

Coordination chemistry of mononuclear iron carbonyl complexes

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Contents

Abstract	331
1. Introduction	332
2. Coordination chemistry from $M^+[HFe(CO)_4]^-$ complexes	333
2.1. Results	333
2.1.1. Reaction with phosphines	333
2.1.2. Reaction with phosphites	336
2.1.3. Reaction with phosphinites	338
2.1.4. Reaction with phosphinite-ammonium ligands	339
2.1.5. Reaction with aminophosphines	340
2.2. Mechanistic considerations	342
3. Coordination chemistry from $RCO(Li)Fe(CO)_4$	346
3.1. α -Iminoacyl ligand in carbonylmetallates	346
3.2. Tandem acylation-complexation of chlorophosphines	347
4. Conclusion	349
Acknowledgments	349
References	349

Abstract

This review is devoted to recent advances in mononuclear iron carbonyl coordination chemistry starting from $M^+[EFe(CO)_4]^-$ complexes ($E=H$, RCO) easily obtained from $Fe(CO)_5$.

$E=H$. The reaction of $K^+[HFe(CO)_4]^-$ with phosphines, phosphites and phosphinites (abbreviated “P”) allows selective syntheses for a large range of (phosphane)iron carbonyl

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complexes such as $\text{Fe}(\text{CO})_3\text{P}_2$, $\text{Fe}(\text{CO})_2\text{P}_3$, $\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$, $\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$ and $\text{K}^+[\text{HFe}(\text{CO})_2\text{P}_2]^-$. In the special case of the new optically active phosphinite–ammonium ligands $\text{P}^-(*)-\text{N}^+$ named “ephosium” and “valphosium”, optically active zwitterionic complexes $[\text{HFe}(\text{CO})_3\text{P}]^--(*)-\text{N}^+$ have been obtained, the structures of which have been studied both in the solid state and in solution. The above reactions have been shown to involve first a CO substitution, generating $[\text{HFe}(\text{CO})_3\text{P}]^-$ species which then react further, the final product depending on both the nature of the solvent (protic or not) and the steric and electronic properties of the phosphane. In contrast, reaction with tri(amino)phosphines proceeds by substitution at the phosphorus atom, affording the Collman dianion $[\text{Fe}(\text{CO})_4]^{2-}$ and $[(\text{R}_2\text{N})_2\text{PH}]\text{Fe}(\text{CO})_4$ complexes the reactivities of which with KH have been studied.

$E=\text{RCO}$. The reaction of lithium aldimines such as $[t\text{-BuN}=\text{C}(t\text{-Bu})]\text{Li}$ with $\text{Fe}(\text{CO})_5$ generates lithium (α -iminoacyl)tetracarbonylferrates, which are imino-protected equivalents of the rare $[(\text{CO})_4\text{Fe}-\text{CO}-\text{CO}-\text{Z}]^-$ sequence. Alkylation with Me_3OBF_4 yields the corresponding α,β -unsaturated Fischer carbene complexes. The reaction of $\text{RCO}(\text{Li})\text{Fe}(\text{CO})_4$ ($\text{R}=\text{alkyl}$) with PPh_2Cl (or PPhCl_2) cleanly proceeds by a tandem acylation–complexation to afford the complexed acylphosphines $[\text{RCOPPh}_2]\text{Fe}(\text{CO})_4$ (or $[\text{RCOPPhCl}]\text{Fe}(\text{CO})_4$) in good yield. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron pentacarbonyl; Hydridocarbonylferrates; Acylcarbonylferrates; Phosphanes; Chiral phosphinite–ammonium ligands; Zwitterionic chiral hydridocarbonylferrates; Ligand substitution processes; Acylphosphine complexes

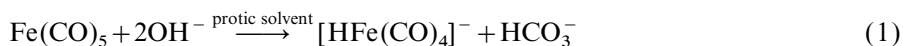
1. Introduction

Since its discovery at the end of the 19th century [1,2], iron pentacarbonyl has played a central role in the field of transition metal carbonyl chemistry [3–6]. Its early use as additive for fuels and as a source of very pure iron for the manufacture of magnets made this compound commercially available in large amounts, thus encouraging chemists to study its possible applications in chemical synthesis [4–6].

It was soon recognized that $\text{Fe}(\text{CO})_5$, which is insoluble in water, reacts with aqueous alkali metal hydroxides to yield solutions which exhibit reducing properties. It was postulated early that these solutions contained mixtures of dianionic and hydridoanionic iron carbonyl complexes. The most famous application of this property is the so-called “Reppe-modification of the hydroformylation reaction” which has been used for the industrial production of butanols [7].

Hydridocarbonylferrates are weak acids of the general formula $[\text{HFe}_n(\text{CO})_{[n(11-n)/2]-1}]^-$ ($n=1-4$). Their conjugated bases, the dianionic $[\text{Fe}_n(\text{CO})_{[n(11-n)/2]-1}]^{2-}$ complexes are also known [3]. The most popular of these dianionic carbonylferrates is $\text{Na}_2\text{Fe}(\text{CO})_4$, commercially available as the dioxane complex (“Collman reagent”). Its use for the stoichiometric carbonylation of reactive alkyl halides has met with large success [8] and evidence exists for the involvement of $[\text{Fe}(\text{CO})_4]^{2-}$ in the catalytic carbonylation of benzyl halides [9].

We were particularly interested in studying the properties of the simplest hydridocarbonylferrates, $\text{M}^+[\text{HFe}(\text{CO})_4]^-$, easily prepared according to (Eq. (1)).



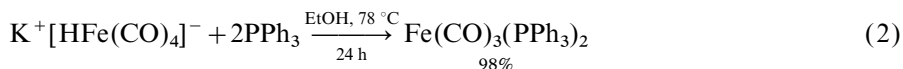
The main motivation was that $M^+[HFe(CO)_4]^-$ complexes appeared, *a priori*, as versatile reagents. Firstly, they exhibit a hydrogen–metal bond and are therefore expected to react with unsaturated substrates. Secondly, the negative charge makes them potential nucleophiles or electron-transfer agents. Finally, the carbonyl ligands make them potential carbonylation reagents or catalysts. The main applications of hydridotetracarbonylferrates in organic synthesis and catalysis were reviewed in 1990 [10] and some other properties have been recently reported from this laboratory [11–16].

This review is devoted to the coordination chemistry of mononuclear iron carbonyl complexes performed in this laboratory during the last ten years; it will be shown that $K^+[HFe(CO)_4]^-$, and more generally complexes of the type $M^+[EFe(CO)_4]^-$ ($E=H, RCO$ or $ArCO$), are versatile precursors for a rich coordination chemistry in the field of mononuclear iron carbonyl complexes.

2. Coordination chemistry from $M^+[HFe(CO)_4]^-$ complexes

2.1. Results

During the course of studies on the reactivity of $M^+[HFe(CO)_4]^-$ for the carbonylation of ethyl acrylate [17] and norbornene [18], it was incidentally observed that triphenylphosphine reacts with $K^+[HFe(CO)_4]^-$ in ethanol to form the disubstituted neutral complex $Fe(CO)_3(PPh_3)_2$. Further studies showed that this reaction is the best route to selectively obtain $Fe(CO)_3(PPh_3)_2$ in high yield (Eq. (2)) [19].



