ELSEVIER

Coordination Chemistry Reviews 178–180
(1998) 353–379

COORDINATION
CHEMISTRY
REVIEWS

Cis octahedral iron complexes $Fe[(CO)_xR][(CO)_yR'](CO)_4$ $(x+y=0, 1, 2, 3, 4)$
Thermolysis and carbon–carbon coupling: a personal survey

Jean-Yves Salaün *, Pascale Laurent, Hervé des Abbayes

Laboratoire de chimie, Electrochimie Molculaires et Chimie Analytique UMR CNRS 6521,
Université de Bretagne Occidentale, UFR Sciences et Techniques, 6 avenue Le Gorgeu, BP 809,
29285 Brest, Cedex, France

Received 6 November 1997; accepted 25 March 1998

Contents

---

* Corresponding author. Fax: +33 2 98 01 65 94; e-mail: jean-yves.salaun@univ-brest.fr

PII S0010-8545(98)00103-9

Abstract

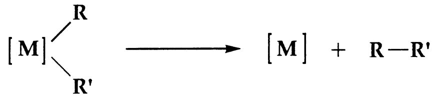
The synthesis of a homogeneous series of *cis* bis substituted iron complexes is described. These complexes which display the $[M]\{[C(O)]_xR\}\{[C(O))_yR']\}$ ($x+y=0$, 1, 2, 3, 4; x, $y \leqslant 2$) pattern are models for the study of carbon–carbon coupling processes including mono- and polycarbonylations. Their reactivity is reviewed and particularly that of bis alkoxycarbonyl, bis carbamoyl and metalla γ ketoester iron compounds. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbene; Carbon–carbon coupling; Chain–ring isomerization; Dicarbonylation; Iron; Monocarbonylation

---

1. Introduction

Coupling reactions of organic compounds catalysed by transition metals are important methods for generating carbon–carbon bonds. It is generally admitted that the final step of this process requires the elimination and coupling of two organic ligands from the transition metal. For this reason the process of reductive elimination described in Eq. (1) has been extensively studied on model complexes and the essential requirements for the achievement of this reaction have been determined [1–3]:



(1)

These different studies have established the influence of the nature of the metal [1,3,4] and of its electronic density [1] on the course of the reaction. They have also revealed the importance of the geometry of the starting complex [5] and also of the nature of the intermediates [6–10] leading to carbon–carbon couplings.

The two organic ligands involved in the carbon–carbon coupling process are also found to influence the reaction either via their electronic effects [6] or the hybridization of their carbon directly bound to the metal centre [1,3].

Most of the previous studies were realized on d^8 square planar complexes and, curiously, only a very small number of hexacoordinate complexes of the type $M(R)(R')(CO)_4$ are reported.

In the present paper we survey recent results concerning the synthesis and study of the properties of octahedral iron(II) complexes bearing two organic ligands in a *cis* position. According to the nature of their ligands, these complexes are possible models either for the study of catalytic dimerization of organic halides ($R=R'=$ alkyl) or for the realization of mono ($R=$alkyl, $R'=$acyl) or di ($R=R'=$acyl) carbonylation processes which are of industrial importance.

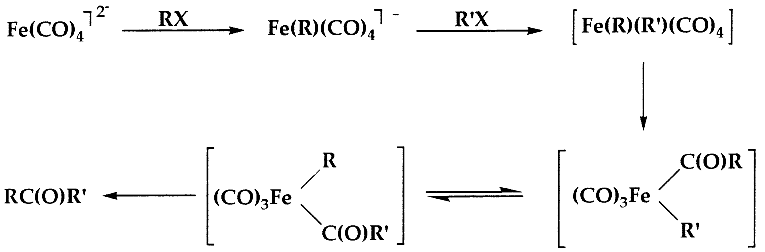
We will successively describe the preparation and reactivity of bis alkyl, alkyl–acyl, alkyl–alkoxycarbonyl, bis alkoxycarbonyl, bis carbamoyl, alkoxycarbonyl–alkyloxalyl, acyl–alkyloxalyl, alkoxycarbonyl–pyruvoyl, bis alkyloxalyl and bis pyruvoyl tetracarbonyl iron complexes. Probably due to the strong *trans* influence of their organic ligands, all these complexes display the *cis* configuration required for a concerted coupling between these two organic ligands. The possible involvement of these complexes in catalytic carbon–carbon coupling processes will also be discussed.

2. Bis alkyl complexes

As suggested by numerous remarkably stable bis alkyl complexes described in the literature, carbon–carbon coupling between two alkyl ligands is not favoured [1,3]. Curiously, only a small number of hexacoordinate iron complexes of the type $Fe(R)(R')(L)_4$ have been reported and most of them are stabilized by electron donor bis phosphine or bis amine ligands [11–17].

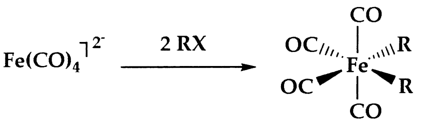
Their carbonyl homologues, $Fe(R)(R')(CO)_4$, have only been described as metallacycles: $Fe–(CH_2)_n–(CO)_4$, $n=4$ [18]; $Fe[CH_2C(O)CH_2CH_2](CO)_4$ [19]; or display electron-withdrawing perfluoroalkyl ligands [20–25].

Attempts to synthesize non-fluoro bis alkyl iron tetracarbonyl complexes by reaction of two organic halides with $[Fe(CO)_4]^{2-}$ [26] [Eq. (2)] failed, due to their rapid decomposition reactions probably by migration of an alkyl to a carbonyl ligand followed by a rapid elimination of a dissymmetric ketone [27]:



(2)

Similar results were obtained in our laboratory under phase transfer conditions for $R=R'=CH_2Ar$ [28]; $R=CH_2Ph$, CH_2CN, $CH_2CHCHPh$, $CH_2CO_2{}^tBu$; $R'=Me$ [29]. Meanwhile, the use of less electron donor ligands has allowed the synthesis of the first two iron complexes bearing two non-fluoro alkyl ligands [30,31] [Eq. (3)]:



1

$R = CH_2CO_2Me$: **1a** [29]

$R = CH_2CN$: **1b** [30]

(3)

Since the electronic properties of the alkyl ligands probably prevent their migration to a terminal carbonyl, these complexes are stable until 30 °C, consistent with the reluctance of carbon–carbon coupling between two alkyl ligands.

3. Model compounds for monocarbonylation

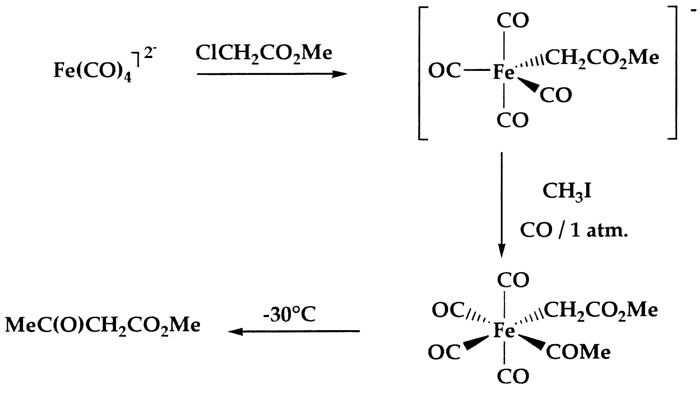
We have already mentioned in the previous section that elimination of ketones from acyl–alkyl transition metal complexes occurs rapidly compared with the reductive coupling of two alkyl ligands; in view of this high reactivity these complexes have often been supposed to be undetectable intermediates in ketone formation [27] and only few examples of well-characterized entities of this type have been described in the literature.

3.1. Acyl–alkyl complexes

Isolable acyl–alkyl complexes are more the exception than the rule. Such platinum(II) [32] and ruthenium(II) [33,34] complexes have, however, been described, but they readily undergo decomposition reactions giving rise, below room temperature, to formation of ketones. On the other hand, acyl–alkyl complexes of rhenium appear more stable and $[Re(Me)[C(O)Ph](CO)_4]^-$ [35] and $ReCp[C(O)Me](Me)(CO)_2$ [36] have been isolated and characterized. They undergo a reductive elimination at 30 °C to form, respectively, benzophenone and acetone.

Iron tetracarbonyl acyl–alkyl complexes are, like their bis alkyl homologues, either cyclic or present perfluoroalkyl ligands [19,37,38]. Cyclic complexes induce thermally the formation of cyclic ketones, and perfluoro analogues by a decarbonylation reaction give rise to bis alkyl complexes.

By reacting successively $ClCH_2CO_2Me$ and CH_3I on $[Fe(CO)_4]^{2-}$ we have realized the synthesis of $Fe[C(O)Me](CH_2CO_2Me)(CO)_4$ **2** [Eq. (4)] which is the first iron non-fluoro alkyl–acyl complex [31]:



2 (4)

This easy formation confirms the rapid migration of methyl ligands on terminal carbonyls already invoked in ketone formation processes induced by bis alkyl complexes. The presence on our complex of an alkyl ligand bearing an electron-withdrawing group (CH_2CO_2Me) probably makes its coupling with the acyl ligand more difficult; this occurs however at −30 °C to give rise to quantitative formation of methyl acetyl acetate [Eq. (4)].

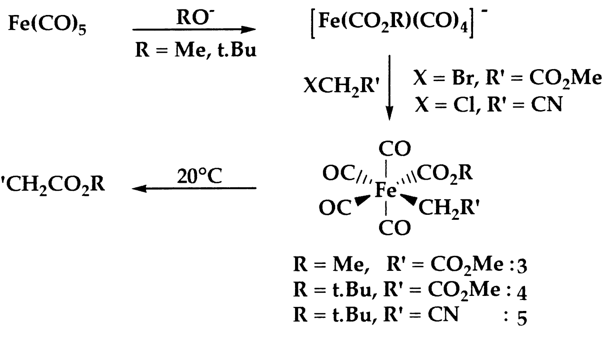
3.2. Alkoxycarbonyl–alkyl complexes

Monoalkoxycarbonyl complexes have been extensively studied because of their basic role in the nucleophilic activation of carbon monoxide [39]. These complexes and their closely related hydroxycarbonyl species are often invoked as key intermediates in catalytic processes such as the water gas shift reaction [39–41]. Alkyl–alkoxycarbonyl intermediates are thought to be involved in stoichiometric or catalytic processes of carbonylation of organic halides to give esters [42,43]. These complexes, resulting from the addition of the halide on an anion (e.g. $[Fe(CO_2R)(CO)_4]^-$), are supposed to induce carbon–carbon coupling reactions between their two organic ligands, affording the final ester.

