not in the reactions with OH^- ion,[27] indicates a different mechanism for the latter. We now recall that the first method to be reported for the synthesis of **7** involved the

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(24) (a) Whitmire, K.; Ross, J.; Cooper, C. B. III; Schriver, D. F. *Inorg. Synth.* **1982**, *21*, 66. (b) In almost all of the reactions run in THF, a variable-intensity absorption at 1969 cm^{-1} was observed in the IR spectrum of the solutions. However, THF has an absorption at this frequency and a perfect compensation of the solvent was not possible, due to the variable amount of water contained in the THF phase, depending on the identity and on the amounts of the species dissolved in both phases. We consider that this absorption, which could not be assigned to any known species, is at least mainly due to THF, but we cannot exclude that it underlines an absorption of an unidentified metal species.

(25) Upon addition of water, almost all of **1** precipitated out of the THF solution and then slowly dissolved again as the reaction proceeded.

(26) To test that the amount of **5** eventually formed is not just so low as to escape detection by IR but large enough to bring about reduction of nitrobenzene, we added this last compound to the $[Et_4N]$-**2**−THF/NaOH (5 M)−H_2O mixture. Only an 18% conversion was observed after stirring for 4 days, indicating that, if any **5** is in equilibrium with **2** under the reaction conditions, its amount must be extremely low and not significant for the reduction reaction.

(27) Although it may be argued that **4** may be formed and rapidly consumed, this does not appear to be the case, since the reaction of **4** with OH^- under these conditions has been shown to afford **3** as a product and no **3** was detected in the early stages of the reaction, although **1** had already been completely converted at this point.

synproportionation of **1** and **5**[28] in THF as solvent (eq 3). This reaction generates **7** without **4** being a byproduct.

$$\underset{\mathbf{1}}{Fe_3(CO)_{12}} + \underset{\mathbf{5}}{[Fe_3(CO)_{11}]^{2-}} \rightarrow \underset{\mathbf{7}}{2[Fe_3(CO)_{11}]^{\bullet -}} \quad (3)$$

Cluster **5** in turn is known to be formed by the action of methanolic KOH on **1**,[29] and this reaction, coupled with reaction 3, easily explains the selectivity observed.

Now that we have clarified at least in part the reactions occurring when **1** is subjected to biphasic conditions, we can turn back to the reactions also involving nitrobenzene.

An aqueous 1 M NaOH solution also containing $[Et_4N][Cl]$ was added to a THF solution of **1**, leading to the almost instantaneous formation of **7**. To this solution was added $PhNO_2$ (1:1 molar amount with respect to the starting **1**). The red-purple solution immediately became a brown suspension, and an IR spectrum of the organic layer showed that most of **7** was consumed in the first 2 min of reaction. All of the remaining **7** was then consumed in about 10 min. At this point the IR spectrum of the almost colorless organic solution showed only the presence of **4**, a very small amount of **8**, and some unreacted $PhNO_2$. Only a trace amount of **2** could be observed. The reaction proceeded then more slowly, and it took 2 h to consume all of the remaining $PhNO_2$. During this time, **4** was the almost exclusive organometallic product observable in solution, apart from a trace amount of **8**. Only after all of the $PhNO_2$ was consumed was an increasing amount of **3** also observable.

As we have shown that **5** is probably an intermediate in the generation of **7** from **1** and since we have previously shown that **5** reacts with nitroarenes at a faster rate than **7**,[19] it is possible that **5** is trapped by $PhNO_2$ before it can react with **1**. We also recall that the reaction of **5** with $PhNO_2$ generates **7** in the early stages of the reaction.[19,30] Several experiments were performed, even inverting the addition of $PhNO_2$ and $NaOH/H_2O$. Unambiguous evidence for an active role of **5** could not be obtained, but a mixture of **7** and **4** was immediately formed even when the order of addition of the reagents was reversed, confirming the active role of **7** in the reduction.

We have already mentioned that NaOH promotes the decomposition of **7** to afford **3** as the dominant product.[31] When $PhNO_2$ was added to the solution of **3** so obtained, a rapid reaction was observed, consuming part of **3** and producing aniline and **2**. This shows that **2** not only is not a reagent for the biphasic reduction of $PhNO_2$, but also, depending on the experimental conditions, may be a product!