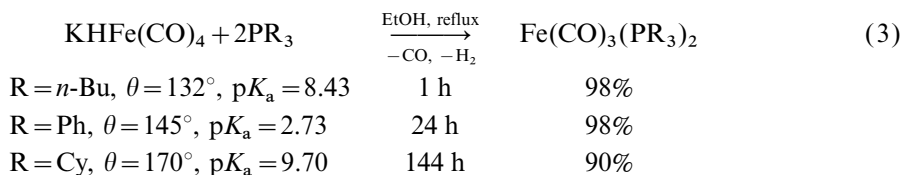
This result was somewhat unexpected since Collman *et al.* previously reported that $Na^+[HFe(CO)_4]^-$ does not react with PPh_3 in THF at room temperature [20]. Similarly, Siegl reported that $P(CH_2CH_2CN)_3$ does not react with $[PPN]^+[HFe(CO)_4]^-$ in refluxing THF [21]. It was thus decided to investigate the reaction of $K^+[HFe(CO)_4]^-$ with various phosphines and phosphites in a systematic manner, both in protic and aprotic solvents. The study was further extended to phosphinites, phosphinite–ammoniums and aminophosphines and general reaction mechanisms for CO substitution processes were proposed.

In the following sections, reactions involving $K^+[HFe(CO)_4]^-$ in *protic media* were conducted in the presence of $KHCO_3$ (see Eq. (1)), whereas reactions conducted in *aprotic solvents* (THF in general) refer to reactions carried out in the absence of $KHCO_3$.

2.1.1. Reaction with phosphines

2.1.1.1. Reactions in protic media. According to our starting observation, phosphines exhibiting various steric and electronic properties do react with

$K^+[HFe(CO)_4]^-$ in refluxing ethanol to afford *selectively* the corresponding $Fe(CO)_3(PR_3)_2$ complexes (Eq. (3)) [19,22].

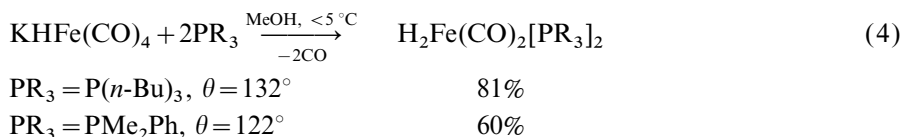


These complexes exhibit a TBP geometry with apical *trans* phosphines, as previously established by IR data [23] and confirmed by multinuclear NMR analysis [22].

Control experiments indicated that the monosubstituted derivatives $Fe(CO)_4(PR_3)$, prepared independently, do not react with PR_3 under the conditions of Eq. (3), and thus are not intermediates in the formation of the disubstituted derivatives $Fe(CO)_3(PR_3)_2$ [22].

As may be seen, the necessary reaction time (Eq. (3)) seems to be related to the Tolman cone angle (θ) of the phosphines [24] rather than to their pK_a values [25].

As a matter of fact, whereas PPh_3 ($\theta = 145^\circ$) and PCy_3 ($\theta = 170^\circ$) do not react with $K^+[HFe(CO)_4]^-$ in ethanol at room temperature, $P(n\text{-Bu})_3$ ($\theta = 132^\circ$) does react (even below $5^\circ C$) but does not lead to the corresponding $Fe(CO)_3[P(n\text{-Bu})_3]_2$ derivative. Under these conditions, the reaction proceeds with evolution of 2 equiv. of CO, leading to the dihydride $H_2Fe(CO)_2[P(n\text{-Bu})_3]_2$ (Eq. (4)). Similarly, use of PMe_2Ph ($\theta = 122^\circ$) leads to the dihydride $H_2Fe(CO)_2[PMe_2Ph]_2$ [26].



Spectral data are in agreement with a *cis*-dihydridotrans-bis(phosphine)dicarbonyliron geometry (Fig. 1).

The stability of these dihydrides appears to be the main factor that determines whether the reaction of $K^+[HFe(CO)_4]^-$ with a phosphine leads to $Fe(CO)_3(PR_3)_2$ or $H_2Fe(CO)_2(PR_3)_2$ derivatives. Indeed, the final product of these reactions is dramatically determined by the reaction conditions, as evidenced in the case of $P(n\text{-Bu})_3$ (Scheme 1).

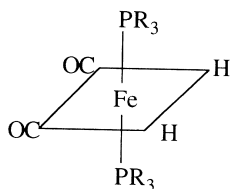
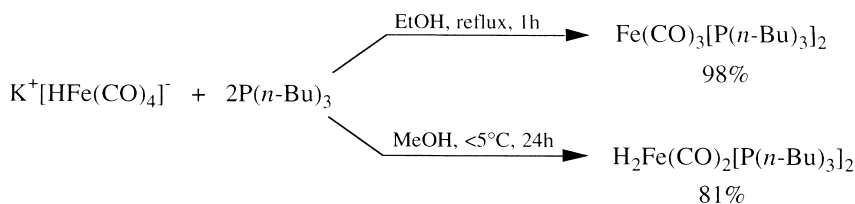
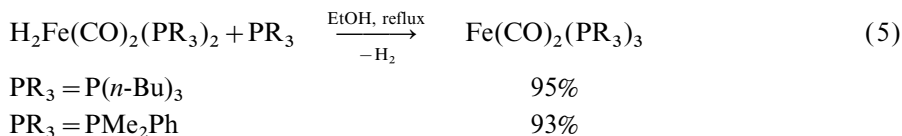


Fig. 1. Geometry of $H_2Fe(CO)_2(PR_3)_2$ complexes.

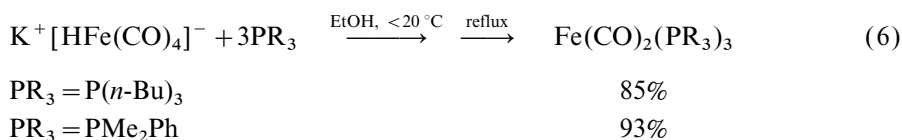
Scheme 1. Reaction of $\text{P}(n\text{-Bu})_3$ with KHFe(CO)_4 in protic media

Only a very few complexes of the type $\text{H}_2\text{Fe(CO)}_2(\text{PR}_3)_2$ have been reported previously [27] and the only one structurally-characterized is $\text{H}_2\text{Fe(CO)}_2[\text{dppe}]$ (dppe = 1,2-bis (diphenylphosphino)ethane), which obviously exhibits a *cis* geometry of the phosphorus atoms [28]. The now easy access to these complexes according to Eq. (4) has been confirmed recently [29].

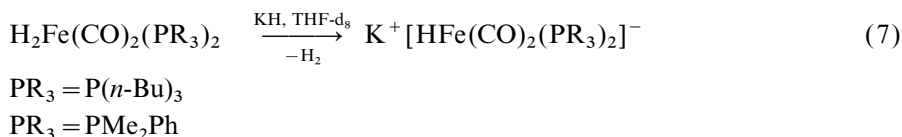
The dihydrides $\text{H}_2\text{Fe(CO)}_2(\text{PR}_3)_2$ react with added phosphine to afford quantitatively the trisubstituted complexes $\text{Fe(CO)}_2(\text{PR}_3)_3$ (Eq. (5)).



The trisubstituted complexes can also be obtained directly from $\text{K}^+[\text{HFe(CO)}_4]^-$ and 3 equiv. of PR_3 by a one-pot, two-step reaction sequence (Eq. (6)) [22].



Deprotonation of the dihydrides with KH allowed to generate, for the first time, the corresponding disubstituted hydridodicarbonylferrates (Eq. (7)).



In both cases, ^{31}P and ^{13}C NMR data suggest a *cis* H–P arrangement of the two equivalent phosphorus atoms and the equivalence of the two carbonyl ligands [22].