Probably due to their high instability, only few examples of this type of complex have been described in the literature. A methyl–methoxycarbonyl platinum complex stabilized by a strong electron donor bis phosphine ligand is stable at −20 °C [44]; its hydroxycarbonyl homologues undergo rapid decarboxylation at room temperature [45,46]. On the other hand, the *cis* $Pd(Me)(CO_2Me)$(bisphosphine) gives rise to the formation of methylacetate even at −50 °C [47].

Only one iron alkyl–alkoxycarbonyl complex has been reported previously to our work. This compound, $Fe(Me)(CO_2Me)(CO)_4$ [48], was obtained by reaction of $MeSO_3F$ with $[Fe(CO_2Me)(CO)_4]^-$ [49,50] at −78 °C. It rapidly decomposes at 0 °C, affording methylacetate.

We have realized the synthesis of a series of fairly stable alkyl–alkoxycarbonyl iron complexes by reacting the anions $[Fe(CO_2R)(CO)_4]^-$, formed by nucleophilic addition of the appropriate alcoholate (MeONa, ^tBuONa) to a terminal carbonyl of $Fe(CO)_5$ [49,50], with organic halides bearing electron-withdrawing groups: $BrCH_2CO_2Me$, $ClCH_2CN$ [Eq. (5)] [30,31]:



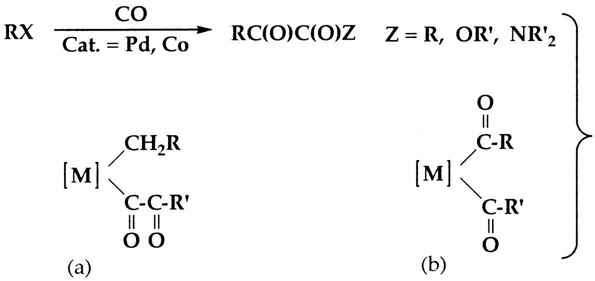
(5)

Complexes **3**, **4** and **5** are stable below +15 °C; at +20 °C they slowly decompose, inducing the quantitative formation of dimethylmalonate (**3**), methyl t-butyl malonate (**4**) and t-butyl cyanoacetate (**5**), respectively. The enhanced stability of **3**, **4** and **5** compared with that of $Fe(CO_2Me)(Me)(CO)_4$ is certainly due to the presence on these complexes of weaker electron donor alkyl ligands.

The case of these observed reductive eliminations strongly suggests that this type of complex is a possible intermediate in catalytic processes of monocarbonylation.

4. Model compounds for dicarbonylation

The recent discovery of the double carbonylation process, essentially realized with Co (see for example refs. [51–54]) or Pd [55] as catalysts has drawn interest to the synthesis and the study of organometallic models reproducing several steps of this process. The double carbonylation of organic halides gives rise to α, β diketones, α ketoesters or α ketoamides [Eq. (6)]. This process a priori involves a carbon–carbon coupling either between an alkyl and an α ketoacyl, α ketoester or α ketoamide ligands (a) or between two acyl ligands (b) [Eq. (6)]:



(6)

Both models will be described in the following section.

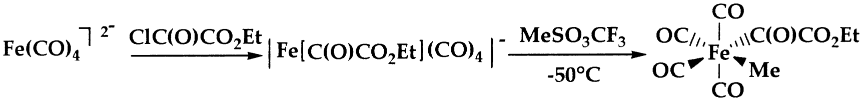
4.1. Alkyl–alkyloxalyl compounds

Though numerous attempts have been carried out to observe the migration of an acyl group from the metal to a carbonyl ligand, this process has never been reported except by oxidation under CO pressure [56,57]. This has to be related to the fact that the reverse reaction, the decarbonylation of complexes bearing ligands such as C(O)C(O)R, occurs readily [58,59].

All these observations make the realization of double carbonylation reactions via complexes of type (a) highly improbable. It was, however, interesting to check the possible accomplishment of double carbonylations by thermolysis of well-characterized alkyloxalyl complexes. To our knowledge only one series of this type of complex has been described. However, these platinum complexes $Pt[C(O)C(O)R](R')(PPh_3)_2$ (R = Me, Et, Ph, OMe; R′ = Me, Et, Ph) display the unfavourable *trans* geometry [60,61]. Thermally, the *trans* $Pt[C(O)C(O)Ph](Et)(PPh_3)_2$ undergoes a spontaneous intramolecular CO transfer to form *trans* $Pt[C(O)Ph][C(O)Et](PPh_3)_2$.

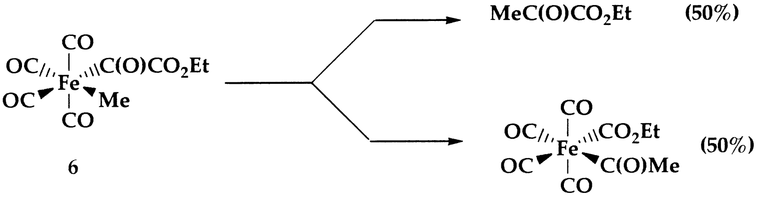
We have reported the preparation of complex **6** by reaction of ethyloxalyl chloride with $Na_2Fe(CO)_4$ [27] followed by methylation of the so-formed

$\{Fe[C(O)CO_2Et](CO)_4\}^-$ anion with the powerful methylating agent $MeSO_3CF_3$ [Eq. (7)] [62]:



6 (7)

Complex **6** is very unstable: it decomposes at −10 °C to afford, according to two different pathways: (1) ethylpyruvate by reductive elimination; (2) the acyl–alkoxycarbonyl complex **7a** by intramolecular CO transfer [Eq. (8)]:



7a (8)

This reaction is the first example of double carbonylation realized from an alkyl–alkyloxalyl complex; however, this process remains in competition with the decarbonylation of the alkyloxalyl ligand.

4.2. Complexes bearing two RCO ligands

We will limit our study to bis acyl and acyl–alkoxycarbonyl (or carbamoyl) complexes. Bis alkoxycarbonyl and bis carbamoyl compounds will be described in special sections.

4.2.1. Bis acyl complexes

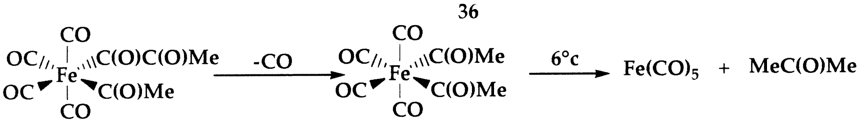
The first bis acyl complexes were described 20 years ago. They are anionic and display the same general formula: $\{M[C(O)R][C(O)R'](CO)_4\}^-$, M = Mn [63–67], M = Re [35,68]; R, R′ = Me, Et, ^iPr, $PhCH_2$. These anions are stable at room temperature. At +50 °C, manganese compounds induced the formation of monoketones [64] supposed to occur by decarbonylation of one acyl ligand giving rise to alkyl acyl complexes. These last complexes easily eliminated their two ligands via carbon–carbon coupling (see Section 3.1). This formation of the alkyl–acyl intermediate by CO de-insertion was demonstrated for Re complexes [35] which are stable at relatively high temperature.

The reductive elimination without decarbonylation of the two acyl ligands from bis acyl complexes did, however, occur under oxidation conditions. Starting from acetyl benzoyl Mn [64] or Re [68] complexes, PhC(O)C(O)Me was then formed quantitatively.

Neutral bis acyl Pt(II) complexes were synthesized later [32,61,69]. These compounds were stabilized by two electron donor phosphine ligands. Thermally, they induced the formation, by reductive elimination, of a mixture of mono- and diketones. Whatever the nature of the two substituents R and R′, the yield of diketones remained low (from 0 to 20%). However, when the reaction was performed under CO pressure, no decarbonylation occurred and the only product of reaction was the diketone.

The only bis acyl iron complexes already described are again either cyclic [37,70–76] or display perfluoro substituents [37,77]. Thermally these complexes undergo decarbonylations giving rise to acyl–alkyl complexes (see Section 3.1). Only one complex displays non-fluoro substituents; however, it is anionic: $\{FeCp(CO)[C(O)R]_2\}^-$, and no study of its thermal behaviour is reported [78].[1]

We have isolated the first neutral bis acetyl iron complex. This compound, *cis* $Fe[C(O)Me]_2(CO)_4$ **8**, is formed by decarbonylation of *cis* $Fe[C(O)C(O)Me][C(O)Me](CO)_4^*$ [Eq. (9)] [79]:

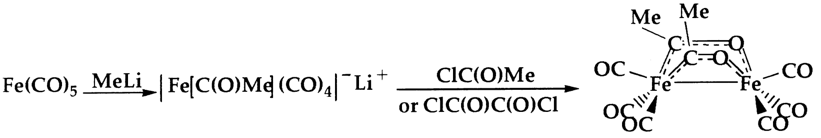


8 (9)

Complex **8**, bearing no electron-withdrawing groups, is unstable; at +6 °C it affords acetone quantitatively by reductive elimination. No trace of butanedione that would result from a direct coupling between the two acetyl ligands has been detected.

Several attempts to prepare complex **8** by reaction of either acetyl chloride or oxalyl chloride with the anion $\{Fe[C(O)Me](CO)_4\}^-$, itself obtained by nucleophilic addition of MeLi on a CO ligand of $Fe(CO)_5$, failed [Eq. (10)].

The only complex formed by these reactions is the $\mu_2\eta_2$ bis acetyl bridged dimer **9a** with the two acetyl carbon atoms bound to one metal centre and the acetyl oxygens linked to the other iron [79].



9a (10)

These bis (η_2 acyl) hexacarbonyl diiron complexes have already been prepared by one-electron oxidation of the corresponding alkyl or acyl ferrate [80–82].

It is not inconceivable that the reaction observed in Eq. (10) could occur via the same oxidative pathway; oxidation of the relatively electron-rich acetyl anion would then be induced by the organic halides.

These difficulties encountered to synthesise iron bis acyl complexes could explain their absence in the literature.

---

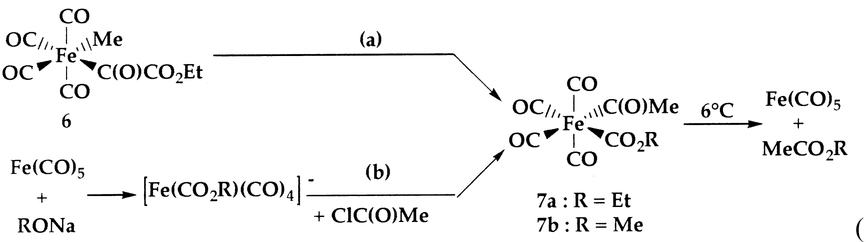
[1] The preparation and study of this complex will be examined in Section 5.

4.2.2. Alkoxycarbonyl or carbamoyl–acyl complexes

Acyl–alkoxycarbonyl or acyl–carbamoyl complexes have been proposed as key intermediates in catalytic palladium double carbonylation reactions of alkyl or aryl halides which lead to the formation of α ketoesters or α ketoamides [3,83–85].