Now that we have evidenced the role of **7** in the phase-tranfer-catalyzed reduction of nitroarenes by **1**, we can also understand the reason for an apparent anomaly. It has been reported that replacing the nitrogen atmosphere in the reaction with CO lowered the yield of aniline.[4] The effect was proposed to arise from the need for a vacant site during the conversion of **1** to **6** (which has, however, been shown by one of us not to be an intermediate[19]) or to the retardation by CO of a ligand dissociation necessary during the reaction.[4,7] Although we cannot exclude that this explanation plays a role,[32] we recall that CO induces an immediate disproportionation of **7** to **4** and **5**.[19] Since, in the presence of excess **1**, **5** transfers an electron to $Fe_3(CO)_{12}$ to generate 2 equiv of **7** (eq 3) that can further disproportionate, the generation of a small amount of **7** in the presence of **1** and under a CO atmosphere initiates an autocatalytic conversion of $Fe_3(CO)_{12}$ to $Fe(CO)_5$. This process has already been observed in the case of the reaction between **1** and chloride under a CO atmosphere.[19] Conversely, reaction of **1** with CO to yield **4** was reported to be catalyzed by an electron-transfer path and $[Fe_3(CO)_{11}]^{\bullet -}$ (**7**) was detected by EPR, along with $[Fe_3(CO)_{12}]^{\bullet -}$ and $[Fe_2(CO)_8]^{\bullet -}$ during the reaction.[33] Thus, in the phase-transfer-catalyzed reduction of nitroarenes, CO has the effect of transforming **1** into the less reactive **4**, thus accounting for the lower yields obtained.

$Fe_3(CO)_{12}$ in the Presence of Fluoride. It has been reported[5] that the reduction of nitroarenes by $Fe_3(CO)_{12}$ can also be promoted by fluoride, either in the form of $[Bu_4N][F]$ or as KF in the presence of a crown ether. Since at least some moisture was always present in the active solutions, it was proposed that the presence of the basic fluoride induced the formation of an equilibrium amount of hydroxide, which was considered to convert **1** into **2**. A red solid was also isolated from a stoichiometric reaction of **1** with KF and wet 18-crown-6, which was identified as **2** on the basis of its UV spectrum. However, it should be noted that the color of **2** in solution (red-purple) is virtually indistinguishable from that of **7** and, as a matter of fact, **5** and **9** also have very similar colors. Thus, UV-visible spectroscopy is not the best technique for identifying these products. At the time the paper on the use of fluoride was published, the report on the disproportionation reactions of **1** in the presence of halides[19,20] was still far in the future and the eventual formation of **7** was not taken into consideration. Since we now know that Cl^-, Br^-, I^-, NCO^-,[19,20] and even OH^- promote the formation of **7** from **1**, it appears unlikely that F^- yielded **2**. Indeed, when we reproduced the reaction[5] between **1** and $[Bu_4N][F]$, the immediate formation of **7** with high selectivity was observed, with only very small amounts of **9**, **4**, and **2** being formed (Figure 3).[34] Since the fluoride solution employed also contains some water,[34] it is impossible to say if the active anion is indeed fluoride or hydroxide. Addition of $PhNO_2$ to this

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[28] (a) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (b) Furuya, F. R.; Gladfelter, W. L. *J. Chem. Soc., Chem. Commun.* **1986**, 129.

[29] (a) Lo, F. Y.-K.; Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, 102, 7691. (b) Hodali, H. A.; Shriver, D. F. *Inorg. Synth.* **1980**, 20, 222. (c) The cluster $[Fe_3(CO)_{11}]^{2-}$ is stable towards synproportionation in methanol. This may partially be due to the very limited solubility of **1** in methanolic KOH, so that it dissolves only as it reacts with hydroxide and its concentration in solution is always very low.

[30] Belousov, Yu. A.; Kolosova, T. A. *Polyhedron* **1987**, *6*, 1959.

[31] When **4** is also present, as in the disproportionation of **1** promoted by halides, it is also quickly converted to **3**, in contrast to a slow reaction when pure **4** is used. Thus, it appears that decomposition of **7** generates some intermediate compound which is able to activate **4**.