2.1.1.2. Reaction in aprotic media. $\text{K}^+[\text{HFe(CO)}_4]^-$ does not react significantly with PPh_3 in THF at room temperature, in agreement with the observation of Collman about $\text{Na}^+[\text{HFe(CO)}_4]^-$ [20]. However, in refluxing THF, a gas evolution

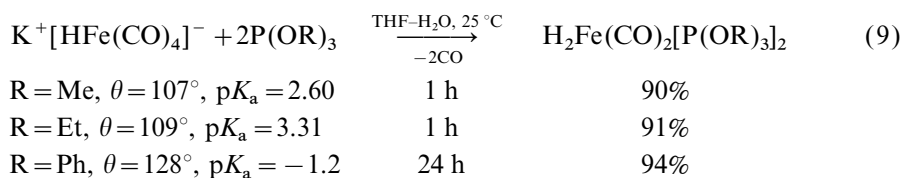
is observed with precipitation of the THF-insoluble $\text{K}_2\text{Fe}(\text{CO})_4$ (Eq. (8)).



This reaction also occurs with $\text{P}(n\text{-Bu})_3$ and constitutes a very convenient preparation (developed on a 10 g scale) of $\text{K}_2\text{Fe}(\text{CO})_4$, a non-pyrophoric analogue of the Collman reagent. In DMAC, or in THF–DMAC mixtures, $\text{K}_2\text{Fe}(\text{CO})_4$ exhibits the same reactivity as $\text{Na}_2\text{Fe}(\text{CO})_4$ in THF for the carbonylation of reactive alkyl halides [30].

2.1.2. Reaction with phosphites

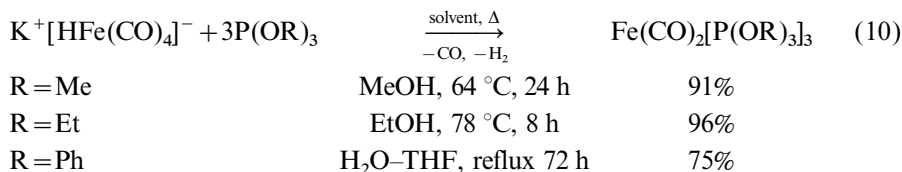
2.1.2.1. Reactions in protic media. The reaction of 2 equiv. of common phosphites $\text{P}(\text{OR})_3$ ($\text{R} = \text{Me, Et, Ph}$) with $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ in THF– H_2O mixtures at 25°C affords the dihydrides $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OR})_3]_2$ in 90–94% (Eq. (9)) with evolution of 2 equiv. of CO [31].



Spectral data are in agreement with an octahedral geometry with phosphites in a *trans* position as in the case of the dihydrides $\text{H}_2\text{Fe}(\text{CO})_2(\text{PR}_3)_2$ (see Fig. 1).

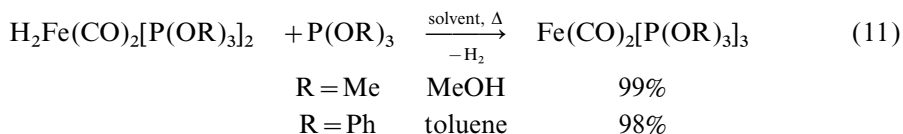
With phosphites exhibiting larger Tolman cone angles, such as tris(*o*-phenylphenyl) phosphite ($\theta = 152^\circ$), no reaction is observed at 25°C , thus suggesting that, as for phosphines, the reaction is mainly governed by the steric bulk of the phosphite. At 70°C , the reaction with tris(*o*-phenylphenyl) phosphite proceeds with evolution of a 1/1 mixture of CO and H_2 gas to afford the *trans* disubstituted complex $\text{Fe}(\text{CO})_3[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{Ph})_3]_2$ in 94% yield [31].

When the reaction of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ with 2 equiv. of $\text{P}(\text{OMe})_3$ is conducted at 70°C , the reaction yields a mixture of the dihydride formed by Eq. (9) and of the trisubstituted $\text{Fe}(\text{CO})_2[\text{P}(\text{OMe})_3]_3$ complexes. By using 3 equiv. of phosphite, the reaction selectively affords the trisubstituted complex in high yield (Eq. (10)) [31]. Previously reported preparation of this complex involved difficult separations of multistep-sequences from commercially available materials [32–34]. This new route was thus extended to some other phosphites and proved to be very convenient (Eq. (10)) [31].

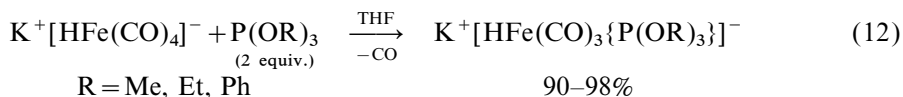


On the basis of the previously reported X-ray structure of $\text{Fe}(\text{CO})_2[\text{P}(\text{OMe})_3]_3$ [34] these complexes are believed to exhibit a TBP geometry with two apical and one equatorial phosphite ligands. In solution, however, $\text{Fe}(\text{CO})_2[\text{P}(\text{OMe})_3]_3$ is fluxional, at least down to 183 K, as previously observed for $\text{Fe}(\text{CO})_2(\text{PMe}_3)_3$ [35].

Control experiments showed that the trisubstituted complexes are formed by reaction of phosphites with the intermediate dihydrides $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OR})_3]_2$ (Eq. (11)).



2.1.2.2. Reaction in aprotic media. $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ readily reacts with phosphites $\text{P}(\text{OR})_3$ (R = Me, Et, Ph) in THF at room temperature to afford the monosubstituted hydridocarbonylferrates $\text{K}^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OR})_3\}]^-$ (Eq. (12)) [31].



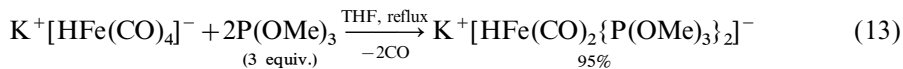
$[\text{PPN}]^+[\text{HFe}(\text{CO})_4]^-$ does not react with the above phosphites, even in refluxing THF, thus confirming the dramatic role of the counterion. In contrast, this reaction proceeds very well in CH_2Cl_2 to afford the hydridocarbonylferrates $[\text{PPN}]^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OR})_3\}]^-$ (R = Me, Et, Ph) in more than 95% yield [31].

The synthesis of $[\text{HFe}(\text{CO})_3\{\text{P}(\text{OR})_3\}]^-$ complexes was first reported by Ellis *et al.* by reaction of $\text{Fe}(\text{CO})_4[\text{P}(\text{OR})_3]$ with $[\text{Et}_4\text{N}]^+\text{OH}^-$ [36,37] and has been further developed by Darensbourg *et al.* [38,39]. However, since the preparation of $\text{Fe}(\text{CO})_4[\text{P}(\text{OR})_3]$ derivatives is often time-consuming, Eq. (12) is a more convenient access to $[\text{HFe}(\text{CO})_3\{\text{P}(\text{OR})_3\}]^-$ derivatives. The complex $\text{K}^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OMe})_3\}]^-$ has been shown to be more reactive than $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ for the selective monoreduction of α -dicarbonyl compounds [13].

The geometry of $\text{M}^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OR})_3\}]^-$ complexes has been thoroughly studied by Darensbourg *et al.* For R = Me and Et, they have been shown to exist in a *trans* configuration of H and $\text{P}(\text{OR})_3$ (TBP geometry). These *trans* complexes exhibit a special behaviour in solution since their NMR parameters, particularly the $^2J_{\text{PH}}$ coupling constant, show a great dependence on both the temperature and the polarity of the solvent [40]. Curiously, for R = Ph the phosphorus ligand is in the equatorial plane, *cis* to the hydride in the crystalline state (X-ray structure) [41] and the complex does not experience the ^1H NMR phenomena described above in solution. In the latter case, the *trans* isomer has never been observed.

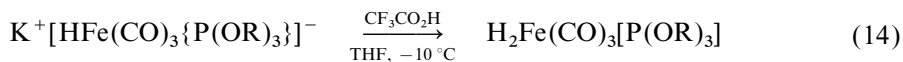
Interestingly, reacting the phosphite which exhibits the smallest Tolman cone angle, $\text{P}(\text{OMe})_3$, with $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ in refluxing THF provided the first example

of a double carbonyl ligand substitution on a carbonylmethylate (Eq. (13)) [31].