In order to study these catalytic processes, platinum acyl–carbamoyl [59,86] and acyl–alkoxycarbonyl [59,87] have been synthesized. These complexes are found to afford thermally α ketoamides or α ketoesters in low yields. However, the direct coupling between an acyl and a carbamoyl appears easier (17% yield) than the reaction between the same acyl and an alkoxycarbonyl ($<1\%$ yield) [86]. One platinum acyl–hydroxycarbonyl complex: $Pt(CO_2H)[C(O)C_6H_9]$(diphosphine), has also been reported. Probably due to the presence of a non-dissociating strongly electron donor diphosphine ligand, this complex is stable and no decarboxylation of the hydroxycarbonyl ligand is observed [45]. Only one acyl–carbamoyl complex of ruthenium: $Ru[C(O)Et][C(O)NR_2](CO)(PPh_3)_2$, has been described. However, the authors suggest that the iron homologues are not stable [88].

We have prepared acyl–alkoxycarbonyl tetracarbonyl iron complexes according to the two methods described by Eq. (11):



(11)

The first synthesis (a) has already been detailed in Eq. (8), the formation of **7a** then results from an intramolecular transfer of CO [62]. The second method of preparation (synthesis of **7b**) occurs by reaction of acetyl chloride with methoxycarbonyl tetracarbonyl ferrate (path b) [79]. Probably due to the lower electronegativity of the alkoxycarbonyl ferrate, the difficulties encountered for the same reaction realized with acyl ferrates are not found here. **7a** and **7b** are the first characterized acyl–alkoxycarbonyl iron complexes; they decompose at 6 °C affording quantitatively ethyl or methyl acetate. No trace of methyl or ethyl pyruvate products of double carbonylation is detected even if the thermolysis is performed under CO atmosphere.

The carbamoyl homologues of **7a** and **7b**: $Fe[C(O)NR_2][C(O)CH_3](CO)_4$, are found unstable, they decompose at low temperature giving rise to acetamides and $Fe(CO)_5$.

4.3. Bis alkoxycarbonyl complexes

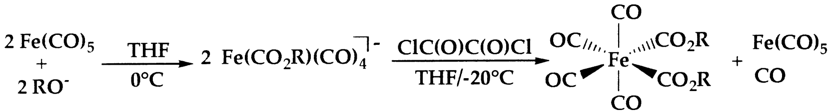
The syngas (mixture of CO and H_2) route to ethylene glycol is an important industrial reaction. A crucial step in this process is the production of oxalates which are subsequently reduced by H_2 to give ethylene glycol.

Another attractive route to oxalates and then to ethylene glycol is the oxidative carbonylation of alcohols. This reaction is reported to give dialkyloxalates in the presence of palladium salts [89–91]. The proposed key intermediate of this reaction is a bis alkoxycarbonyl palladium species which would release oxalate by reductive coupling of the two alkoxycarbonyl ligands.

Only one well-characterized complex: $Pd(CO_2Me)_2(PPh_3)_2$ [92], thermally induces the formation of dimethyloxalate. Though numerous *cis* bis alkoxycarbonyl complexes have been described, none of these Pd [93], Pt [44,94–96], Co [97–99], Rh [100] or Ru [101,102] compounds thermally affords the formation of oxalates but only dialkyl carbonates or alcohols [44,93,94,97,100,101]. Elimination of oxalates from these bis alkoxycarbonyl complexes requires the action of oxidizing agents which also give some organic side products [44,100].

4.3.1. *Preparation of bis alkoxycarbonyl iron complexes*

4.3.1.1. By reaction of oxalyl chloride on methoxy, ethoxy and i-propyloxy carbonyl ferrates. Surprisingly, iron bis alkoxycarbonyl complexes are not described in the literature. We successfully synthesised them via a novel preparation [Eq. (12)] [103]:



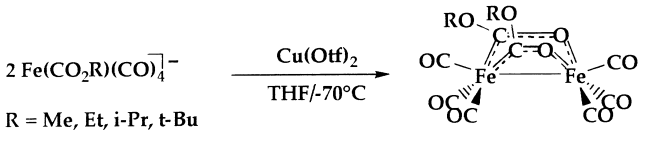
10a : R = Me
10b : R = Et
10c : R = i-Pr
10d : R = allyl

(12)

The alkoxycarbonyl ligand is formed by nucleophilic attack of the appropriate alcoholate on a terminal carbonyl of $Fe(CO)_5$ leading to formation of the corresponding alkoxycarbonyl tetracarbonyl ferrate which, by reaction with 1/2 equivalent of oxalyl chloride, affords *cis* bis alkoxycarbonyl tetracarbonyl iron complexes.

The overall yields of these straightforward reactions are about 70%; however their mechanism remains unclear.

An oxidation process analogous to that responsible for the formation of the di $\mu_2\eta_2$ acetyl iron dimer **9a** by reaction of acetyl halide with $\{Fe[C(O)Me](CO)_4\}^-$ (see Section 4.2.1) was first considered. However, one-electron oxidation reactions of $[Fe(CO_2R)(CO)_4]^-$ realized by copper(II) trifluoromethane sulfonate are found to induce specifically the formation [Eq. (13)] of di $\mu_2\eta_2$ alkoxycarbonyl dimers analogous to that obtained for $\{Fe[C(O)Me](CO)_4\}^-$ [104]:



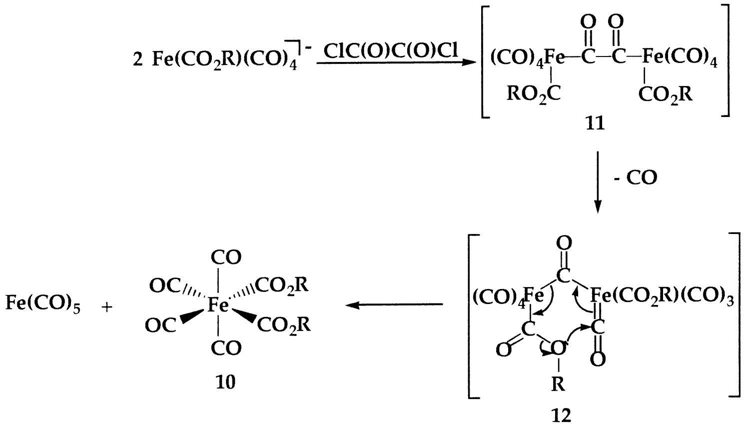
9b : R = Me
9c : R = Et
9d : R = i-Pr
9e : R = t-Bu

(13)

These di $\mu_2\eta_2$ alkoxycarbonyl dimers have never been described as iron examples of this type are limited to acyl [80–82,105] or carbamoyl [106] complexes.

Alkoxycarbonyl bridging ligands of **9b–e** present a carbenoid character as their carbonyl resonance in ^{13}C NMR is found at ~230 ppm.

The achievement of complexes **9** by one-electron oxidation of $[Fe(CO_2R)(CO)_4]^-$ rules out the possible intervention of such a reaction pathway in the formation of the monomer compounds **10**. Another mechanism may explain the formation of **10** [Eq. (14)]:



(14)

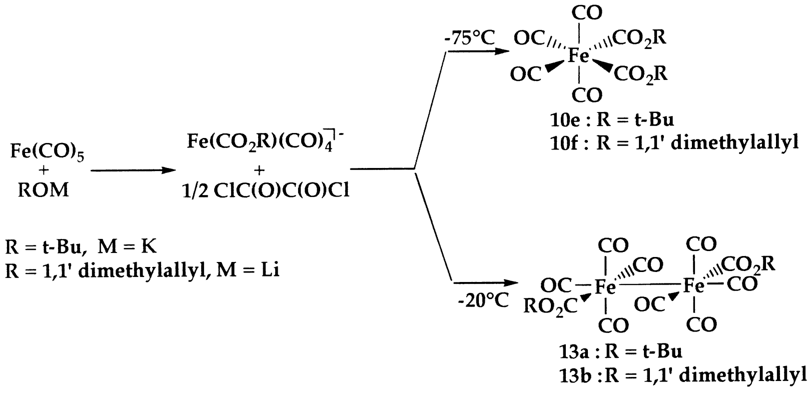
According to this pathway, reactions of oxalyl chloride on the ferrates are supposed to afford dicarbonyl monobridged complexes **11**, iron analogous to the products of the reactions between oxalylchloride and the anions $[M(CO)_5]^-$, M = Mn, Re [107]. Monocarbonyl monobridged complexes **12** would then be formed by decarbonylation of **11** and after rearrangement would give rise to $Fe(CO)_5$ and $Fe(CO_2R)_2(CO)_4$ **10**.

The next example will show that the reality of the intervention of a di- and a monocarbonyl monobridged complex cannot be precluded.

4.3.1.2. By reaction of oxalyl chloride with ferrates bearing bulky alkoxycarbonyl ligands. When the process described in Eq. (12) is performed with bulky alcoholates as reagents, the nature of the final products depends on the temperature of the reaction [Eq. (15)] [108].

With addition of oxalyl chloride to ferrates at −20 °C, new complexes (**13**) are formed. Their IR and NMR data and a crystallographic study of **13a** reveal that these complexes display a dimeric structure formed by two $Fe(CO_2R)(CO)_4$ entities linked by their metal centre. Their alkoxycarbonyl ligands are *cis* to the metal–metal bond and they present no bridging ligands.

Complexes **13a** and **13b** are of importance: only a few dimers without bridging ligands and displaying one organic ligand on each metal centre have been described. $Os_2H_2(CO)_8$ [109] and $Os_2(Me)_2(CO)_8$ [110] are stable but several attempts to realize



(15)

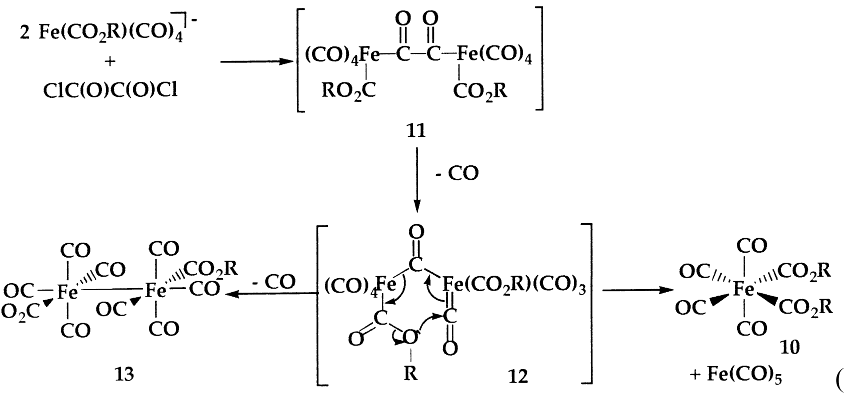
the preparation of $(CO)_4[C(O)Me]Fe–Fe[C(O)Me](CO)_4$ by addition of MeCOCl to $[Fe_2(CO)_8]^{2-}$ failed [111].