[32] For example, an inhibiting effect of small amounts of CO on the reaction between **1** and chloride anion has been reported.[19] This last effect was ascribed to the reversibility of the formation of an intermediate proposed to be $[Fe_3(CO)_{11}(Cl)]^-$.

[33] Yang, S. L.; Li, C. S.; Cheng, C. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1872.

[34] In ref 5 it was reported that a "1 M $[Bu_4N][F]$ solution (Aldrich)" was used; the solvent was not specified. Since the only 1 M $[Bu_4N][F]$ solution sold by Aldrich is a THF solution, we used this in our experiments. This commercial solution is reported also to contain ~5% H_2O (that is, ~2.5 M H_2O).

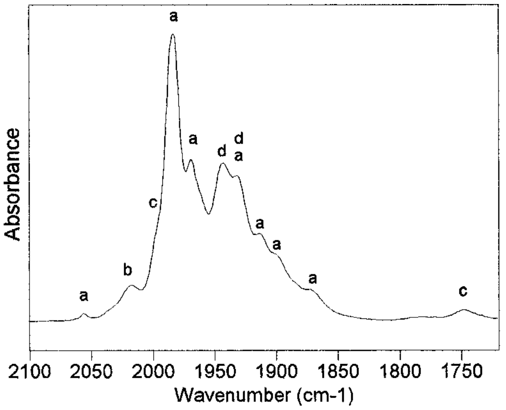

Figure 3. IR spectrum of the solution of the reaction between $Fe_3(CO)_{12}$ and a stoichiometric amount of $[Bu_4N][F]$ in THF. For the meaning of symbols, see the caption to Figure 2.

solution resulted in an immediate reaction. After 20 min the IR spectrum of the solution showed a set of bands (1992 w, 1926 vs, 1900 m, 1872 mw) attributable to $[Fe_3(CO)_9(\mu_3\text{-NPh})]^{2-}$ (**10**)[19] and trace amounts of **9**, **4**, and **2**. Gas-chromatographic analysis of the solution at this stage evidenced a complete conversion of $PhNO_2$, with a 57% selectivity in aniline.[35] An experiment has also been reported[5] employing a catalytic amount of fluoride. We have also reproduced this experiment, and the details are reported in the Experimental Section. We merely evidence here that in this case as well water has only the function of decomposing some intermediately formed nitrogen-containing complex (and eventually to increase the rate of formation of **7** by generating OH^-), not of generating **2**.

$Fe(CO)_5$ in the Presence of Hydroxide. Since $Fe(CO)_5$ (**4**) is formed during most reactions and is responsible for part of the reduction, we also examined its reactivity to some extent. This complex has already been reported to reduce nitroarenes under biphasic conditions.[2] In ref 2, the intriguing observation was made that the presence of the nitroarene was required to induce a reaction between **4** and OH^-, since no reaction was observed in its absence, but no explanation was proposed for this fact. We ran two parallel reactions between a toluene solution of **4** and an aqueous 1 M NaOH solution. To one of the solutions was also added $PhNO_2$. The concentration of **4** in the toluene solution had to be kept lower than the one in ref 2, in order to be able to follow the decrease of its concentration by IR. Our results indicate that the rate of disappearance of **4** in the solution also containing $PhNO_2$ is about twice as fast as that in the other solution, at least in the first hours, but a reaction (to produce **3** as the largely predominant product) is observed even in the absence of nitroarene. Although other pathways may also act in competition, our results suggest that some **3** is generated, which initiates the reduction of $PhNO_2$, also generating other species which may activate other molecules of **4**. Such chain mechanisms are quite likely in these systems[19,36] and the apparently higher difference of rates in the consumption of **4** when more concentrated solutions are used[2] supports this view.