This complex can also be obtained by deprotonation of the dihydride $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$ with KH [31]. NMR data are in agreement with a TBP or a distorted square planar geometry in solution. The $J_{\text{P-H}}$ coupling constant of the hydride resonance (triplet) is invariant with temperature (253–307 K), in contrast to what has been observed for the monosubstituted derivatives *trans* $\text{M}^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OMe})_3\}]^-$ ($\text{M}^+ = \text{Na}^+, (n\text{-Bu})_4\text{N}^+, \text{PPN}^+$) [40].

The now easily accessible $\text{K}^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OR})_3\}]^-$ derivatives have been used for the preparation of the corresponding neutral dihydrides by protonation with trifluoroacetic acid (Eq. (14)) [31]. These monosubstituted dihydrides could not be obtained directly from $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ and $\text{P}(\text{OR})_3$ in protic solvents.

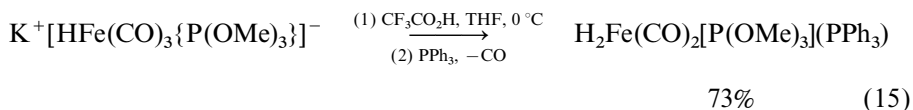


$\text{R} = \text{Me, Et, Ph}$

>95%

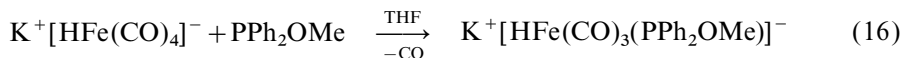
This two-step synthesis from $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ is the most efficient method for the preparation of these complexes which are stable monosubstituted derivatives of the unstable $\text{H}_2\text{Fe}(\text{CO})_4$ [42]. The spectroscopic data of $\text{H}_2\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]$ have been previously interpreted as a “ $\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]$ ” tetrahedron capped with the two hydride ligands [34].

The monosubstituted dihydrides $\text{H}_2\text{Fe}(\text{CO})_3[\text{P}(\text{OR})_3]$ readily react with the corresponding phosphite to give the disubstituted dihydrides $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OR})_3]_2$ with CO evolution. No hydrogen evolution is detected, confirming a dihydride character of the complex (vs a dihydrogen character). Adding a different phosphite generally leads to a mixture of three complexes resulting from phosphite ligands redistribution [31]. Adding a phosphine results in a slow reaction affording the mixed complex as the major product, isolated in the case of triphenylphosphine (Eq. (15)).



2.1.3. Reaction with phosphinites

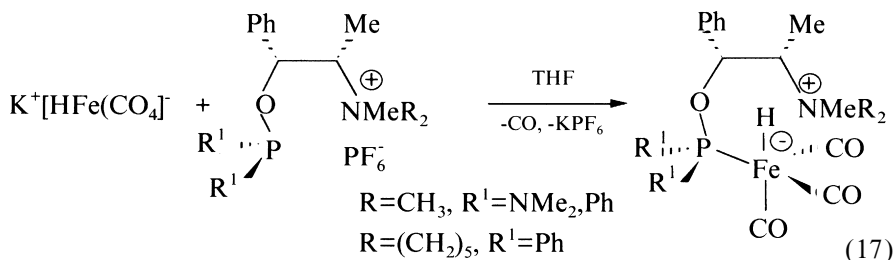
The basicity of phosphinites is intermediate between those of phosphines and phosphites. The reaction of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ with PPh_2OMe ($\theta = 132^\circ$, $\text{p}K_{\text{a}} = 2.69$) in THF leads to the monosubstituted hydridocarbonylferrate $\text{K}^+[\text{HFe}(\text{CO})_3(\text{PPh}_2\text{OMe})]^-$ (Eq. (16)) [43], as in the case of phosphites.



85%

2.1.4. Reaction with phosphinite–ammonium ligands

The reactivity of $\text{K}^+[\text{HFe}(\text{CO})_3\{\text{P}(\text{OMe})_3\}]^-$ for the selective reduction of α -dicarbonyl compounds [13] opens the way to possible enantioselective reductions by introducing a chirality centre on the phosphorus ligand. Beyond this possibility, a new concept has been introduced which relies on the zwitterionic control of the chirality transfer [44]. Zwitterionic, chiral non-racemic monosubstituted hydridocarbonylferrates have been synthesized from “ephosiums”, which are new phosphinite–ammonium ligands derived from the ephedrine skeleton (Eq. (17)).



For $\text{R}=\text{Me}$ and $\text{R}^1=\text{Ph}$, the X-ray structure (Fig. 2) indicates an unexpected *cis* H to P arrangement in a TBP geometry with the phosphorus atom in the equatorial plane. Such a *cis* geometry has been observed only for $[\text{PPN}]^+$

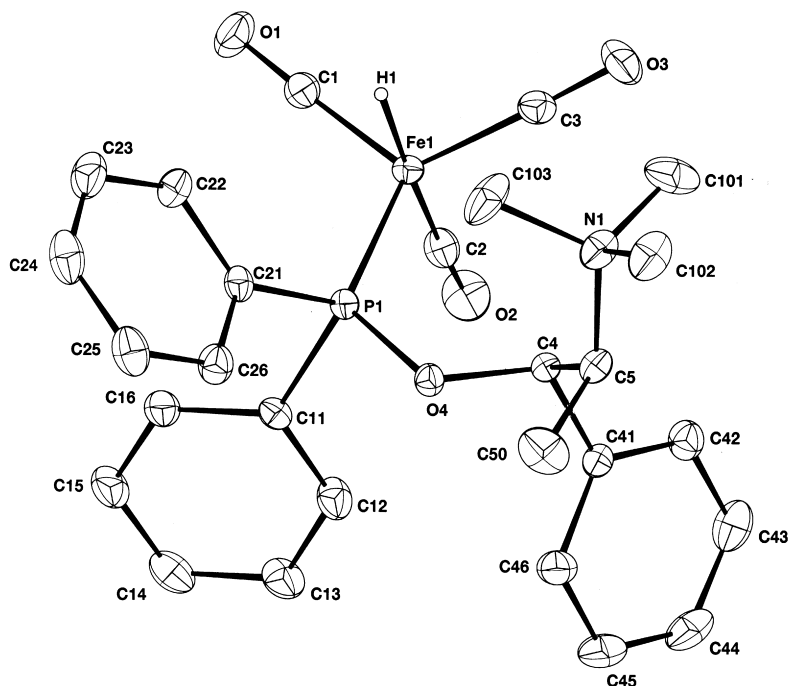
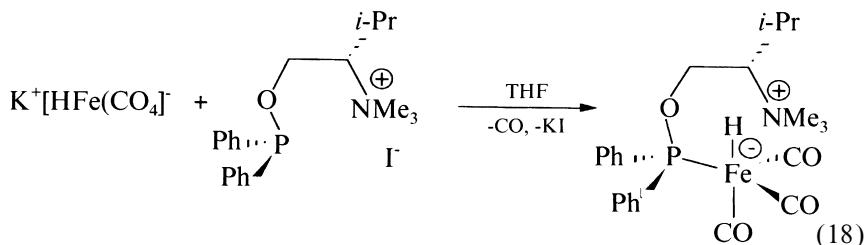


Fig. 2. X-ray structure of diphenyl-*N,N*-dimethylephosium hydridotricarbonylferrate.

$[\text{HFe}(\text{CO})_3\{\text{P}(\text{O}^+\text{Ph})_3\}]^-$ (vide supra). An electrostatic interaction between the hydride and the ammonium centre is also apparent. Interestingly, this interaction is still present in solution (CD_3CN), as evidenced by a strong (36%) NOE effect between the methyl groups of the ammonium centre and the hydride.