The only compound isoelectronic to **13** which displays two alkoxycarbonyl ligands is $[Ru(CO_2Me)(CO)_2(bipyridine)]_2$ [112]. However, its two alkoxycarbonyl ligands are *trans* to the metal–metal bond.

When reaction (15) is performed at −78 °C, bis alkoxycarbonyl monomers **10d** and **10e** are the only products of the process.

A crystallographic study of **10e** has been realized [104].

These results strongly suggest that the formation of bis alkoxycarbonyl monomers or dimers by reaction of oxalyl chloride on alkoxycarbonyl ferrates occurs via the monocarbonyl monobridged intermediate **12** which either after rearrangement gives rise to **10** or after decarbonylation affords **13** [Eq. (16)]:

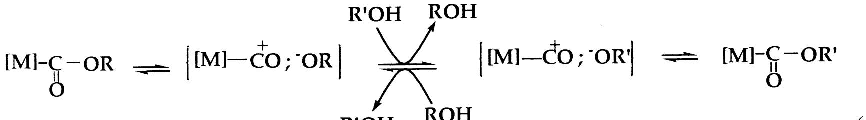


(16)

4.3.2. Properties of iron bis alkoxycarbonyl complexes

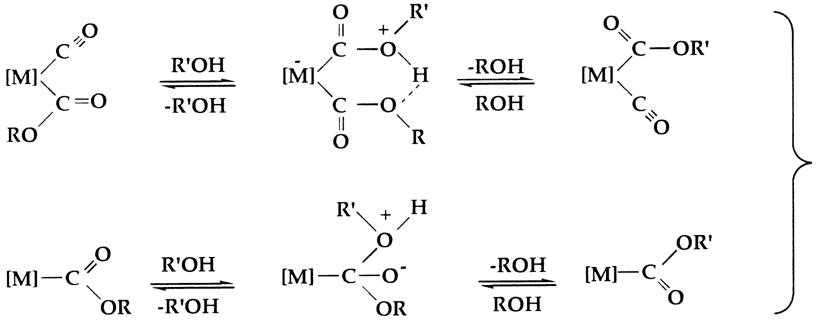
4.3.2.1. The "mobility" of their alkoxy groups. A well-known property of alkoxycarbonyl ligands is their easy transesterification under very mild conditions. Thus a methoxycarbonyl ligand is rapidly converted into the corresponding ethyl ester upon treatment with ethanol without added acid or base catalyst in contrast to the transesterification of organic esters. This process has been observed for a wide range of alkoxycarbonyl complexes: Pt [113], Re [114], Ir [115], Mn [116,117], Ru [118] and Fe [116,117,119,120].

However, the mechanism of this reaction remains unclear. Depending on the nature of the metal centre or on the electronic effects of the ancillary ligands, two different pathways have been suggested. A dissociative mechanism [Eq. (17)] has been postulated for the exchange reactions observed on rhenium: ReCp(NO)(CO_2Me)L, L = CO, PPh_3 [114] or on iron complexes: FeCp (CO_2menthyl)(CO)(PPh_3) [116,117] whose homologues FeCp[C(O)R](CO)(PPh_3), R = OMe, OPh, SMe, SPh, exhibit spontaneous ionization in polar solvents [119,120].

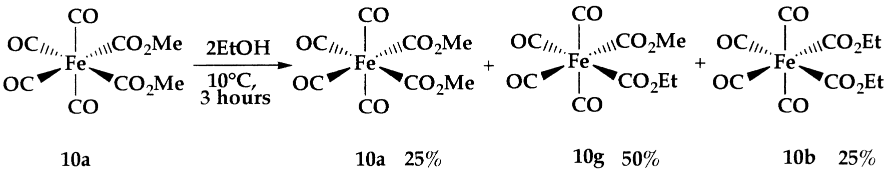


(17)

On the other hand, associative routes where a nucleophilic attack of alcohol occurs prior to the elimination of the alkoxy group have been proposed for Mn(Cp)(NO)(CO_2menthyl)$(CO)_2$(PPh_3) [116,117] or Ru$(CO_2Me)_2(CO)_2$(dppe)[2] [118]. However, little has been done to determine the site of the nucleophilic attack on the complex (terminal CO or carbonyl of the alkoxycarbonyl [Eq. (18)]):



(18)



(19)

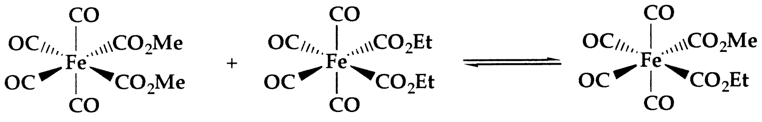
The mobility of the alkoxy groups of complexes **10** is evidenced by rapid exchanges with alcohols or with dialkyl oxalates. Thus **10a** reacts rapidly with two equivalents

---

[2] dppe = ethylene bis diphenylphosphine.

of ethanol or with one mole of diethyl oxalate to afford a statistical mixture of **10a**: 25%, **10b**: 25% and $Fe(CO_2Me)(CO_2Et)(CO)_4$ **10g**: 50% [Eq. (19)]:

The same mixture is obtained when equal quantities of **10a** and **10b** are mixed in CH_2Cl_2 at 10 °C [Eq. (20)]:

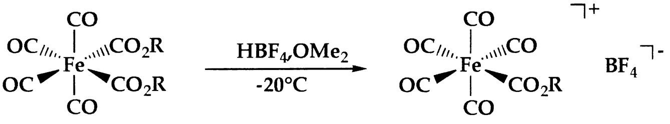


10a 25% **10b** 25% **10g** 50%

(20)

This last result can explain our unsuccessful attempts to isolate pure **10g** as this complex probably evolves toward the equilibrium of Eq. (20).

The mechanism of exchange reactions — Contrary to $FeCp[C(O)R](CO)(PPh_3)$ (R=OMe, OPh, SMe, SPh) [119,120], complexes **10** do not undergo spontaneous dissociation even in solution in polar solvents. However, we showed that **10** loses one alkoxy group by reaction with strong nucleophiles (HBF_4) [Eq. (21)] [121]:



10

14a : R = Me
14b : R = Et
14c : R = t-Bu

(21)

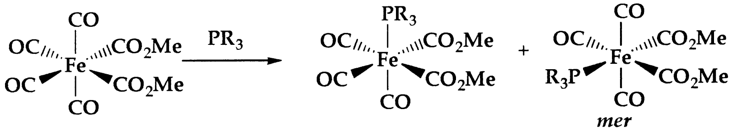
Compounds **14** represent the second example of cationic complexes bearing an alkoxycarbonyl carbonyl ligand after $[CoCp(CO_2Me)(CO)(PPh_3)]^+$ [98] which has already been described.

Though these last results indicate that spontaneous dissociation does not occur on complexes **10**, they do not preclude the intervention of a dissociative mechanism in the exchange reactions observed for these compounds. In order to get more information about this mechanism, we have prepared bis alkoxycarbonyl complexes of higher electron density than **10** by substitution of one CO ligand of **10a** by different phosphanes.

Indeed, an increase of the electron density of the metal centre is expected to favour a dissociative pathway [122] and to make the nucleophilic attack of the associative mechanism more difficult. The preparation of monophosphane bis alkoxycarbonyl complexes occurs by heating a CH_2Cl_2 solution of complex **10a** in the presence of the appropriate phosphane for 24 h at 28 °C. After recrystallization the yield of $Fe(CO_2Me)_2(CO)_3(PR_3)$ is about 40% [Eq. (22)] [79].

The substitution of one terminal carbonyl of **10a** by PMe_3 affords 95% of **15a** (isomer *fac*) while the same reaction realized with PPh_3 or $P(OEt)_3$ gives rise to 100% of the *mer* isomers of **15b** or **15c**.

Careful monitoring of the early stages of these reactions of substitution realized



10a

fac

R = Me **15a** : 95%

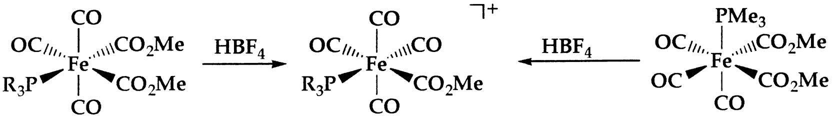
mer

R = Me **15'a** : 5%
R = Ph **15b**
R = OEt **15c**

(22)

by ^{31}P NMR have not revealed the transitory formation of the *fac* isomers of **15b** or **15c** or any change in the relative proportions of complexes **15a** and **15a**′. As the primary product of the reaction of substitution of one CO of $Fe(CO_2Me)_2(CO)_4$ by a phosphane is expected to be the *fac* compound [123,124], the rapid formation of **15b** and **15c** leads us to assume that, at 28 °C, rapid isomerization between *fac* and *mer* isomers could occur. These processes possibly occur via methoxy hopping from one CO to another as proposed for the ruthenium homologues [118].

Like **10**, phosphane complexes **15a**, **15b** or **15c** do not display spontaneous dissociation in polar solvents. However, by reaction with HBF_4 they easily give rise to cationic compounds **16** [Eq. (23)]:



15b : R = Ph
15c : R = OEt

16a : R = Me
16b : R = Ph
16c : R = OEt

15a

(23)

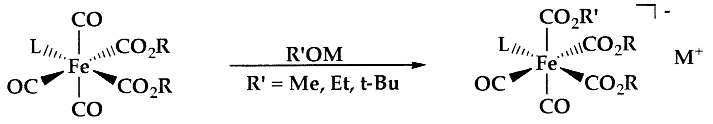
The specific formation of **16b** and **16c** indicates that a phosphane ligand induces the dissociation of the alkoxycarbonyl *trans* to itself. Whereas this enhanced mobility should favour a *trans* esterification process realized via a dissociative mechanism, complexes **15a** or **15b** are unreactive towards alcohols even at room temperature. Only **15c** undergoes a slow *trans* esterification reaction (24 h at 30 °C).

These last results strongly suggest that the exchange reactions observed on complexes **10** occur via an associative mechanism. This mechanism involves, prior to the dissociation of the alkoxy group, a nucleophilic attack of alcohol on a carbonyl of the compound. On complex **10**, this addition can occur either on a terminal carbonyl or on an alkoxycarbonyl itself.

Determination of the site of nucleophilic addition on iron bis alkoxycarbonyl complexes — When a complex displays no terminal CO, nucleophilic additions can occur on the alkoxycarbonyl ligands [125]. It has also been proven that for complexes bearing acyl and CO ligands the same addition is specifically realized on the CO [35]. However, since alkoxycarbonyl ligands are more electrophilic than acyl ones, a nucleophilic addition of alcohols on their carbonyl cannot be precluded.