In this paper we have investigated the identity of the active species in the biphasic reduction of nitroarenes by $Fe_3(CO)_{12}$ and $Fe(CO)_5$. Concerning the use of $Fe_3(CO)_{12}$, the traditional view involved the generation of $[HFe_3(CO)_{11}]^-$ and its following reaction with the nitroarene to generate $[HFe_3(CO)_9(\mu_3\text{-NPh})]^-$. In a previous paper,[19] we had already shown that this last imido cluster is not part of the reaction pathway and that radical processes were involved at several stages of the reaction. In this paper, we have shown that the reaction proceeds through several, and not simply one, active species. The radical anion $[Fe_3(CO)_{11}]^{\bullet-}$ is surely involved in the first part of the reaction, whereas $[HFe(CO)_4]^-$ is responsible for the reduction in the latest part, when the cluster compound is no longer present in solution. The dianion $[Fe_3(CO)_{11}]^{2-}$, which appears to be an intermediate in the formation of the radical monoanion, may also be responsible for the initial reduction of some nitroarene. Ironically, the only compound among those observed that *surely does not take part in the reaction* is $[HFe_3(CO)_{11}]^-$. At our actual level of knowledge, describing the mechanism of the reaction appears to be inappropriate and considering the mechanisms of the reactions is more adequate. The data collected clearly show that the selectivity in aniline observed is not the consequence of a particular reaction pathway largely prevailing over all the others but of different competing pathways, all of which eventually yield the same *organic* product.

The apparently widespread acceptance that the proposal of **2** as an active species in the reduction of nitroarenes has met appears to be influenced by the well-known reducing ability of classical hydridic reagents such as $[Na][BH_4]$ and $[Li][AlH_4]$. However, the importance of the hydridic character of a reductant should not be taken for granted in the field of the reduction reactions of nitroarenes. Indeed, the first step of the activation of these substrates has been shown to involve an electron transfer from the complex to the nitro compound in all of the cases in which this possibility has been investigated.[19,30,37] Thus, a reagent with a high tendency to transfer an electron should be looked for, rather than one capable of transferring an H^- ion. Viewed in this context, the much higher reducing activity of $[Fe_3(CO)_{11}]^{2-}$ and $[Fe_3(CO)_{11}]^{\bullet-}$

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[35] The lower selectivity with respect to that reported in ref 5 is likely to be due to the chromatographic workup (in the air) performed in this last case, which probably decomposes **10**, affording aniline. We recall that decomposition of $[HFe_3(CO)_9(\mu_3\text{-NPh})]^-$ *in the presence of oxidants* can afford aniline, although no reaction is observed in their absence.[19]

[36] In one experiment, we treated a mixture of **7** and **4**, with a strong prevalence of **4**, derived from the reaction of **1** with $[Et_4N][Cl]$ in THF, with 1 M NaOH. The usual strong decrease of intensity of the bands of **7** in the first few minutes was accompanied by the complete disappearance of the bands of **4** and by the formation of **3**. In the absence of **7**, reaction of **4** with OH^- under these conditions takes several hours. Thus, at least in this case it is clear that some products deriving from the decomposition of **7** activate **4** in a chain reaction.

[37] (a) Skoog, S. J.; Campbell, J. P.; Gladfelter, W. L. *Organometallics* **1994**, *13*, 4137. (b) Sherlock, S. J.; Boyd, D. C.; Moasser, B.; Gladfelter, W. L. *Inorg. Chem.* **1991**, *30*, 3626. (c) Kunin, A. G.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2739. (d) Ragaini, F.; Cenini, S.; Demartin, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1467. (e) Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1994**, *13*, 1178. (f) Berman, R. S.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 248. (g) Liu, P. H.; Liao, H.-Y.; Cheng, C.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 2441. (h) An electron transfer was proposed to be involved even in the case of the reactions of **4**, but there was no experimental evidence.[2]

toward nitroarenes with respect to $[HFe_3(CO)_{11}]^-$ appears not to be surprising.[38]