The series of zwitterionic hydridotricarbonylferrates has also been extended to a phosphinite–ammonium ligand “valphosium” derived from valinol (Eq. (18)) [43].

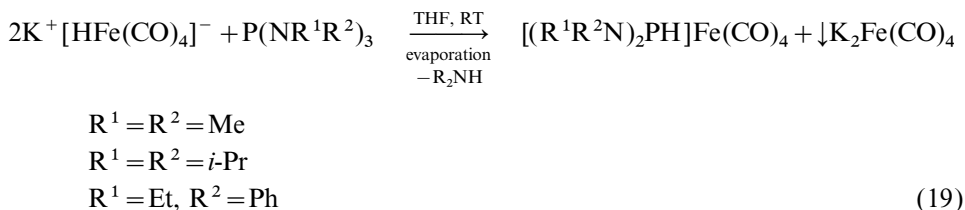


This *N,N,N*-trimethyldiphenylvalphosium hydridotricarbonylferrate exhibits spectroscopic properties similar to those of the corresponding ephosium hydridotricarbonylferrate (Eq. (17)) and similar structural features (in particular the *cis* H–Fe–P arrangement) are likely.

Variable-temperature NMR study (CD_3CN) of the zwitterionic ephosium and valphosium hydridotricarbonylferrates showed dependence of their $^2J_{\text{PH}}$ coupling constants with temperature [43]. A similar behaviour has been previously observed only for (phosphane) hydridotricarbonylferrates having the *trans* H–Fe–P geometry (vide supra). These zwitterionic complexes are thus special hydridotricarbonylferrates displaying both a *cis* H–Fe–P geometry and a dependence of the $^2J_{\text{PH}}$ coupling constant with temperature: the *cis* geometry could be dictated by a stabilizing effect of the electrostatic interaction which could not take place in a *trans* form because of the steric hindrance of the equatorial CO ligands. These coupling constant variations could reveal a variation of the H–Fe–P angles with temperature-dependent average opening of a seven-membered chelation ring with a labile electrostatic edge $\text{HFe}^- \cdots \text{N}^+$ [43].

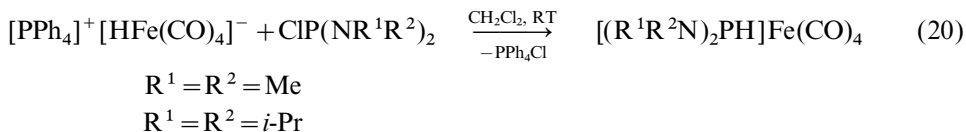
2.1.5. Reaction with aminophosphines

In contrast to phosphites, phosphines and phosphinites, tri(amino)phosphines do not react with $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ by CO substitution. Instead, substitution at phosphorus is observed, affording the neutral iron tetracarbonyl complexes $[(\text{R}_2\text{N})_2\text{PH}](\text{Fe}(\text{CO})_4)$ and $\text{K}_2\text{Fe}(\text{CO})_4$ according to the stoichiometry of Eq. (19) [45].



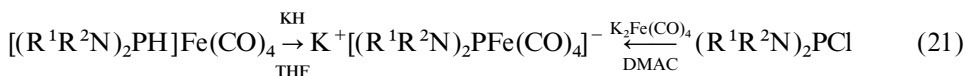
This reaction provides a rapid (30 min, $R^1 = R^2 = \text{Me}$) laboratory scale preparation of Collman-type reagents $M_2\text{Fe}(\text{CO})_4$ ($M = \text{Na}, \text{K}$) for immediate use [45].

Some $[(R_2N)_2\text{PH}]\text{Fe}(\text{CO})_4$ complexes have been previously reported by reaction of $[\text{PPh}_4]^+[\text{HFe}(\text{CO})_4]^-$ with the corresponding bis(dialkylamino)chlorophosphine (Eq. (20)) [46].

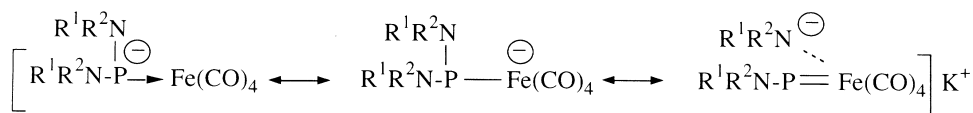


The synthesis of these secondary aminophosphine tetracarbonyliron complexes from tri(amino)phosphines (Eq. (19)) may be an interesting alternative to Eq. (20). Nevertheless, tri(amino)phosphines are not always easy to prepare and Eq. (20) has been used to obtain the previously unreported $[(\text{Ph}_2\text{N})_2\text{PH}]\text{Fe}(\text{CO})_4$, whose structure has been determined by X-ray diffraction analysis [47].

The chemistry of $[(R^1R^2N)_2\text{PH}]\text{Fe}(\text{CO})_4$ complexes has been briefly investigated. In particular, they can be deprotonated by reaction with KH in THF to afford the corresponding phosphido complexes (Eq. (21)) which can be prepared, alternately, by reaction of $\text{K}_2\text{Fe}(\text{CO})_4$ with the corresponding di(amino)chlorophosphines [47].



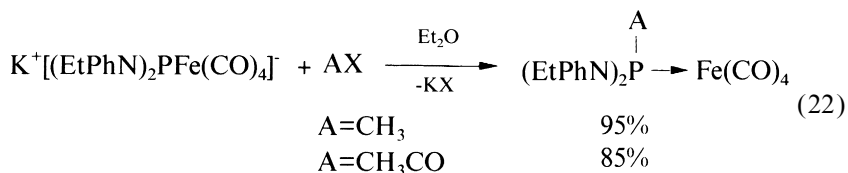
These phosphidotetracarbonylferrates are characterized by a low-field ^{31}P NMR signal in the range 220–230 ppm. This deshielding suggests the participation of the amido stabilized phosphinidene resonance form to the description of the complex (Scheme 2).



Scheme 2. Resonance forms of the phosphido complexes $[(R^1R^2N)_2\text{P}]\text{Fe}(\text{CO})_4]^-K^+$

This participation is supported by analogy with literature data on base-stabilized ironsilylene complexes, e.g. $[\text{Fe}(\text{CO})_4\{\text{SiMe}_2-(\text{Me}_2\text{NH})\}]$ [48] and by the behaviour of the complex with $R^1 = R^2 = \text{Me}$ [47].

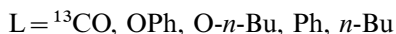
By contrast, the phosphido character of these complexes (Scheme 2) is revealed by their reaction with CH_3I or CH_3COCl to afford the expected alkyl or acyldi(amino)phosphine tetracarbonyliron complexes (Eq. (22)).



2.2. Mechanistic considerations

Ligand substitution processes have attracted much attention both for the study of mechanisms and for the synthesis of new heteroleptic complexes [49]. Most of these studies deal with neutral carbonyl metal derivatives [50].

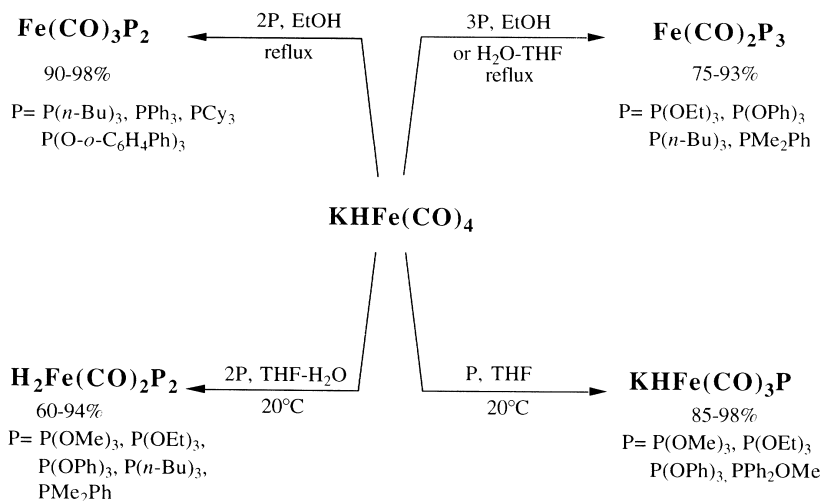
Only very few data are available on CO substitution by phosphanes on *carbonylmetallates* without photochemical activation. The only reported example concerns the direct replacement of a CO ligand in salts of $[\text{Co}(\text{CO})_4]^-$ (Eq. (23)) [51].



