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Mechanism of formation of the metallacyclic iron carbenes $(CO)_3\overline{Fe[=C(NR_2)OC(O}})NR_2]$ formed by thermal evolution of bis carbamoyl complexes, characterization of η^2-carbamoyl intermediates

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Abstract

The reaction of oxalyl chloride with carbamoyl ferrates: $\{Fe[C(O)NR_2](CO)_4\}^-$ or alkoxy–amine exchanges from $Fe(CO_2R)_2(CO)_4$ (**1**) are found to afford the same metallacyclic carbene complexes: $(CO)_3\overline{Fe[=C(NR_2)OC(O}})NR_2]$ (**3**) instead of the expected bis carbamoyl: $Fe[C(O)NR_2]_2(CO)_4$ (**2**) compounds. Low temperature monitorings and trapping experiments (carried out with phosphines) of the two reactions leading to **3** establish the rapid evolution of **2** into **3** and the easy achievement of η^2-carbamoyl bonding modes for these iron complexes. It is also shown that the formation of the metallacycle pattern of **3** is obtained by a carbon–oxygen-coupling process performed between the two carbamoyl ligands of $[\eta^1\text{-}C(O)NR_2][\eta^2\text{-}C(O)NR_2]Fe(CO)_3$ intermediates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene; Iron; Carbamoyl; η^2-Carbamoyl; Carbon–oxygen coupling

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1. Introduction

Catalytic carbonylation of alcohols is reported to afford dialkyloxalates which can be subsequently reduced by H_2 into ethylene glycol. As the key step of oxalate formation is supposed to be a reductive carbon–carbon coupling process between two alkoxycarbonyl ligands situated in close position on the catalyst, numerous bis-alkoxycarbonyl complexes of Pd, Pt, Co, Rh and Ru were synthesized and studied [1]. With the exception of one palladium compound: $Pd(CO_2Me)_2(PPh_3)_2$, complexes of this series were not found to induce thermally the formation of oxalates but to give rise to alcohols and dialkyl-carbonates. With the aim of studying such a carbon–carbon coupling reaction performed from well characterized complexes of metals of poor catalytic activity, we carried out the preparation of *cis* bis alkoxycarbonyl iron complexes: $Fe(CO_2R)_2(CO)_4$ (**1**). These compounds were obtained by an original method: the reaction of 0.5 equivalent of oxalyl chloride with the appropriate alkoxycarbonylferrate: $[Fe(CO_2R)(CO)_4]^-$ [2] itself prepared by a nucleophilic addition of an alcoholate on a carbonyl of $Fe(CO)_5$. As observed for compounds displaying a *cis* $[M](CO_2R)_2$ pattern, **1** was not found to induce thermally the formation of oxalates [3].

In order to get a better understanding of the properties of *cis* bis substituted iron complexes, we achieved the preparation of a number of these compounds by reaction of oxalyl chloride with the appropriate ferrate. Among these ferrates, the anions $\{Fe[C(O)NR_2](CO)_4\}^-$ were supposed to give rise to the *cis* bis carbamoyl series: $Fe[C(O)NR_2\}_2(CO)_4$ (**2**). Synthesis of **2** was of interest as bis-carbamoyl compounds de-

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scribed in the literature are scarce. $Hg[C(O)NEt_2]_2$ [4], the ruthenium and platinum complexes stabilized by electron-donor phosphines: $Ru[C(O)NEt_2]_2(CO)_2(dppe)$ [5] and $Pt[C(O)NR_2]_2[P(Ph)_2R]_2$ [6] the uranium and thorium compounds of the series: U or $Th(C_5Me_5)_2[\eta^2\text{-}C(O)NR_2]_2$ [7] and the Mo trimetallic complex: $Mo_3[C(O)NMe_2]_6(NHCMe_3)_2(CO)_6$ [8] displaying three different binding modes of its carbamoyl ligands are the most representative examples of this series. Though displaying two carbamoyl ligands, $\{W[C(O)N(i\text{-}Pr)_2]_2(CO)_4\}^{2-}$ [9]; $(CO)_3Fe[C(O)NR_2]_2Sn(CH_3)_2$ and $\{(CO)_3Fe[C(O)NR_2]_2\}_2Sn$ [10] are better described as carbenic compounds. None of the above described bis-carbamoyl complexes were reported to induce a carbon–carbon coupling process between its two carbamoyl ligands.