Experimental Section

General Procedure. Unless otherwise specified, all reactions and manipulations were performed under a prepurified N_2 atmosphere using standard Schlenk apparatus, cannula techniques, and magnetic stirring. Toluene and THF were distilled from Na/benzophenone before use to eliminate oxygen impurities. Water was degassed by three freeze−pump−thaw cycles. Compounds **1**,[39] $[Et_4N]$**2**,[10] [PPN]**5**,[29b] [PPN]**9**,[24a] [PPN]**7**,[19] $[Me_3NCH_2Ph]$**8**,[23] and $[Et_4N]$**3**[40] were synthesized by methods reported in the literature or by slight modifications thereof. $Fe(CO)_5$ was distilled *in vacuo* prior to use. Nitrobenzene was purified by shaking with 10% H_2SO_4, washing with water, and drying with Na_2SO_4, followed by distillation under nitrogen and storage under an inert atmosphere. All other compounds were commercial products and were used as received Gas chromatographic analyses were performed on a Perkin-Elmer 8420 capillary gas chromatograph equipped with a PSS 255 column. Ri values (Ri = response factor, relative to naphthalene as an internal standard) were determined by the use of solutions of known concentrations of the compounds. IR and GC monitoring of the reactions were performed by sampling the organic layer only, but, at the end of the reactions, extraction of the aqueous phase with CH_2Cl_2 (2 × 10 mL) was also applied in order to recover all of the organic products. When appropriate, hexane was added to the withdrawn samples before injection in the gas chromatograph, in order to precipitate the ionic metal complexes.

Reagents Amounts. The amounts of the reagents were chosen as to maintain the same concentrations reported in refs 2 and 8. Unless otherwise stated, all reactions were performed using **1** (125 mg, 0.25 mmol) or $[Et_4N]$**2** (152 mg, 0.25 mmol) dissolved (or suspended) in 5 mL of solvent (toluene or THF). When required, the stoichiometric amount of $[Et_4N][Cl]$ (41.4 mg, 0.25 mmol) or a catalytic amount of $[Et_3NCH_2Ph][Cl]$ (11 mg, 0.05 mmol) were also added to the aqueous solution before mixing with the organic one. Naphthalene (50 mg) was used as a GC internal standard and was added to the organic solution before the addition of $PhNO_2$. The same amount of nitrobenzene (30.8 mg, 25.6 μL, 0.25 mmol) was always added when required, unless otherwise stated. A 1 M NaOH solution in water (5 mL) was always used as the aqueous phase, except for the experiment on the stability of $[Et_4N]$**2**, in which additional NaOH was added after 2 h so that the total NaOH concentration increased to 5 M, and the one in which no NaOH but only $[Et_4N][Cl]$ in water was added. Several of the experiments performed have already been discussed in the text and will not be further described here.

Synthesis and Decomposition of $[Fe_3(CO)_{11}]^{\bullet-}$ (7) in THF/1 M NaOH-H_2O. In a Schlenk tube, **1** was dissolved in THF and the 1 M NaOH solution, also containing $[Et_4N][Cl]$, was added. The dark green color immediately changed to red-purple, and the IR spectrum of the THF phase showed bands at 2057 (vw), 2019 (vw, sh), 1982 (vs), 1969 (m), 1960 (m, sh), 1933 (mw), and 1916 (w, sh) cm^{-1} due to **7**. A very weak absorption was observed at 1879 cm^{-1}, indicating the presence of a trace amount of $[HFe(CO)_4]^-$ (**3**). The intensity of the absorptions due to **7** then rapidly decreased over a few minutes, although complete disappearance took 1.5 h. At the same time it was possible to observe an increase of new bands at 1937 (**8**), 1945 (**9**), and 1910 and 1878 (**3**) cm^{-1} and very weak absorptions at 1998, 1974, and 1747 (**2**) cm^{-1}. Other weak bands were overlapped and not resolved. The attribution of the band at 1945 cm^{-1} to **9** was confirmed by a very short (a few seconds) exposure of part of the solution to the air, followed by an IR spectrum. The bands of all other compounds completely disappeared, and the single absorption, with a characteristic asymmetric shape, of **9** was observable as the only band, except for a small amount of **2** being also detectable. After 2 h the highest absorption was that for **8**, followed by that for **3**, but the last increased upon stirring overnight, accompanied by an increase of the bands of **2** and a decrease of all of the other bands, which, in the case of **8**, is at least in part due to precipitation of some of the compound. An orange residue was also present, which was filtered off through a frit, washed with THF, and finally treated with CH_3CN. The CH_3CN solution showed bands at 2000 (vw), 1931 (vs), 1901 (m), and 1881 (w) cm^{-1} assigned to **8** by comparison with an authentic sample. Only two weak shoulders were observed at 1974 and 1955 cm^{-1} which do not belong to the spectrum of **8**. An insoluble residue still remained, which showed no IR bands in the carbonyl region and was identified as α-FeOOH by X-ray powder diffraction. The same reaction was repeated in the absence of $[Et_4N][Cl]$. The same general outcome was observed, but **8** did not precipitate in the absence of the ammonium salt. After 5.5 h the main species in solution was **3**, together with a discrete amount of **8** and a small amount of **2**. To this solution were added naphthalene and $PhNO_2$. After 40 min GC analysis of the solution showed the complete disappearance of $PhNO_2$ and the formation of aniline (80% yield). The IR spectrum of the solution at this stage showed a sharp decrease in intensity of the bands of **3** and an increase of the ones due to **2**.