One important observation about Eq. (23) is the dramatic role of ion-pairing phenomena, as evidenced by the fact that the use of $[\text{PPN}]^+$ or $[(n\text{-Bu})_4\text{N}]^+$ as the counterion completely inhibits the CO substitution on $[\text{Co}(\text{CO})_4]^-$ [51].

When this work was initiated, the only reported direct ligand substitution on $[\text{HFe}(\text{CO})_4]^-$ was the reaction of $\text{Na}^+[\text{HFe}(\text{CO})_4]^-$ with ${}^{13}\text{CO}$ [52]. In this case again, the role of the counterion is very important since $\text{Na}^+[\text{HFe}(\text{CO})_4]^-$ readily exchanges carbonyl ligands with ${}^{13}\text{CO}$ in THF whereas $[\text{PPN}]^+[\text{HFe}(\text{CO})_4]^-$ does not. No proven example of direct substitution of a carbonyl ligand by a weaker π -acceptor ligand has been reported before and disinclination towards thermal ligand substitution has been reported for $[\text{HFe}(\text{CO})_4]^-$, $\text{V}(\text{CO})_6^-$ and $\text{CpMo}(\text{CO})_5^-$ [53].

From our results (Scheme 3), the reaction of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ with phosphanes (hereafter abbreviated “P”) under various conditions now appears as the best



Scheme 3. Synthesis of mononuclear phosphane-substituted iron carbonyl complexes from $\text{KHF}(\text{CO})_4$

synthetic route to a large variety of iron carbonyl complexes containing one, two or three phosphane ligand(s) [54–56].

From a mechanistic point of view, interesting information could be obtained by IR and ^{31}P NMR monitoring, by analysis of evolved gas and by separate experiments on the reactivity of isolated complexes. The main conclusions emphasize the role of the cation, the nature of the solvent and the steric and electronic properties of the phosphane.

2.2.1. Nature of the counterion

The IR spectra of $\text{M}^+[\text{HFe}(\text{CO})_4]^-$ in THF have been thoroughly studied [38,39]. When M^+ is Na^+ , an interaction has been evidenced between the latter and an equatorial carbon monoxide ligand (ν_{CO} absorption band at 1854 cm^{-1}). This interaction makes the “axial” carbon monoxide ligand more labile. In contrast, when the cation is $[\text{PPN}]^+$, this interaction no longer occurs, and the complex is much more resistant than $\text{Na}^+[\text{HFe}(\text{CO})_4]^-$ to ligand exchange with ^{13}CO [52]. This can explain the lack of reactivity of $[\text{PPN}]^+[\text{HFe}(\text{CO})_4]^-$ with phosphanes in most cases. The reason why $[\text{PPN}]^+[\text{HFe}(\text{CO})_4]^-$ does react with phosphites in CH_2Cl_2 is not clear. At last, for what concerns ephosium and valphosium ligands (vide supra) the question whether ligand substitution occurs before or after cation metathesis is opened.

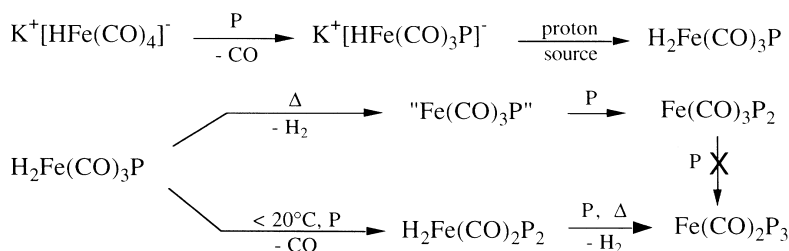
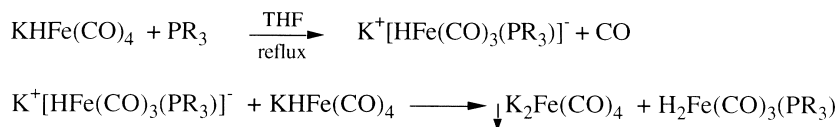
With regard to reactions of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$, the first ligand substitution generates the anionic hydrides $\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$. The course of the reaction then depends on both the nature of the solvent and the steric and electronic properties of the phosphane.

2.2.2. Nature of the solvent (protic or aprotic)

In protic solvents, $\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$ derivatives are readily protonated to generate the dihydrides $\text{H}_2\text{Fe}(\text{CO})_3\text{P}$ which, depending on the reaction temperature, either (i) evolve by loss of H_2 to generate the coordinatively unsaturated “ $\text{Fe}(\text{CO})_3\text{P}$ ” species which react further with an excess ligand to give the disubstituted $\text{Fe}(\text{CO})_3\text{P}_2$ derivatives, or (ii) evolve by loss of CO to generate the coordinatively unsaturated $\text{H}_2\text{Fe}(\text{CO})_2\text{P}$ which react with an excess ligand to give the corresponding dihydrides $\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$. In most cases the dihydrides $\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$ may react further if an excess of P is present to yield the corresponding trisubstituted $\text{Fe}(\text{CO})_2\text{P}_3$ derivatives. A generalized reaction pathway has been established (Scheme 4).

In an aprotic solvent, the $\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$ derivatives can be isolated from reactions at room temperature when P is a phosphite or a phosphinite. In contrast, when P is a phosphine, this complex is basic enough to deprotonate $[\text{HFe}(\text{CO})_4]^-$, thus generating $\text{K}_2\text{Fe}(\text{CO})_4$ and the dihydride $\text{H}_2\text{Fe}(\text{CO})_3\text{P}$ which evolves as in a protic medium (Scheme 5).

Solutions of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ in THF exhibit the same interaction ($\nu_{\text{CO}} = 1856\text{ cm}^{-1}$) as noted before for $\text{Na}^+[\text{HFe}(\text{CO})_4]^-$ whereas solutions in methanol do not. Thus, it could be expected that CO substitution on $\text{K}^+[\text{HFe}(\text{CO})_4]^-$

Scheme 4. General reaction pathway for the reaction of $\text{KHFe}(\text{CO})_4$ with phosphanes (P)Scheme 5. Reaction of phosphines with $\text{KHFe}(\text{CO})_4$ in refluxing THF

would occur more readily in THF than in methanol. In fact, the reverse is observed for $\text{P}(n\text{-Bu})_3$ and PMe_2Ph (vide infra, Table 2). Actually, in methanol, *all* the IR carbonyl absorption bands of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ are shifted to higher frequencies (Table 1). The Fe–CO bonds are weaker, and hence CO substitution occurs more readily in hydroxylic solvents than in THF.

In other words, in protic media, the back-bonding onto the carbonyl ligands of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ is less important than in THF. This observation suggests an interaction between K^+ and the charge on the $[\text{Fe}-\text{H}]^-$ moiety. Comparison of the ^1H NMR hydride chemical shifts of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ in CD_3OD and in $\text{THF}-d_8$ (Table 1) shows that the hydridic character is more pronounced in methanol than in THF, in agreement with a more important back-bonding to the CO ligands in the latter (IR data). This observation leads to the proposed representations for $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ in THF and in protic media (Fig. 3).