To our knowledge only one example of nucleophilic addition of alcoholate on a complex bearing terminal CO and alkoxycarbonyl ligands has been described: complex $Co(CO_2Me)(CO)_4$ by reaction with MeO^- affords the anion $[Co(CO_2Me)_2(CO)_3]^-$ formally formed by addition of MeO^- on a terminal CO [97]. However, due to the same nature of the alcoholate and the alkoxy group, a rapid exchange resulting from an attack of the alcoholate on the alkoxycarbonyl ligand cannot be dismissed.

Similar reactions realized on complexes **10a–e** led us to synthesize a series of new *tris* alkoxycarbonyl anions [Eq. (24)] [126]:



10a : R = Me, L = CO
10e : R = t-Bu, L = CO
15c : R = Me, L = $P(OEt)_3$

17a : R = R' = Me, L = CO, M = Na
17b : R = R' = t-Bu, L = CO, M = K
17c : R = Me, R' = t-Bu, L = CO, M = K
17d : R = t-Bu, R' = Me, L = CO, M = Na
17e : R = Me, R' = Et, L = CO, M = Na
17f : R = R' = Me, L = $P(OEt)_3$, M = Na

(24)

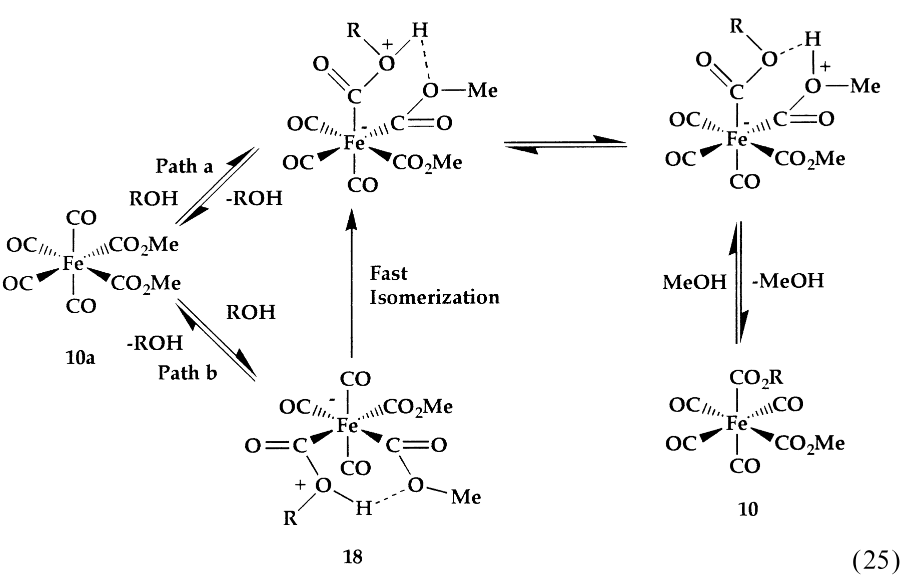
All these complexes present a *fac* geometry of their alkoxycarbonyl ligands. This geometry is attributed to these compounds according to their IR and NMR data; it has been confirmed by the crystallographic study of **17b**.

Specific formation of complexes **17c**, **17d**, and **17e** demonstrate that nucleophilic additions of alcoholates occur specifically on a terminal CO since fast nucleophilic attack of alcoholates on alkoxycarbonyl ligands would induce the formation of complex mixtures composed of $[Fe(CO_2R)_3(CO)_3]^-$, $[Fe(CO_2R)_2(CO_2R')(CO)_3]^-$, $[Fe(CO_2R)(CO_2R')_2(CO)_3]^-$ and $[Fe(CO_2R')_3(CO)_3]^-$.

Tris alkoxycarbonyl complexes have never been described previously; nevertheless, they are close to the *tris* acyl dianions $\{M[C(O)R]_3(CO)_3\}^{2-}$ formed by addition of an excess of alkyl lithium on $M[C(O)R](CO)_5$, M = Mn, Re [66,127].

Probably due to the strong electron donor effect of their phosphorus ligand, no reaction is observed by addition of RONa to the phosphine complexes $Fe(CO_2Me)_2(CO)_3L$, $L = PMe_3$: **15a**, $L = PPh_3$: **15b**. However, the reaction occurs on complex **15c**: $L = P(OEt)_3$, affording the phosphite anion **17f**. Exchange reactions are only observed for complexes which undergo nucleophilic addition of alcoholate on one terminal CO. These results suggest the following mechanism for the *trans* esterification of **10a** [Eq. (25)].

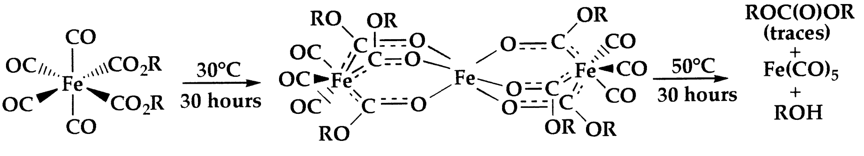
The process is associative, it includes an addition of alcohol on a terminal CO prior to the elimination of the alkoxy group of one alkoxycarbonyl ligand. When addition of alcohols occurs on an equatorial CO (path b), the reaction affords probably the *mer tris* alkoxycarbonyl intermediate **18**. However, this intermediate bearing two ligands of strong *trans* influence in *trans* position probably undergoes a fast isomerization, giving rise to its *fac* isomer which displays the same geometry as anions **17**.



(25)

4.3.2.2. Thermal properties of bis alkoxycarbonyl iron complexes. (a) *Thermolysis of the mononuclear complexes* — We already mentioned that most bis alkoxycarbonyl complexes described in the literature do not thermally induce the formation of oxalates by carbon–carbon coupling but afford dialkylcarbonates and alcohols (see Section 4.3). Consistent with these observations, thermolysis of $Fe(CO_2R)_2(CO)_4$ **10** afford alcohols, traces of dialkylcarbonates and $Fe(CO)_5$.

Careful control of these reactions allowed us to isolate and characterize a new series of intermediates: the iron hexa alkoxycarbonyl trimers **19** [Eq. (26)] formed at 30 °C in ca. 70% yield [104]:



19a : R = Me
19b : R = Et
19c : R = i-Pr
19d : R = allyl
19e : R = t-Bu

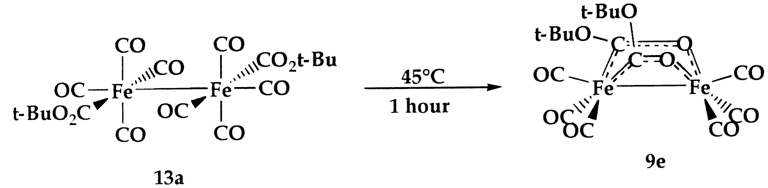
(26)

Complex **19d** has been structurally characterized. These compounds **19** can be considered as two anionic entities $[Fe(CO_2R)_3(CO)_3]^-$ linked by the oxygen of the carbonyl of their alkoxycarbonyl ligands to a central Fe^{2+}. They can be compared to $\{Re[C(O)Me]_2[RC(O)](CO)_3\}_2M$, M = Zr, Hf, described by Lukehart and coworker [127,128]. Complexes **19** are the first characterized intermediates in the thermolysis of bis alkoxycarbonyl complexes. When heated at 50 °C, they give $Fe(CO)_5$, alcohols and traces of dialkylcarbonates.

(b) *Thermolysis of the binuclear bis alkoxycarbonyl complex* $[Fe(CO_2{}^tBu)(CO)_4]_2$ ***13a*** — Bimetallic complexes bearing an organic ligand on each metal centre are of importance since they forge a link between mononuclear complexes used in homogeneous catalysis and polynuclear clusters which may be used as models for heterogeneous catalysts. Studies of carbon–carbon coupling induced by such compounds are not numerous. Very often, due to the presence of bridging ligands on the complexes, the two organic entities are not close enough to induce concerted carbon–carbon coupling and the observed reactions then occur via radical formation [129,130].

Since complex **13a** exhibits two alkoxycarbonyl ligands *cis* to the iron–iron bond, direct coupling between these two ligands cannot be precluded.

When heated for 1 h at 45 °C, **13a** specifically affords the complex **9e** already obtained by monoelectronic oxidation of $[Fe(CO_2{}^tBu)(CO)_4]^-$ (see Section 4.3) [Eq. (27)]:



13a **9e** (27)

This process formally involves the migration of an alkoxycarbonyl ligand from one metal centre to the other and, for this reason, can provide a model for the study of the migration of carbonylated ligands on a metal surface.

To our knowledge this reaction has never been observed for alkoxycarbonyl complexes but only for acyl [105,131–134] or allyl [135–138] bimetallic compounds. Further work to gain mechanistic information about this migration is in progress.

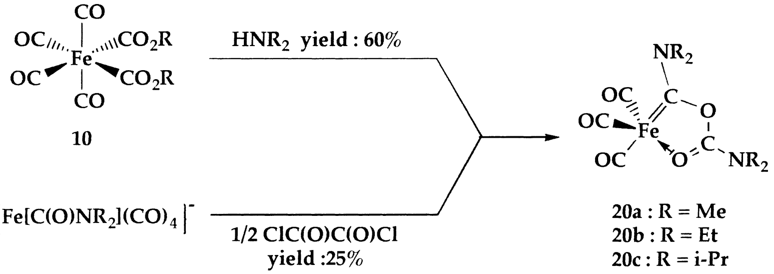
Though thermal decomposition of acyl homologues of **9e** is known to induce the formation of mono- or diketones [81], probably via a diketonic complex [139], further thermolysis of complex **9e** has only afforded $Fe(CO)_5$ and ^tBuOH.

4.4. *Bis carbamoyl iron complexes*

Though carbamoyl ligands are very easily prepared, either by nucleophilic addition of amines on terminal carbonyl [39] or by alkoxy/amine exchange on alkoxycarbonyl ligands [140], only two bis carbamoyl complexes have been structurally characterized [141,142].

Two different procedures were supposed to allow the synthesis of $Fe[C(O)NR_2]_2(CO)_4$: (1) the alkoxy/amine exchange with $Fe(CO_2R)_2(CO)_4$ **10**; and (2) the action of 1/2 equivalent of oxalyl chloride on the carbamoyl ferrates $\{Fe[C(O)NR_2](CO)_4\}^-$.