Confirmation of the Formation of 7. Pure [PPN]**7**[19] (100 mg, 0.1 mmol) was dissolved in THF (5 mL), and 1 M NaOH (5 mL) was added. The reaction was followed by IR. Immediately after mixing the same bands were observed as in the previously described reaction, including a small amount of **3**. The evolution of the reaction then exactly paralleled that starting from **1**.

Reaction of $Fe_3(CO)_{12}$ (1) and $PhNO_2$ with a Stoichiometric Amount of $[Bu_4N][F]$. In a Schlenk tube, **1** (420 mg, 0.835 mmol) was dissolved in THF (5 mL) and 1 mL of a 1 M solution of $[Bu_4N][F]$ in THF (Aldrich) was added. In order to avoid contact with air of the fluoride solution, its bottle was always opened while it was kept inside a Schlenk tube with a wide mouth and while a strong nitrogen flush was maintained. The reaction was immediate, and **7** was the largely predominant product, although small amounts of **4**, **9**, **8**, and **2** were also detected. To this solution were added naphthalene and $PhNO_2$ (142.3 μL, 170.8 mg, 1.39 mmol). The outcome of the reaction is described in the Results and Discussion.

Reaction of $Fe_3(CO)_{12}$ (1) and $PhNO_2$ with a Catalytic Amount of $[Bu_4N][F]$. In a Schlenk tube, **1** (375 mg, 0.743 mmol) was dissolved in THF (5 mL) and naphthalene, $PhNO_2$ (127.1 μL, 152.5 mg, 1.24 mmol), and 100 μL of a 1 M solution of $[Bu_4N][F]$ in THF (Aldrich) were added in this order (see also the preceding reaction; in the original procedure,[5] no solvent was mentioned, but it is clear, from a comparison with the other reactions reported, that THF was employed, otherwise the reaction mixture would be solid, since solid nitrotoluene was used as the organic reagent and the amount of THF coming from the fluoride solution is enormously inferior to that necessary to dissolve the reactants). After 20 min, the IR spectrum of the pale red solution showed the presence of **4** as the only detectable product. GC analysis showed that 64.3% of the starting $PhNO_2$ had been converted, with a 25.5% selectivity in aniline. Only at this point, as required by the procedure,[5] was water (51 μL, 2.8 mmol) added and the

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[38] (a) As previously mentioned, **4** can also be activated by basic alumina[6,11] and the formation of **2** under these conditions appears to be well documented.[38b] Although small amounts of **7** may also be formed under these conditions, the role of **2** in these reactions appears to be indisputable. The higher activity of **2** when supported than when dissolved in solution can be ascribed to strong interactions with the support. In this context, it is useful to recall that the IR spectrum of **2**/Al_2O_3 is completely different from that of the same complex in solution.[38b] (b) Hugues, F.; Smith, A. K.; Ben Taarit, Y.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 68.

[39] McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1965**, *8*, 181.

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solution stirred overnight. GC analysis of the solution at the end of the reaction showed complete conversion of $PhNO_2$, with an 80.8% selectivity in aniline. The amount of aniline formed overnight is too large to come only from the $PhNO_2$ that had not been converted during the first 20 min and must be partially derived from decomposition by water of some metal-containing compound formed in this period. The rest of the nitrobenzene must have been reduced overnight by the $Fe(CO)_5$ formed in the initial phase of the reaction.

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Supporting Information Available: Infrared spectra of several reaction mixtures and of some pure reference compounds (2 pages). Ordering information is given on any current masthead page.

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