2.2.3. Steric and electronic properties of the phosphane

It is interesting to compare the reactivity of the various phosphanes in order to gain information concerning the influence of their steric and electronic properties in ligand substitution reactions on an 18-electron complex like $[\text{HFe}(\text{CO})_4]^-$. Most of the isolated products, however, result from consecutive reactions and it is difficult

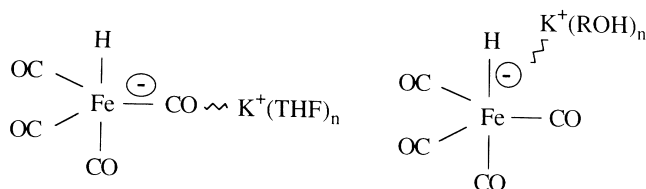
Fig. 3. Sites of interaction of $\text{K}^+(\text{THF})_n$ and $\text{K}^+(\text{ROH})_n$ with $[\text{HFe}(\text{CO})_4]^-$.

Table 1
Spectroscopic characteristics of $\text{KHFe}(\text{CO})_4$ as a function of the solvent

Solvent	IR: ν_{CO} (cm^{-1})	^1H NMR: δ (ppm)
THF- d_8	1999 (w); 1911 (sh); 1878 (S); 1856 (sh)	−8.75
MeOD	2008 (w); 1921 (sh); 1893 (S)	−9.05

to determine the influence of the nature of the phosphane on the first ligand substitution step. It is possible, however, to compare the results of reactions conducted *near room temperature*, that is the formation of the early detectable products.

In THF, the reaction of $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ with phosphanes allows the isolation of the monosubstituted hydridocarbonylferrate $[\text{HFe}(\text{CO})_3\text{P}]^-$ in four cases (Table 2). As may be seen, the Tolman cone angle of the phosphane is an important parameter, as evidenced by the difference in reactivity between PPh_3 and $\text{P}(\text{OMe})_3$, which have similar $\text{p}K_{\text{a}}$ values [57]. However, the basicity of the phosphane also plays an important role since $\text{P}(\text{OPh})_3$ ($\text{p}K_{\text{a}} = -1.20$) and PPh_2OMe ($\text{p}K_{\text{a}} = 2.69$) react much more rapidly than $\text{P}(n\text{-Bu})_3$ and even PMe_2Ph which exhibit cone angles in the same range, but much higher $\text{p}K_{\text{a}}$ values (Table 2).

In a protic solvent, the reaction directly leads to the dihydrides $\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$, and the intermediate $\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$ cannot be observed. It has been found, however, that protonation of the latter, and the second CO substitution on $\text{H}_2\text{Fe}(\text{CO})_3\text{P}$ are very fast. Hence, the first ligand substitution on $\text{K}^+[\text{HFe}(\text{CO})_4]^-$ is the rate-determining step, and reaction times given in Table 3 are a good reflection of the order of reactivity [57].

As may be seen from Table 3, the reactivity of phosphanes in protic media is clearly determined by their cone angle but not by their basicity, in contrast to what was observed in THF. Indeed, the poorly basic $\text{P}(\text{OPh})_3$ and the highly basic $\text{P}(n\text{-Bu})_3$, which exhibit comparable cone angles, react in a similar manner whereas

Table 2
Reaction of phosphanes “P” (2 equiv.) with $\text{KHFe}(\text{CO})_4$ in THF at 20 °C

“P”	θ	$\text{p}K_{\text{a}}$	Reaction time (h)	Product	Yield (%) (isolated)
$\text{P}(\text{OMe})_3$	107	2.60	1	$\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$	91
$\text{P}(\text{OEt})_3$	109	3.35	1	$\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$	97
PMe_2Ph	122	6.49	No significant reaction after 24 h		
$\text{P}(\text{OPh})_3$	128	−1.20	2	$\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$	98
PPh_2OMe	132	2.69	4	$\text{K}^+[\text{HFe}(\text{CO})_3\text{P}]^-$	85
$\text{P}(n\text{-Bu})_3$	132	8.43	No significant reaction after 24 h		
PPh_3	145	2.73	No significant reaction after 24 h		
PCy_3	170	9.70	No significant reaction after 24 h		

Table 3

Reaction of phosphanes “P” (2 equiv.) with $\text{KHF}(\text{CO})_4$ in protic media (15–20 °C, $\text{H}_2\text{O}/\text{THF}$ or MeOH)

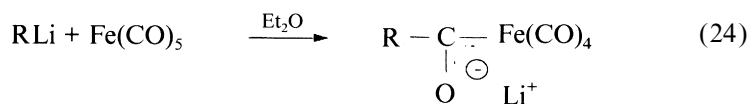
“P”	θ	$\text{p}K_{\text{a}}$	Reaction time (h)	Product	Yield (%) (isolated)
$\text{P}(\text{OMe})_3$	107	2.60	1	$\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$	90
$\text{P}(\text{OEt})_3$	109	3.35	1	$\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$	91
PMe_2Ph	122	6.49	20	$\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$	60 ^a
$\text{P}(\text{OPh})_3$	128	–1.20	24	$\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$	94
$\text{P}(n\text{-Bu})_3$	132	8.43	24	$\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$	81
PPh_3	145	2.73	No significant reaction after 48 h		
PCy_3	170	9.70	No significant reaction after 48 h		

^a Due to difficulties in product isolation.

$\text{P}(\text{OMe})_3$ and PPh_3 , which have similar $\text{p}K_{\text{a}}$ values, but different cone angles, exhibit a dramatically different reactivity.

3. Coordination chemistry from $\text{RCO}(\text{Li})\text{Fe}(\text{CO})_4$

The reaction of alkyl (or aryl)- lithium derivatives with $\text{Fe}(\text{CO})_5$ to give acyl (or aryl)- carbonylferrates has been known for a long time (Eq. (24)) [58].



Hereafter are briefly presented both the extension of this reaction to lithium aldimines — generating new α,β -unsaturated acylferrates — and the reaction of common acylferrates with chlorophosphines, an easy route to complexed acylphosphines.

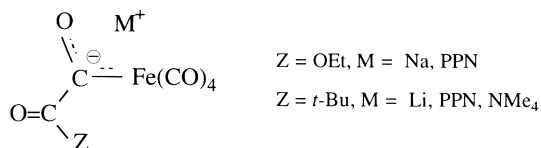
3.1. α -Iminoacyl ligand in carbonylmetallates

Recent studies have shown α,β -unsaturated Fischer carbene complexes to have potential in a number of reactions [59,60]. Alkylation of (acyl)carbonylmetallates $[\text{R}(\text{COLi})\text{M}(\text{CO})_n]$ in which the R group contains an α,β -unsaturated function is a possible route to α,β -unsaturated Fischer carbene complexes.

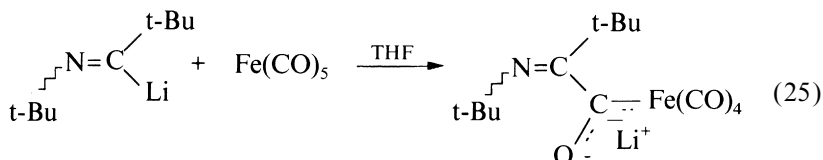
Although some α,β -unsaturated acylferrates are known [61,62], only two examples of the sequence $[(\text{CO})_4\text{FeCOCOZ}]^-$, which is relevant to double carbonylation processes [63,64], have been reported. One is the ethoxy oxalyl tetracarbonylferrate ($\text{Z}=\text{OEt}$) [64]. The second is the (pivaloylacyl)tetracarbonylferrate ($\text{Z}=t\text{-Bu}$) generated by a tedious procedure (Fig. 4) [65].