The present paper describes several attempts to synthesize complexes of the *cis* $Fe[C(O)NR_2]_2(CO)_4$ series. Thermal evolution of these bis carbamoyl intermediates will also be reported and the possible mechanism of this transformation will be discussed [11].

2. Results and discussion

2.1. Attempts at preparation of cis bis carbamoyl complexes $Fe[C(O)NR_2]_2(CO)_4$ (2)

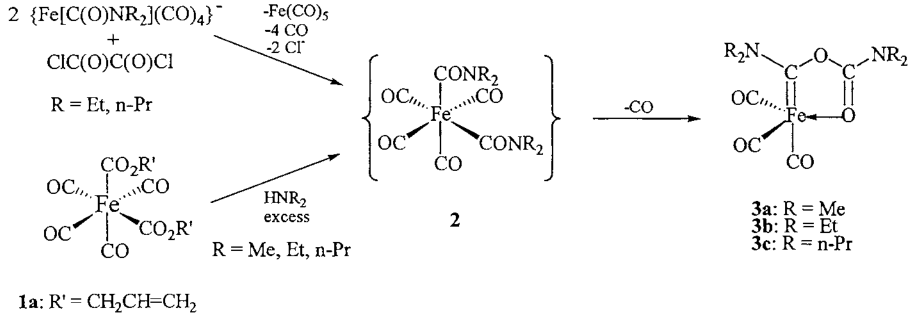
Two methods were considered to prepare **2**. The first one which was already mentioned is the reaction of 0.5 equivalents of oxalyl chloride with the carbamoyl ferrates: $[Fe[C(O)NR_2](CO)_4]^-$ (R = Et, *n*-Pr) was found to afford about 25% yields of very air sensitive orange–red powders **3**. The second one used originated from the well known exchange ability of the alkoxy groups of alkoxycarbonyl ligands [5,12,13] and consisted of reacting *cis* $Fe(CO_2R)_2(CO)_4$ complexes (**1**) in solution at − 5°C in THF or CH_2Cl_2 with an appropriate amine (the allyl derivative: **1a** whose preparation is easier than that of the other complexes of the series was used to perform the reaction). This reaction again gave rise to the same orange–red compounds **3**. When performed with $HNMe_2$ the process was very rapid and required only the stoichiometric amount of amine. After a reaction time of 1 h, a compound **3a** was obtained in 70% yield. However, longer reaction times were required for bulkier amines and complexes **3b** (R = Et, 63% yield) and **3c** (R = *n*-Pr, 45% yield) were only formed after 3 and 5 h of reaction of **1a** with an excess of $HNEt_2$ or $HN(n\text{-}Pr)_2$ (HNR_2–Fe molar ratio = 12). No reaction was observed with $HN(i\text{-}Pr)_2$. As it has been shown that these exchange processes occurred by associative pathways via the formation of trifunctionalized *fac* $\{Fe[C(O)NR_2]_n(CO_2R')_{3-n}(CO)_3\}^-$ intermediates (n = 1, 2) [12] resulting from a nucleophilic addition of HNR_2 to an axial terminal carbonyl, the difference in reactivity between $HNMe_2$ and bulkier amines underlines the importance of steric factors in nucleophilic additions at terminal carbonyl carbons.

2.2. Characterization of complexes 3

2.2.1. Crystallographic study of 3b

As the spectroscopic characteristics of complex **3** did not fit with those expected for *cis* $Fe[C(O)NR_2]_2(CO)_4$, an X-ray single-crystal diffraction study of the ethyl derivative was carried out. This study allowed us to characterize the product of the reaction as the iron carbene $(CO)_3Fe[=C(NEt_2)OC(O)NEt_2]$ (**3b**) (Scheme 1) whose molecular structure is shown in Fig. 1 and selected bond lengths and angles are collected in Table 1.

The ORTEP diagram of **3b** shows the molecule to display a metallacyclic carbenic structure. The coordination around the metal center of **3b** appears as a slightly distorted trigonal bipyramid. The carbenic carbon occupies one of the axial positions of this bipyramid. This carbon is substituted by a carbamate group also bound to the metal by the oxygen of its carbonyl. Owing to the presence on the complex of the five-member chelate, the C(4)–Fe–O(4) angle value is lowered (79.3°). The carbenic character of the chelate is shown by the presence of a short Fe–C(4) bond (1.911(5) Å)



Scheme 1.