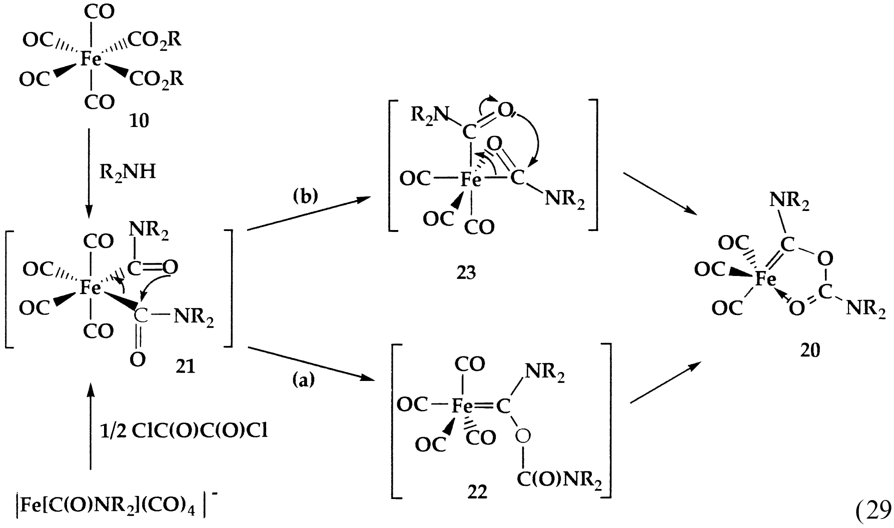
These two reactions occurring for $NR_2=NMe_2$, NEt_2 or $NiPr_2$ afford the same type of complex which exhibit the carbenic metallacyclic structure displayed in Eq. (28) [104]:



(28)

20b, which has been characterized structurally, is found to present a quasi-planar five-membered metallacycle.

Though bis carbamoyl complexes have never been found to induce the formation of such carbenic compounds, it is highly probable that formation of complexes **20** occurs via the bis carbamoyl intermediates **21** [Eq. (29)]:

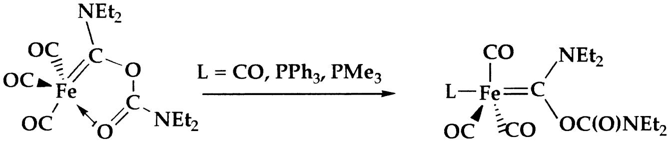


(29)

Two reaction pathways may explain the formation of carbenes **20** from bis carbamoyl intermediates **21**. Path (a) requires an initial nucleophilic attack of the oxygen of a carbamoyl on the carbon of the carbonyl of the second carbamoyl. This would be followed by a rearrangement which is supposed to afford carbenes **22** whose decarbonylation gives rise to metallacyclic carbenes **20**. According to path (b) the decarbonylation would occur prior to the nucleophilic attack affording the η_2 carbamoyl intermediate **23**, which after addition of the oxygen of the η_1 carbamoyl on the carbon of the carbonyl of the η_2 carbamoyl and rearrangement would afford **20**.

Later we will see that carbenes **22** are stable under the reaction conditions; path (b) then represents the more likely route for the formation of **20** from **21**. Further work is in progress to confirm the formation of the intermediate η_2 carbamoyl **23**.

To our knowledge these results constitute the first example of evolution of bis carbamoyl complexes into metallacyclic carbenes. Though less numerous than other metal carbenes, iron carbenes are well known [143]. $Fe[C(NiPr_2)OC(O)Et](CO)_3$, whose structure is very close to that of **20**, has been characterized structurally [144]. This complex, which is a side product of a classical Fischer type reaction, is formed in very low yield and has not been studied. Since coordination between neutral iron complexes and oxygen atoms is generally weak, the η_2 carbene ligand of complexes **20** can be considered as a potential hemilabile ligand. Indeed, complex **20b** reacts rapidly with CO or phosphines to afford the non-cyclic carbenes **24** [Eq. (30)]:



20b

24a : L = CO
24b : L = PPh_3
24c : L = PMe_3

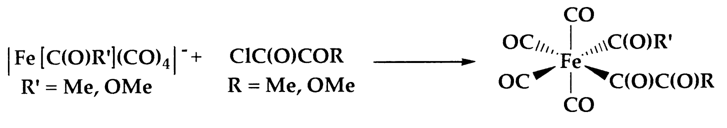
(30)

Complexes **24** are stable even in the absence of added phosphines or under inert atmosphere.

5. Potential models for tricarbonyl chaining

Stoichiometric or catalytic triple carbonylation processes inducing the formation of tricarbonyl organic compounds have never been described. However, a series of platinum complexes: *cis* $Pt[C(O)C(O)R][C(O)R'](PPh_3)_2$, has been designed to study the possibility of such a reaction from well-characterized complexes. This attempt was not successful since thermolysis of these complexes afforded *trans* diacyl– or acyl–alkoxycarbonyl complexes after decarbonylation of their α ketoacyl or alkyloxalyl ligands [61].

In order to check the possible occurrence of carbon–carbon coupling induced by iron complexes of a similar type, we prepared the $Fe[C(O)C(O)R][C(O)R'](CO)_4$ series by reaction of $\{Fe[C(O)R'](CO)_4\}^-$ anions with $ClC(O)C(O)R$ [Eq. (31)] [145]:



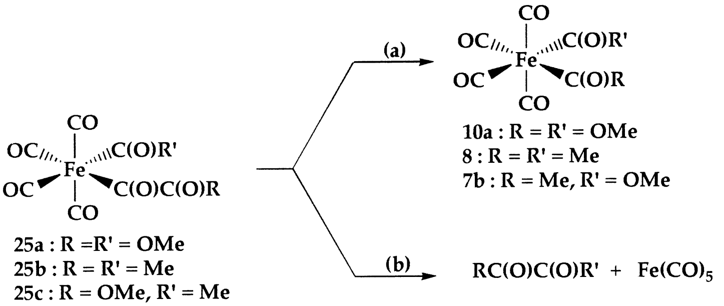
25a : R = R' = OMe
25b : R = R' = Me
25c : R = OMe, R' = Me
25d : R = Me, R' = OMe

(31)

The yield of these reactions varies from 30% (**25a**) to 55% (**25d**).

With these complexes, exchange reactions with alcohols are only observed for the alkoxycarbonyl directly linked to the metal centre and not for the ester group of alkoxycarbonyl ligands.

25a and **25b**, which display an alkoxycarbonyl ligand, decompose respectively at 25 and 15 °C. They are more stable than their acyl homologues which undergo thermal decomposition at 0 °C. Complexes **25a**, **25b** and **25c** decompose thermally according to two different routes [Eq. (32)]:



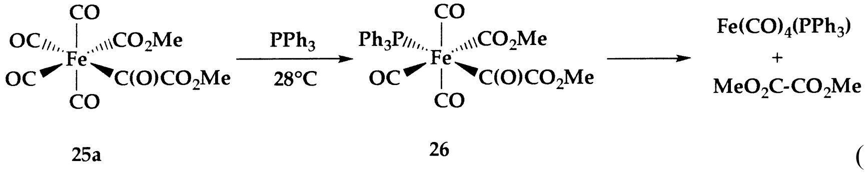
(32)

Path (a) consists of a decarbonylation reaction affording bis alkoxycarbonyl (**10a**), acyl–alkoxycarbonyl (**7b**) or bis acyl (**8**) complexes. Decarbonylation of **25b** is the only method of preparation of the bis acyl compound **8** (see Section 4.2.1).

According to path (b), **25a**, **25b** and **25c** afford $Fe(CO)_5$ and a dicarbonylated organic compound: RC(O)C(O)R′ (dimethyl oxalate, methyl pyruvate or butanedione). The formation of these last products formally results from a carbon–carbon coupling between a carbonyl α to the metal (on the acyl or on the alkoxycarbonyl ligands) and a second carbonyl in the β position on the dicarbonylated ligand (alkyloxalyl or pyruvoyl).

The ratio between the two processes (a) and (b) varies from 85% decarbonylation and 15% oxalate formation for **25a** to 65% decarbonylation and 35% oxalate formation for **25c**.

Since no α, β dicarbonyl organic compounds are formed by thermolysis of complexes **10a**, **8** and **7b** [see Section 4.2.1 (**8**), Section 4.2.2 (**7b**) and Section 4.3.2.2 (**10a**)], the observed reactions are undoubtedly the result of decomposition of **25**. When the thermolysis is performed under CO pressure, the rate of the two processes is reduced dramatically. Furthermore, thermolysis of **25a** occuring in the presence of one equivalent of PPh_3 affords the phosphine complex **26** which itself induces at 28 °C the quantitative formation of oxalate [Eq. (33)] [145]:

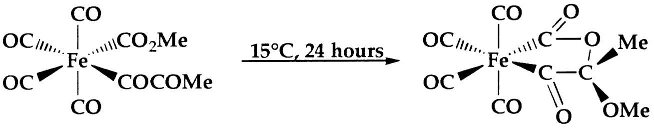


(33)

These last results strongly suggest that the formation of RC(O)C(O)R′ by thermal decomposition of complexes **25** could occur via the formation of a pentacoordinated intermediate formed by decoordination of a terminal CO.

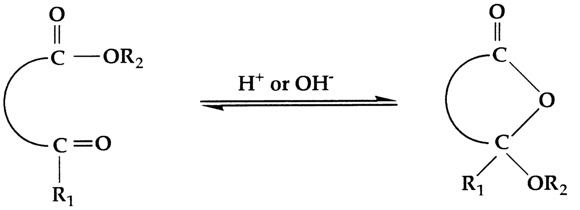
To our knowledge complexes **25** and **26** are the first well-characterized complexes displaying the [M][C(O)R][C(O)C(O)R′] pattern whose decomposition affords dicarbonyl organic products in reasonable yield.

Surprisingly, complex **25d** when heated under the same conditions as **25a**, **25b** and **25c** does not afford decarbonylation or carbon–carbon coupling but isomerizes into the metalla methoxy ketolactone **27a** [Eq. (34)] [146]:



25d **27a** (34)

The formation of **27a**, which has been structurally characterized, results from a chain–ring isomerization analogous to those observed in organic chemistry for γ ketoesters [Eq. (35)] [147]:



(35)

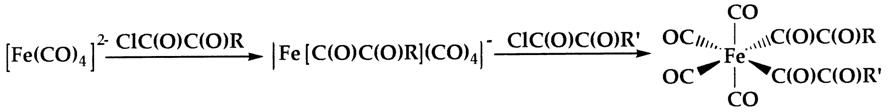
Complex **25d** can be considered as a γ ketoester which possesses a metal inserted in the chain connecting the two carbonylated groups. Contrary to the reaction observed for organic γ ketoesters, the isomerisation of **25d** is irreversible and does not require any catalyst. Since this cyclisation is not observed for **25c**, $Fe[C(O)CO_2Me][C(O)Me](CO)_4$, which is also a metalla γ ketoester, it is clear that the isomerization is made possible by the specific properties of the alkoxycarbonyl ligand displayed by **25d**. The proximity of this ligand to the metal increases the nucleophilic character and the mobility of its alkoxy group which can migrate to the ketonic carbon. The rate of the reaction is greatly enhanced in methanol, this last result suggests that the mechanism of this cyclisation could be of associative type.