We became interested in the synthesis of carbonylferrates containing the unprecedented α -iminoacyl ligand, akin to the above α -ketoacyl ligand.

The lithium aldimine generated from $t\text{-BuLi}$ and $t\text{-BuNC}$ [66] reacts with

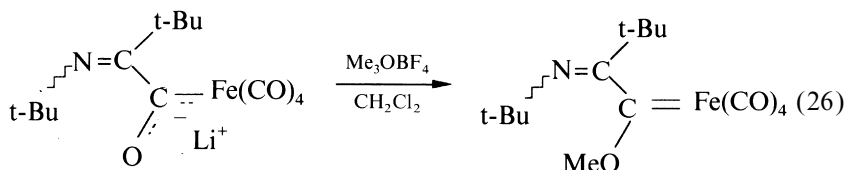
Fig. 4. (α -Ketoacyl)tetracarbonylferrates $[(\text{CO})_4\text{FeCOCOZ}]^- \text{M}^+$.

$\text{Fe}(\text{CO})_5$ in THF (Eq. (25)) to give the imino-protected equivalent of the (pivaloylacyl)tetracarbonylferrate cited above [67]. Contrary to the latter, this imino derivative is stable as lithium salt, at least overnight at 55 °C in THF.



This complex is characterized by a low-field ^{13}C NMR signal (298.4 ppm) for the acyl carbon atom. This is the first example of an α -iminoacyl ligand in the carbonyl-metallate series. The above strategy has been extended to chromium and manganese carbonyls [67].

In situ alkylation of this lithium (α -iminoacyl)tetracarbonylferrate with Me_3OBF_4 gives the stable methoxycarbene complex (mixture of two isomers) in 45% isolated yield (Eq. (26)). The latter exhibits a ^{13}C NMR signal at 335.2 ppm for the carbenic carbon atom.

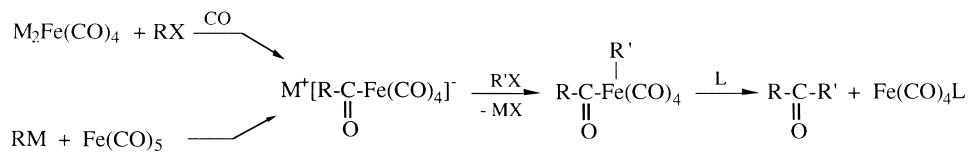


By comparison, the (pivaloylacyl)tetracarbonylferrate ($[\text{Me}_4\text{N}]^+$ salt) has been reported to react with electrophiles (e.g. FSO_3Et) to give thermolabile products (decomposition above -40°C) resulting from alkylation at the acyl oxygen atom [65]. On the contrary, $[(\text{CO})_4\text{FeCOCOOEt}]^- \text{Na}^+$ is alkylated at the metal by reaction with $\text{CF}_3\text{SO}_3\text{Me}$ [64].

3.2. Tandem acylation–complexation of chlorophosphines

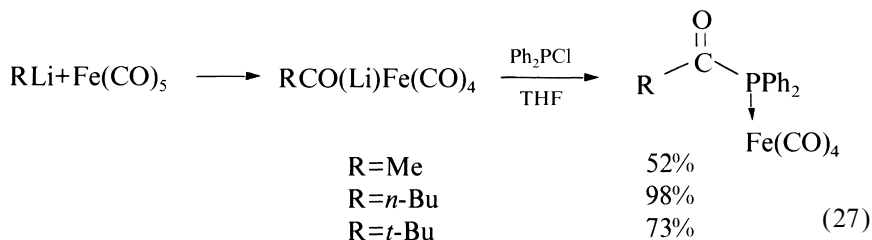
The synthesis of ketones promoted by iron carbonyl derivatives involves generation of acyltetracarbonylferrates by either pathway shown in Scheme 6 [8].

It was possible to imagine that a chlorophosphine R_2PCl could act both as the alkyl halide $\text{R}'\text{X}$ by substitution of Cl and as the ligand L by its phosphorus atom. This proved to be the case and this reaction constitutes a very easy route to

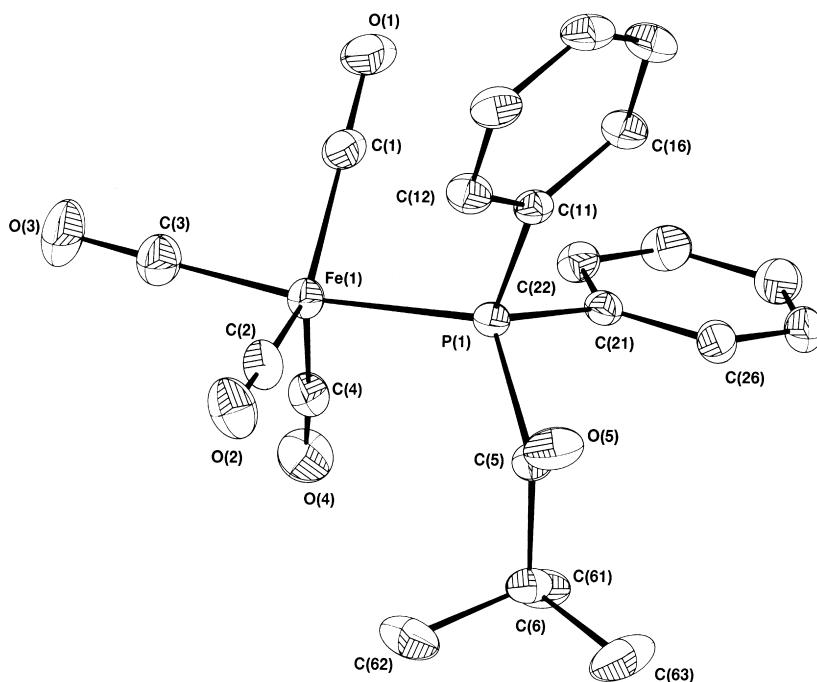


Scheme 6. Synthesis of dialkylketones from acylferrates

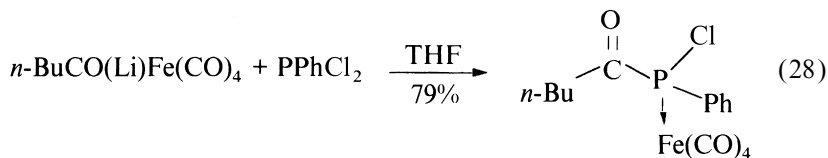
acylphosphine iron tetracarbonyl complexes, isolated in fair to high yield (Eq. (27)) [68,69].



In the cases where R = *t*-Bu or Me, the structures have been determined by X-ray diffraction studies (Fig. 5 for R = *t*-Bu) [68,69].

Fig. 5. X-ray structure of [*t*-BuC(O)PPh₂]Fe(CO)₄.

The same strategy also applies to dichlorophenylphosphine (Eq. (28)), but not to PCl_3 [69].



4. Conclusion

Nowadays, the main goal of coordination chemistry is both to provide a better knowledge and understanding of nature, i.e. the possible arrangements of atoms around metal centres, and to make available efficient syntheses for the design of a large variety of new complexes in view of their possible applications in organic synthesis and homogeneous catalysis.

The results summarized in this review show that tetracarbonylferrates $\text{M}^+[\text{EFe}(\text{CO})_4]^-$ ($\text{E}=\text{H}, \text{RCO}$), easily obtained from the inexpensive $\text{Fe}(\text{CO})_5$ in a one-step reaction, are versatile, efficient, *in situ* precursors for the design of a large variety of new mononuclear iron carbonyl complexes. Study of the possible applications of the latter in selective organic synthesis, stoichiometric or catalytic, is underway, as well as extension of the strategies developed for iron to other transition metals of the first row, in particular to chromium [70].

Acknowledgements

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