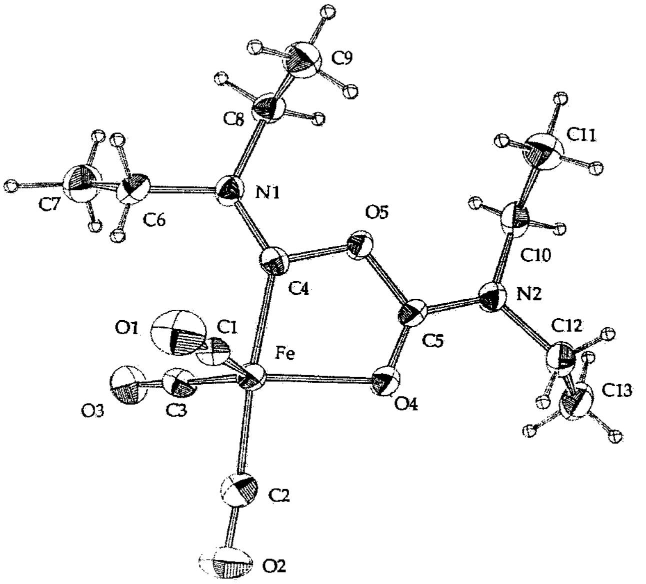


Fig. 1. ORTEP diagram for the metallacyclic carbene **3b**.

Table 1
Selected bond lengths (Å) and angles (°) for **3b**

Bond lengths			
Fe–C(1)	1.756(4)	Fe–C(2)	1.801(5)
Fe–C(3)	1.745(5)	Fe–C(4)	1.911(5)
C(4)–N(1)	1.314(6)	C(4)–O(5)	1.394(5)
Fe–O(4)	2.066(3)	C(5)–O(5)	1.364(6)
		C(5)–O(4)	1.237(6)
Bond angles			
O(4)–Fe–C(4)	79.3(2)	Fe–C(4)–O(5)	115.0(3)
C(4)–O(5)–C(5)	113.3(3)	O(4)–C(5)–O(5)	120.0(3)
Fe–O(4)–C(5)	112.3(3)	C(1)–Fe–C(3)	121.5(5)
C(1)–Fe–O(4)	117.5(2)	O(4)–Fe–C(3)	120.5(2)
C(1)–Fe–C(2)	89.4(2)	C(2)–Fe–C(3)	91.6(2)
O(4)–Fe–C(2)	95.8(2)		

analogous to those already described for many iron carbenes and by reduced carbenic carbon hetero-atom distances C(4)–N(1) (1.314) and C(4)–O(5) (1.394 Å) which are intermediates between those found for organic C–N (1.47 Å) and C–O (1.44 Å) single bonds and C=N (1.28 Å) and C=O (1.20 Å) double bonds [14]. Due to the complexation of its oxygen to the metal, the C=O bond of the carbamate group is relatively long (1.237 Å). As shown by the values of the torsion angles: O(4)–Fe–C(4)–O(5): 2.77, Fe–C(4)–O(5)–C(5): −1.84, C(4)–O(5)–C(5)–O(4): −1.44, O(5)–C(5)–O(4)–Fe: 3.68 and C(5)–O(4)–Fe–C(4): −3.53°, the metallacycle is nearly planar. Such a planar geometry, which has already been observed for analogous chromium complexes [15] suggests an efficient electron delocalization along the metallacycle. The values observed for the torsion angles C(5)–O(5)–C(4)–N(1): 176.31, O(4)–Fe–C(4)–N(1): −174.66, C(4)–O(5)–C(5)–N(2): −179.00, Fe–O(4)–C(5)–N(2): −179.11, C(10)–N(2)–C(5)–O(5): 8.95, C(12)–N(2)–C(5)–O(4): −9.29, O(5)–C(4)–N(1)–C(8): −6.85 and Fe–C(4)–N(1)–C(6): 170.69° show that the two nitrogen atoms N(1) and N(2) and the carbons C(6), C(8), C(10) and C(12) of their ethyl substituents are nearly coplanar with the metallacycle. This is indicative of a delocalization of the nitrogen atoms' electrons confirmed by the presence of short C(4)–N(1) (1.314) and C(5)–N(2) (1.321 Å) distances.

To our knowledge, only one iron complex presenting a carbenic metallacyclic structure analogous to that displayed by **3b** has been described in the literature. This compound: Fe{=C[N(*i*-Pr)$_2$]OC(O)C$_2$H$_5$}(CO)$_3$ [16] was obtained in low yield (6%) as a by-product of the reaction of formation of the Fischer's carbene Fe{=C[N(*i*-Pr)$_2$]OC$_2$H$_5$}(CO)$_4$ by the usual method.