To our knowledge reaction (33) represents the first example of cyclisation of a γ ketoester with a metal inserted in the bridge between the two organic groups.

6. Potential models for tetracarbonyl chaining

Complexes which can be considered as model compounds for the study of the tetracarbonylation reaction and which should display the

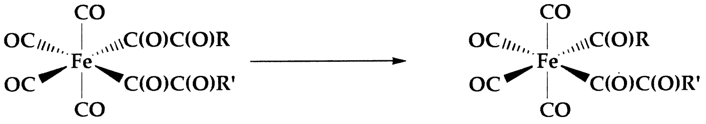
[M][C(O)C(O)R][C(O)C(O)R′] pattern have never been described. Our work gave us the possibility of preparing such iron complexes by reaction of $[Fe(CO)_4]^{2-}$ with pyruvoyl chloride or alkyloxalyl chloride [Eq. (36)] [79,145]:



28a : R = R' = OMe, 40% yield
28b : R = R' = Me, 20% yield
28c : R = OMe, R = Me, 25% yield

(36)

Surprisingly, these complexes are found relatively stable; they evolve between 10 °C and 15 °C giving rise to complexes **25a**, **25b** and **25d** by decarbonylation reactions [Eq. (37)] [145]. At these temperatures no carbon–carbon coupling is observed.



28a : R = R' = OMe
28b : R = R' = Me
28c : R = OMe, R' = Me

25a : R = R' = OMe
25b : R = R' = Me
25c : R = OMe, R' = Me

(37)

As expected, decarbonylation of the alkyloxalyl of **28c** occurs more rapidly than that of the pyruvoyl ligand, affording specifically **25d**. This result confirms that ligands bearing electron-withdrawing groups undergo easy decarbonylation [35].

7. Conclusion

Specific synthetic methods for the preparation of *cis* bis substituted iron complexes have been developed. Since these compounds display the *cis* $[Fe][(CO)_xR][(CO)_yR']$ pattern they are good models for the study of carbon–carbon coupling processes with octahedral complexes. Studies of the reactivity of these complexes have confirmed that carbon–carbon coupling reactions between two ligands linked to the metal centre via two sp^3 or two sp^2 carbons (carbonyl groups) are difficult to realize, contrary to the same reductive elimination between an sp^3 and an sp^2 carbon, which occurs readily.

The model compounds for the dicarbonylation: $x=y=1$, are found unable to thermally induce such a process. Nevertheless, bis alkoxycarbonyl and bis carbamoyl complexes afford respectively original trimeric clusters and metallacyclic carbenes.

Model compounds for the tricarbonylation: $x=2$, $y=1$, give rise to bis carbonylated organic compounds except the metalla γ ketoester

$Fe(CO_2Me)[C(O)C(O)Me](CO)_4$ which undergoes isomerization into a metalla ketolactone.

Finally, the first models for the tetracarbonylation were prepared, but they only undergo decarbonylation reactions.

References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.C. Finke, Principles and Applications of Organotransition Metal Chemistry, University Sciences Books, Mill Valley, CA, 1987.
[2] A. Gillie, J.K. Stille, J. Am. Chem. Soc. 102 (1980) 4933.
[3] J.M. Brown, N.A. Cooley, Chem. Rev. 88 (1988) 1031.
[4] J.S. Thompson, J.D. Atwood, Organometallics 10 (1991) 3525.
[5] F. Ozawa, K. Kurihara, M. Fujimoro, T. Hikada, T. Toyoshima, A. Yamamoto, Organometallics 8 (1989) 180.
[6] K. Tatsumi, R. Hoffman, A. Yamamoto, J.K. Stille, Bull. Chem. Soc. Jpn. 54 (1981) 1857.
[7] T. Yamamoto, A. Yamamoto, S. Ikeda, J. Am. Chem. Soc. 97 (1971) 3350.
[8] P.S. Braterman, R.J. Cross, G.B. Young, J. Chem. Soc., Dalton Trans. (1976) 1310.
[9] P.S. Braterman, R.J. Cross, G.B. Young, J. Chem. Soc., Dalton Trans. (1977) 1892.
[10] S. Komiya, Y. Abe, A. Yamamoto, T. Yamamoto, Organometallics 2 (1983) 1466.
[11] W. Lau, J.C. Huffman, J.K. Kochi, Organometallics 1 (1982) 155.
[12] J. Chatt, B.L. Shaw, J. Chem. Soc. (1961) 285.
[13] A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, A. Misino, J. Am. Chem. Soc. 90 (1968) 1878.
[14] H.H. Karsch, Chem. Ber. 116 (1983) 1656.
[15] S. Komiya, M. Katom, T. Ikariya, R.H. Grubbs, T. Yamamoto, A. Yamamoto, J. Organomet. Chem. 260 (1984) 115.
[16] W.K. Wong, K.W. Chiu, G. Wilkinson, A.J. Howes, M. Motevalli, M.B. Hursthouse, Polyhedron 4 (1985) 603.
[17] G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thorton-Pett, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1985) 1339.
[18] E. Lindner, E.S. Schauss, W. Hiller, R. Fawzi, Angew. Chem., Int. Ed. Engl. 23 (1984) 711.
[19] D. Navarre, H. Rudler, J.C. Daran, J. Organomet. Chem. 314 (1986) C34.
[20] T.A. Manuel, S.L. Stafford, P.M. Treichel, F.G.A. Stone, J. Am. Chem. Soc. 83 (1961) 249.
[21] H.H. Hoehn, L. Pratt, K.F. Watterson, G. Wilkinson, J. Chem. Soc. (1961) 2738.
[22] D.W. Hensley, R.P. Stewart, Inorg. Chem. 17 (1978) 905.
[23] I.I. Guerus, Y.L. Yagupol'skii, J. Organomet. Chem. 247 (1983) 81.
[24] I.I. Guerus, Y.L. Yagupol'skii, S.I. Vdovenko, Zh. Org. Khim. 21 (1985) 145.
[25] W. Ducat, D. Naumann, J. Chem. Soc., Dalton Trans. (1989) 739.
[26] R.G. Finke, T.N. Sorrel, Org. Synth. 59 (1980) 808.
[27] J.P. Collman, Acc. Chem. Res. 8 (1975) 342.
[28] G. Tanguy, B. Weinberger, H. des Abbayes, Tetrahedron Lett. 24 (1983) 4005.
[29] P. Laurent, G. Tanguy, H. des Abbayes, J. Chem. Soc., Chem. Commun. (1986) 1754.
[30] P. Laurent, S. Sabo-Etienne, A.M. Larsonneur, H. des Abbayes, J. Chem. Soc., Chem. Commun. (1988) 929.
[31] P. Laurent, Ph.D. Dissertation, Université de Bretagne Occidentale, Brest, France, 1989.
[32] J.T. Chen, T.-M. Huang, M.-C. Cheng, Y. Wang, Organometallics 9 (1990) 539.
[33] B. Chamberlain, R.J. Mawby, J. Chem. Soc., Dalton Trans. (1991) 2067.
[34] D.R. Saunders, R.J. Mawby, J. Chem. Soc., Chem. Commun. (1984) 140.
[35] C.P. Casey, D.M. Scheck, J. Am. Chem. Soc. 102 (1980) 2723.
[36] K.I. Goldberg, R.G. Bergman, J. Am. Chem. Soc. 111 (1989) 1285.
[37] D.W. Hensley, W.L. Wurster, R.P. Stewart, Inorg. Chem. 20 (1981) 645.

[38] B. Denise, D. Navarre, H. Rudler, J.C. Daran, J. Organomet. Chem. 375 (1989) 273.
[39] P.C. Ford, A. Rokicki, Adv. Organomet. Chem. 28 (1988) 139.
[40] P.C. Ford, Acc. Chem. Res. 14 (1981) 31.
[41] M.A. Bennett, J. Mol. Catal. 41 (1987) 1.
[42] M. Yamashita, K. Mizushima, Y. Watanabe, T. Mitsudo, Y. Takegami, Chem. Lett. (1977) 1355.
[43] G.C. Tustin, R.T. Hembre, J. Org. Chem. 49 (1984) 1761.
[44] H.E. Bryndza, Organometallics 4 (1985) 1686.
[45] M.A. Bennett, A. Rokicki, Organometallics 4 (1985) 180.
[46] I. Torresan, R.A. Michelin, A. Marsella, A. Zanardo, F. Pinna, G. Strukul, Organometallics 10 (1991) 623.
[47] I. Toth, C.J. Elsevier, J. Chem. Soc., Chem. Commun. (1993) 529.
[48] W. Petz, Organometallics 2 (1983) 1044.
[49] J.L. McLean, Ph.D. Dissertation, City University of New York, 1975.
[50] R.J. Trautman, D.C. Gross, P.C. Ford, J. Am. Chem. Soc. 107 (1985) 2355.
[51] R. Perron, French Patent No. 2297200, 1975.
[52] H. Alper, H. des Abbayes, J. Organomet. Chem. 134 (1977) C11.
[53] H. des Abbayes, A. Buloup, J. Chem. Soc., Chem. Commun. (1978) 1090.
[54] M. Foa, F. Francalanci, J. Mol. Catal. 41 (1987) 89.
[55] A. Yamamoto, F. Ozawa, K. Osakada, L. Huang, T.I. Son, N. Nawasaki, M.K. Doh, Pure Appl. Chem. 63 (1991) 687 and references cited therein
[56] J.B. Sheridan, S.H. Han, G.L. Geoffroy, J. Am. Chem. Soc. 109 (1987) 8097.
[57] D.J. Stuffens, J.B. Sheridan, G.L. Geoffroy, Inorg. Chem. 29 (1990) 4347.
[58] E.D. Dobrzynski, R.D. Angelici, Inorg. Chem. 14 (1975) 59.
[59] A. Sen, J.T. Chen, W.M. Vetter, R.R. Whittle, J. Am. Chem. Soc. 109 (1987) 148.
[60] J.T. Chen, T.M. Huang, M.C. Cheng, Y. Wang, Organometallics 10 (1991) 2838.
[61] J.T. Chen, Y.S. Yeh, C.S. Yang, F.Y. Tsai, G.L. Huang, B.C. Shu, T.M. Huang, Y.S. Chen, G.H. Lee, M.C. Cheng, C.C. Wang, Y. Wang, Organometallics 13 (1994) 4804.
[62] S. Sabo-Etienne, A.M. Larsonneur, H. des Abbayes, J. Chem. Soc., Chem. Commun. (1989) 1671.
[63] C.P. Casey, D.M. Scheck, J. Am. Chem. Soc. 102 (1980) 2728.
[64] C.P. Casey, C.A. Bunnel, J. Chem. Soc., Chem. Commun. (1974) 733.
[65] C.P. Casey, C.A. Bunnel, J. Am. Chem. Soc. 98 (1976) 436.
[66] D. Drew, M. Darensbourg, D.J. Darensbourg, J. Organomet. Chem. 85 (1975) 73.
[67] C.M. Lukehart, G.P. Torrence, J.V. Zeile, Inorg. Chem. 15 (1976) 2393.
[68] C.P. Casey, L. Baltusis, J. Am. Chem. Soc. 104 (1982) 6347.
[69] G.L. Huang, T.M. Huang, J.T. Chen, Inorg. Chem. 31 (1992) 4034.
[70] F.R. Pettersen, J.L. Cihonsky, F.R. Young, R.A. Levenson, J. Chem. Soc., Chem. Commun. (1975) 370.
[71] F.R. Young, D.H. O'Brien, R.C. Petersen, R.A. Levenson, D.L. Von Hinden, J. Organomet. Chem. 114 (1976) 157.
[72] F.W. Grewels, J. Buchkremer, E.A. Koerner Von Gustorf, J. Organomet. Chem. 111 (1976) 235.
[73] E. Hoffman, E. Weiss, J. Organomet. Chem. 128 (1977) 399.
[74] R. Victor, V. Usielli, S. Sarel, J. Organomet. Chem. 129 (1977) 387.
[75] S. Aime, L. Milone, E. Sappa, A. Tiripicchio, A.M. Manotti Lanfredi, J. Chem. Soc., Dalton Trans. (1979) 1664.
[76] M.H. Cheng, H.G. Shin, G.H. Lee, S.M. Peng, R.S. Liu, Organometallics 12 (1993) 108.
[77] K.J. Karel, T.H. Tulip, S.D. Ittel, Organometallics 9 (1990) 1276.
[78] C.M. Lukehart, J.V. Zeile, J. Am. Chem. Soc. 99 (1977) 4368.
[79] M. Sellin, Ph.D. Dissertation, Université de Bretagne Occidentale, Brest, France, 1995.
[80] E.O. Fischer, V. Kiener, J. Organomet. Chem. 23 (1970) 215.
[81] G. Sundanarajan, J. San Philippo Jr., Organometallics 4 (1985) 606.
[82] G. Sundanarajan, Organometallics 10 (1991) 1377.
[83] M. Tanaka, T.A. Kobayashi, T. Sakakura, J. Chem. Soc., Chem. Commun. (1985) 837.
[84] F. Ozawa, N. Kawasaki, H. Okamoto, T. Yamamoto, A. Yamamoto, Organometallics 6 (1987) 1640.