2.2.2. Spectroscopic characteristics of 3

The spectroscopic characteristics of **3** (see Section 4) are in accordance with those expected for trigonal bipyramid complexes displaying a carbenic metallacycle. In IR, three bands are observed in the C≡O stretching area between 2010 and 1860 cm^{-1}. This set of bands is characteristic of an Fe(CO)$_3$ group of C_s symmetry implying the presence of two equatorial and one axial terminal carbonyls on the trigonal bipyramid.

In ^{13}C-NMR the resonances of the carbenic carbons are observed near 244 ppm value already quoted for Fe{=C[N(*i*-Pr)$_2$]OC(O)Et}(CO)$_3$ [16].

At −80°C, the three terminal carbonyls of complexes **3** display a single signal near 222 ppm. This result shows the occurrence, even at low temperature, of fast exchange processes between these three ligands. The signal of the carbamate carbonyl is found near 157 ppm. As observed for many carbenes bearing NR$_2$ groups [15–17] or for organic amides [18], the substituents of the two nitrogen atoms are found to be non equivalent in ^{1}H- and ^{13}C-NMR. This implies slow rotations around the two C$_{cyclic}$–N bonds in regard to the NMR detection. The delocalization of the nitrogen's electrons toward the carbene or the carbonyl of the carbamate inducing a marked double bond character of the C–N bonds is then confirmed.

2.3. Mechanism of formation of the metallacyclic carbenes 3

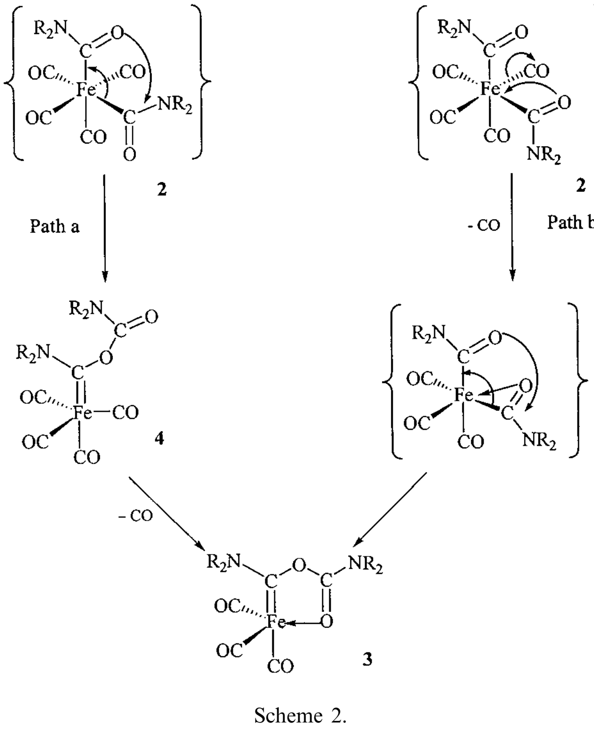
Achievement of carbenes **3** either by reaction of oxalyl chloride with carbamoyl ferrates or by alkoxy–amine exchanges from a bis-alkoxycarbonyl complex strongly suggests that the formation of this complex is brought about by thermal evolution of bis-carbamoyl intermediates. The probable intervention of these intermediates in the process of formation of **3** is also suggested by the structure of the carbenic ligand of **3** which consists in two R$_2$N–C–O groups linked by a carbon–oxygen bond.

Such a pattern could also be formed from the previously mentioned $\{Fe[C(O)NR_2]_n(CO_2R')_{3-n}(CO)_3\}^-$ intermediate. The process would then be analogous to that proposed for the thermal evolution of the bis carbamoyl tungsten anionic intermediate: $\{I(CO)_4W[C(O)NR_2]_2\}^{2-}$ into a second carbamato carbene intermediate: $\{I(CO)_4W[{=}C(NR_2)OC(O)NR_2]\}^-$ [19]. Though rather improbable in the course of the reaction of ClC(O)C(O)Cl with carbamoyl ferrates, the possible involvement of such trifunctionalized anions in the formation of metallacyclic carbenes by alkoxy–amine exchanges from bis alkoxycarbonyl complexes cannot be ruled out and will be studied in the future.

As the thermal evolution of $Fe[C(O)NR_2]_2(CO)_4$ (**2**) could afford the metallacyclic carbenes **3** it was of importance to study the mechanism of formation of **3**.

*2.3.1. Mechanism of transformation of **2** into metallacyclic carbenes **3***

As interactions between the oxygen of a carbonyl and iron are generally weak, the formation of the metallacyclic pattern of **3** by thermal evolution of bis carbamoyl intermediates is rather unexpected. Preparation of homologous complexes has however already been reported starting from carbenic complexes displaying one heteroatom or a double bond in appropriate position on one substituent of the carbene carbon [20]. These compounds are found to afford metallacyclic carbenes after thermal or photochemical decoordination of one of their ancillary ligands (often a CO), followed by the formation of the metallacycle via coordination of one carbene substituent on the metal vacant site. Direct formation of metallacyclic carbene complexes has however been described. The first example concerns the Rh (III) compound: $Cl_3(CO)Rh[C(Ph)N(Me)C(Ph){=}N(Me)]$ whose carbenic ligand is also bound to the metal by a nitrogen atom [21] and a second is the previously mentioned iron complex: $Fe\{{=}C[N(i\text{-}Pr)_2]OC(O)Et\}(CO)_3$ [16]. No mechanism was proposed to account for these two metallacyclic carbenes formation. A last example concerns a Ni sulfur analogue of **3**: $\{[\eta^2\text{-}C(S)NMe_2]Ni[{=}C(NMe_2)SC(S)NMe_2]\}BF_4$ whose formation is supposed to occur via a C–S coupling between two thiocarbamoyl ligands of the cationic $\{[\eta^2\text{-}C(S)NMe_2][\eta^1\text{-}C(S)NMe_2]Cl(CO)_2Ni\}^+$ intermediate [22].



Scheme 2.

Two different reactional paths could explain the formation of carbenes **3** by a carbon–oxygen coupling of the two carbamoyl ligands of intermediates **2** (see Scheme 2).

According to path (a), the oxygen of the first carbamoyl of **2** would attack the carbonyl carbon of the second carbamoyl affording tetracarbonyl carbene complexes **4** which, after decarbonylation followed by coordination of the carbamate oxygen on the metal center, would give **3**. Path (b) considers the decarbonylation of **2** affording (η^1-carbamoyl)(η^2-carbamoyl)$Fe(CO)_3$ intermediates which would evolve directly into the metallacarbenes **3** by a carbon–oxygen coupling between the two carbamoyl ligands.

We succeeded to prepare the intermediates $Fe\{{=}[C(NR_2)]OC(O)NR_2\}(CO)_4$ (**4**) (**4a**: R = Me; **4b**: R = Et) suggested in path (a) by leaving solutions of **3a** (R = Me) or **3b** (R = Et) in CH_2Cl_2 under a carbon monoxide atmosphere. As shown by ^{13}C-NMR monitorings (solvent: CD_2Cl_2) the process is slow and is only achieved after 3 days at 0°C. Tetracarbonyl carbenic complexes **4** were obtained as white micro crystals in 25% yield after chromatography.

The spectroscopic characteristics of **4a** or **4b** (see Section 4) are in good agreement with those displayed by complexes of similar structure [16,17]. Their IR spectra exhibit four signals in the $\nu C{\equiv}O$ area; the two bands observed near 1950 and 1940 cm^{-1} result from a splitting of the E band which is expected for a molecule displaying an asymmetric carbene ligand such as $[{=}C(NR_2)OC(O)NR_2]$ in an axial position on a trigonal bipyramid [16,17a,b,23b,24]. As these $\nu C{\equiv}O$ frequency values fall between 2060 and 1935 cm^{-1}, they represent an energy increase of ca. 50 cm^{-1} from the respective oscillators of the metallacyclic carbenes **3a** and **3b.** This trend is consistent with a decrease of the metal electron density of **4** induced by the replacement on the metal center of the oxygen of the carbamate carbonyl by an electron–withdrawing terminal C≡O. This lowering of the metal center electron density of **4** is also confirmed in ^{13}C-NMR, by a shift of ca. 5 ppm toward the high fields of the terminal carbonyls and the carbenic carbons' signals. The presence, even at −80°C, of a single resonance for the terminal carbonyls of **4** is indicative of fast exchanges between the three equatorial and the axial carbonyls. Such a behavior has already been observed for analogous complexes [16,17a]. As previously mentioned for **3** and as generally noticed for numerous organometallic complexes displaying a carbene carbon substituted by an amino group [16,17a,20d], a large π bonding contribution to the $C_{(carbene)}$–N bond of **4** hinders rapid rotations around this bond and induces in ^{1}H- or ^{13}C-NMR the non equivalence of the two substituents of the nitrogen. Complexes **4** are also found to display an analogous marked double bond character for the C–N bond of their carbamate group.