[85] L. Huang, F. Ozawa, A. Yamamoto, Organometallics 9 (1990) 2612.
[86] T.S. Huang, J.T. Chen, G.H. Lee, Y. Wang, Organometallics 10 (1991) 175.
[87] G.M. Kapteijn, M.J. Verhoef, M.A.F.H. Von Den Broek, D.M. Grove, G. Von Koten, J. Organomet. Chem. 503 (1995) C26.
[88] F. Ozawa, S. Chikaoka, X. Cao, A. Yamamoto, J. Organomet. Chem. 424 (1992) 173.
[89] D.M. Fenton, P.J. Steinwand, J. Org. Chem. 39 (1974) 701.
[90] F. Rivetti, U. Romano, J. Organomet. Chem. 154 (1978) 323.
[91] F. Rivetti, U. Romano, J. Organomet. Chem. 174 (1979) 221.
[92] F. Rivetti, U. Romano, Chim. Ind. 62 (1980) 7.
[93] B.E. Hanson, J.S. Merola, F.J. Waller, Organometallics 12 (1993) 568.
[94] K.V. Werner, W. Beck, Chem. Ber. 105 (1972) 3947.
[95] G. Vasopollo, L. Toniolo, G. Cavinato, F. Bigoli, M. Lanfranchi, M.A. Pellighelli, J. Organomet. Chem. 481 (1994) 173.
[96] G. Minghetti, F. Bonati, G. Banditelli, Synth. Inorg. Met.-Org. Chem. 3 (1973) 415.
[97] G. Fachinetti, T. Funaioli, D. Masi, C. Mealli, J. Organomet. Chem. 417 (1991) C32.
[98] H. Werner, L. Hofmann, R. Zolk, Chem. Ber. 120 (1987) 379.
[99] D. Milstein, J.L. Huckaby, J. Am. Chem. Soc. 104 (1982) 6150.
[100] P.L. Burk, D.V. Van Engen, K.S. Campo, Organometallics 3 (1984) 493.
[101] J.D. Gargulak, A.J. Berry, M.D. Noirot, W.L. Gladfelter, J. Am. Chem. Soc. 114 (1992) 8933.
[102] E.W. Evans, M.B.H. Howlader, M.T. Atlay, Inorg. Chim. Acta 230 (1995) 193.
[103] J.Y. Salaün, G. Le Gall, P. Laurent, H. des Abbayes, J. Organomet. Chem. 441 (1992) 99.
[104] D. Luart, Ph.D. Dissertation, Université de Bretagne Occidentale, Brest, France, 1997.
[105] C.M. Jensen, Y.J. Chen, H.D. Kaesz, J. Am. Chem. Soc. 106 (1984) 4046.
[106] E.O. Fischer, V. Kiener, J. Organomet. Chem. 27 (1971) C56.
[107] E.J.M. de Boer, J. de With, N. Meijboom, Organometallics 4 (1985) 259.
[108] D. Luart, M. Sellin, P. Laurent, J.Y. Salaün, R. Pichon, L. Toupet, H. des Abbayes, Organometallics 14 (1995) 4989.
[109] J.R. Moss, W.A.G. Graham, Inorg. Chem. 16 (1977) 75.
[110] K.M. Motyl, J.R. Norton, C.K. Schauer, O.P. Anderson, J. Am. Chem. Soc. 104 (1982) 7325.
[111] C.E. Summer, J.A. Collier, R. Pettit, Organometallics 1 (1982) 1350.
[112] S. Chardon-Noblat, A. Deronzier, D. Zsoldos, R. Ziessel, M. Haukko, T. Pakkanen, T. Vanälainen, J. Chem. Soc., Dalton Trans. (1996) 2581.
[113] H.C. Clark, K.R. Dixon, W.J. Jacobs, J. Am. Chem. Soc. 91 (1969) 1346.
[114] C.P. Casey, M.A. Andrews, D. McAllister, J.E. Rinz, J. Am. Chem. Soc. 102 (1980) 1927.
[115] P.J. Fraser, W.R. Roper, F.G.A. Stone, J. Organomet. Chem. 66 (1974) 155.
[116] H. Brunner, Angew. Chem., Int. Ed. Engl. 10 (1971) 249.
[117] H. Brunner, E.S. Schmidt, J. Organomet. Chem. 50 (1973) 219.
[118] J.D. Gargulak, W.L. Gladfelter, Organometallics 14 (1994) 698.
[119] N. Grice, S.C. Kao, R. Pettit, J. Am. Chem. Soc. 101 (1979) 1627.
[120] L.K. Liu, U.B. Eke, M.A. Mesubi, Organometallics 14 (1995) 3958.
[121] M.J. Fernandez, M.J. Roriguez, L.A. Oro, J. Organomet. Chem. 438 (1992) 337.
[122] A.R. Cutler, P.K. Hanna, J.C. Vites, Chem. Rev. 88 (1988) 1363.
[123] J.D. Atwood, T.L. Brown, J. Am. Chem. Soc. 98 (1976) 3160.
[124] D.L. Lichtenberger, T.L. Brown, J. Am. Chem. Soc. 100 (1978) 366.
[125] Y. Zhou, M.A. Dewey, J.A. Gladysz, Organometallics 12 (1993) 3918.
[126] M. Sellin, D. Luart, J.Y. Salaün, P. Laurent, L. Toupet, H. des Abbayes, Organometallics 15 (1996) 521.
[127] C.M. Lukehart, Acc. Chem. Res. 14 (1981) 109.
[128] D.T. Hobbs, C.M. Lukehart, Inorg. Chem. 18 (1978) 1247.
[129] R.G. Bergman, Acc. Chem. Res. 13 (1980) 113.
[130] K.W. Kranarz, R. Eisenberg, Organometallics 11 (1992) 1997.
[131] T. Adatia, K. Henrick, A.D. Horton, M.J. Mays, M. Mc. Partlin, J. Chem. Soc., Chem. Commun. (1986) 1206.
[132] P.V. Bonnensen, A.T. Baker, W.H. Hersh, J. Am. Chem. Soc. 108 (1986) 8304.

[133] B.D. Martin, S.A. Matchett, J.R. Norton, O.P. Anderson, J. Am. Chem. Soc. 107 (1985) 7952.
[134] B. Longato, B.D. Martin, J.R. Norton, O.P. Anderson, Inorg. Chem. 24 (1985) 1389.
[135] J.A. Beck, S.A.R. Knox, G.H. Riding, G.E. Taylor, M.J. Winter, J. Organomet. Chem. 202 (1980) C49.
[136] A.D. Clauss, M. Tachikawa, J.R. Shapley, E.G. Pierpont, Inorg. Chem. 20 (1981) 1528.
[137] A.F. Dyke, S.A.R. Knox, M.J. Morris, P.J. Naish, J. Chem. Soc., Dalton Trans. (1983) 1417.
[138] C.P. Casey, S.R. Marder, B.R. Adams, J. Am. Chem. Soc. 107 (1985) 7700.
[139] V. Kiener, E.O. Fischer, J. Organomet. Chem. 42 (1972) 447.
[140] R.J. Angelici, Acc. Chem. Res. 5 (1972) 335.
[141] K. Toman, G.G. Hess, Z. Kristallogr. 142 (1975) 35.
[142] J.D. Gargulak, W.L. Gladfelter, J. Am. Chem. Soc. 116 (1994) 3792.
[143] W. Petz, Iron Carbene Complexes, Springer, Berlin, 1992.
[144] E.O. Fischer, J. Schneider, K. Ackermann, Z. Naturforsch. 39b (1984) 468.
[145] P. Laurent, J.Y. Salaün, G. Le Gall, M. Sellin, H. des Abbayes, J. Organomet. Chem. 466 (1994) 175.
[146] M. Sellin, D. Luart, J.Y. Salaün, P. Laurent, L. Toupet, H. des Abbayes, J. Chem. Soc., Chem. Commun. (1996) 857.
[147] R.E. Valters, W. Flitsh, Ring–Chain Tautomerism, Plenum, New York, 1985.