As reported for iron carbenes of similar structure [16,17b,20d,23], complexes **4** are found to be stable for several hours in solution at 20°C even under nitrogen atmosphere. This stability dismisses their possible intervention in the process of formation of the metallacyclic carbenes **3** (Scheme 2 path (a)) and leaves $Fe[\eta^1\text{-}C(O)NR_2][\eta^2\text{-}C(O)NR_2](CO)_3$ as the probable intermediates of the achievement of **3** (path (b)).

*2.3.2. Characterization of the intermediates responsible for the formation of **3** by ^{13}C-NMR monitoring of the reactions leading to **3b***

2.3.2.1. Reaction of oxalyl chloride with $\{Fe[C(O)NEt_2](CO)_4\}^-$. The reaction performed at low temperature (−70°C in THF-d_8) showed the only appearance of the final product (**3b**) resonances suggesting a very low stability even at low temperature of the bis-carbamoyl intermediate **2b**.

*2.3.2.2. Alkoxy–amine exchange reaction between $Fe[C(O)Oallyl]_2(CO)_4$ (**1a**) and Et_2NH or $(n\text{-}Pr)_2NH$.* Performed at −70°C, monitoring of these exchange reactions clearly showed the formation of relatively stable intermediates (respectively **5b** or **5c**). The appearance of three signals of intensity 2:1:1 (see Section 4) in the terminal carbonyls resonance area (between 205 and 194 ppm) suggested the formation of an octahedral complex substituted in *cis* position by two different organic ligands. Two signals near 185 ppm (C=O) and the presence of the resonances of the O-allyl and the $N(Et)_2$ (or $N(n\text{-}Pr)_2$) carbons confirmed these ligands to be an allyloxycarbonyl and a carbamoyl. By comparison with the ^{13}C spectrum of **1a**, the signal at 187.6 ppm was attributed to the carbonyl of the allyloxycarbonyl and that at 185.0 ppm to the carbonyl of the carbamoyl. Restricted rotations around the C–N bond of the carbamoyl ligand of **5b** and **5c** were again found to induce the nonequivalence of the two nitrogen substituents (ethyl or *n*-propyl). These data suggested for **5b**: R = Et and **5c**: R = *n*-Pr the *cis* $Fe(CO_2allyl)[C(O)NR_2](CO)_4$ structure. Complexes **5b** and **5c** were then formed from **1a** by one alkoxy–amine exchange. Though often postulated as reactional intermediates, complexes bearing an alkoxycarbonyl and a carbamoyl ligands are scarce [25] and, to our knowledge, $Ru(CO_2Me)[C(O)NHAr](CO)_2(dppe)$ [13c] stabilized by a strong electron donor bisphosphine is the only complex of this type described in the literature.

Complexes **5b** or **5c** were found to be very unstable as their NMR signals disappeared at −50°C to give rise to those of the metallacyclic carbenes **3b** or **3c**. This result suggested that at −50°C a second alkoxy–amine exchange could take place from **5b** or **5c** affording probably bis-carbamoyl intermediates that seem to evolve instantaneously into **3b** or **3c**.

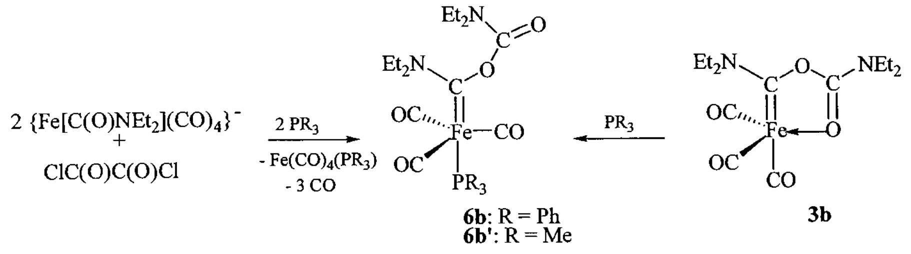
It is noteworthy that no trace of $\{Fe[C(O)NR_2]_2(CO_2allyl)(CO)_3\}HNR_3$ which is a probable intermediate in the alkoxy–amine exchange process can be detected in solution.

These monitoring experiments clearly show the occurrence of an alkoxy–amine exchange from **1a** affording the unstable carbamoyl-alkoxycarbonyl intermediates **5**. They also suggest that iron bis-carbamoyl complexes could be extremely unstable. They however fail in showing the formation of η^2-carbamoyl intermediates that could play an essential role in the reactions affording **3** (Scheme 2, path (b)).

*2.3.3. Stabilization by phosphine complexation of the intermediates giving rise to the metallacyclic carbenes **3***

*2.3.3.1. Formation of **3b** by reaction of oxalyl-chloride with $\{Fe[C(O)NEt_2](CO)_4\}^-$.* With the aim to stabilize η^2-carbamoyl intermediates which could account for the formation of **3**, we carried out this reaction in the presence of phosphines (PPh_3 or PMe_3). Independently of the nature of the phosphine, this process was found to give rise in good yield (70%) to the new complexes **6b** (PPh_3) or **6′b** (PMe_3) which were characterized as the *trans* phosphine homologues of the tetracarbonyl carbenes **4** (Scheme 3).

Spectroscopic data of **6b** and **6′b** (see Section 4) are very close to those displayed by *trans* $Fe(PPh_3)(CO)_3[{=}C(OEt)NiPr_2]$ and $Fe(PPh_3)(CO)_3[{=}C(OEt)R]$ [17e]. Their IR spectra present two bands in the $\nu C{\equiv}O$ area which are expected for D_{3h} *trans* $Fe(CO)_3LL'$ complexes bearing an asymmetric ligand (splitting of the E′ band of the D_{3h} $Fe(CO)_3$ pattern). By comparison with **4b**, the electron donor effect of the phosphine induces in ^{13}C-NMR a shift toward the lower fields of the terminal carbonyls' resonances (doublet at 216 ppm for **6b** and at 221 ppm for **6′b**). A more efficient back bonding toward the C≡O is probably responsible for a higher $J_{C–P}$ value observed for the signals of the



Scheme 3.

terminal carbonyls (30 Hz) than for the carbenic carbon (19 Hz) even located in *trans* position from the phosphine. Again restricted rotations around C–N bonds of **6b** and **6b′** are observed.

The structure attributed to **6b** and **6b′** was confirmed by the quantitative preparation of the same complexes by reaction at −30°C of the metallacyclic carbene **3b** with the appropriate phosphine (Scheme 3). This last result suggests that, during the process of formation of **3b** by reaction of ClC(O)C(O)Cl with a carbamoyl ferrate, PPh_3 or PMe_3 we are unable to quench the very fast transformation of the bis-carbamoyl intermediate **2b** into the metallacyclic carbene **3b**. The achievement of **6b** and **6b′** could then result from a further reaction of **3b** with PPh_3 or PMe_3.

2.3.3.2. *Synthesis of* **3** *by alkoxy–amine exchanges performed from* **1a**.

Performed in the presence of phosphine, the nature of the product formed by alkoxy–amine exchanges from **1a** was found to depend on both the phosphine and the amine used to achieve the process.

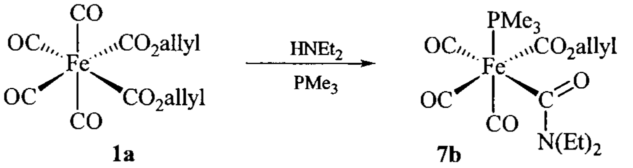
Reaction carried out with PMe_3. When performed with $HNEt_2$ in the presence of the strong electron donor phosphine: PMe_3, the exchange was found to give rise to the *fac* $Fe(CO_2allyl)[C(O)NEt_2](CO)_3(PMe_3)$ (**7b**) (Scheme 4).

The spectroscopic characteristics of **7b** are very close to those observed for bis alkoxycarbonyl homologues: *fac* $Fe(CO_2R)_2(CO)_3(PMe_3)$ [12]. In IR, two bands in the νC≡O area are indicative of a C_{3v} symmetry of the $M(CO)_3$ pattern. In ^{13}C-NMR, the phosphine complexation induces a shift toward the lower fields of the signals of the carbons bound to the metal. The presence of three doublets attributed to the terminal carbonyls (one of them with a large J_{C-P}: 41 Hz) also confirms the *fac* structure of **7b**. By analogy with the signals observed for the alkoxycarbonyl homologues, the resonance at 203.3 ppm is ascribed to the allyloxycarbonyl and the one at 197.2 ppm to the carbamoyl. The absence of rotation around the C–N bond of the carbamoyl is again observed on **7b**.

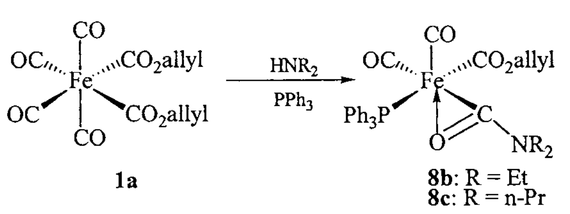
The formation of **7b** is in good accordance with the previous observation of **5b** formed from **1a** by one alkoxy–amine exchange. However, the easiness of the substitution of one terminal carbonyl of the intermediate **5b** by PMe_3 affording **7b**, (1 h at −50°C) compared to the conditions required for the analogous reaction performed from the bis-alkoxycarbonyl complexes **1** (24 h at 28°C), suggests the possible intervention of the carbamoyl ligand in the decoordination process of an axial carbonyl of **5b** and could be indicative of the formation of an η^2 carbamoyl intermediate.

Reaction achieved in the presence of PPh_3. A complex **8c** displaying an original structure was found to be the only product of the reaction when the exchange was performed with $HN(n\text{-}Pr)_2$ (known to react slowly with *bis*-alkoxycarbonyl complexes) in the presence of a less electron donor phosphine: PPh_3. We were unfortunately unable to grow for this complex, suitable crystals for an X-ray study, however its spectroscopic data (see Section 4) suggests the complex displays the η^2 carbamoyl structure described in Scheme 5.

In IR **8c** exhibits two bands at 2007 and 1938 cm^{-1} in the νC≡O area. In ^{31}P-NMR, the signal observed at 50.5 ppm is that of a phosphine linked to the metal center. ^{1}H- and ^{13}C-NMR spectra of **8c** show the presence on the complex of a carbamoyl and of an allyloxycarbonyl ligands. COSY and HMQC sequences allow the attribution of the ^{1}H-NMR signals at 5.84 (1H, m); 5.23 (1H, d) and 5.07 ppm (1H, d) to the ethylenic protons of the allylic group. The resonances of the two aliphatic hydrogens of the same group are



Scheme 4.



Scheme 5.

found at 4.35 (1H, d, d) and 4.30 ppm (1H, d, d). It is noteworthy that, due to the low symmetry of the molecule, these two protons are diastereotopic. This diastereotopy is also observed for the protons of the CH_2 linked to the nitrogen of the carbamoyl whose resonances appear as four multiplets at 3.83, 3.04, 2.91 and 2.75 ppm. The presence of four signals for these CH_2 is again the result of a restricted rotation around the C(O)–N bond which induces the non equivalence of the two *n*-propyl substituents. The ^{13}C-NMR spectrum of **8c** is in good accordance with these observations as three resonances at 133.4, 115.8 and 63.9 ppm (allylic carbons) and six signals at 53.4, 51.1, 21.6, 20.6, 11.1 and 11.0 ppm (*n*-propyl carbons) are displayed by its alkoxycarbonyl and carbamoyl ligands. As ^{1}H–^{13}C interactions between the aliphatic CH_2 resonances of the allylic group at 4.30 and 4.35 ppm in ^{1}H-NMR and the signal at 205.6 ppm in ^{13}C-NMR were revealed by an HMBC sequence, this last resonance was attributed to the alkoxycarbonyl carbonyl. As shown by the high value of the $J_{C–P}$ coupling constant (58 Hz) displayed by this signal the alkoxycarbonyl ligand is clearly situated in *trans* position from the phosphine. In the same way it was shown that the signal at 203.4 ppm was that of the carbonyl of the carbamoyl ligand which is obviously *cis* to the phosphine ($J_{C–P} = 14$ Hz). The ^{13}C-NMR spectrum of **8c** also presents two doublets of equal intensity at 219.4 and 212.1 ppm attributed to two terminal carbonyls. As shown by their $J_{C–P}$ constants (15 and 16 Hz respectively) these two ligands are located in *cis* position from the phosphine. The presence of only two terminal carbonyls and then of five ligands on the complex suggests that one of them (undoubtedly the carbamoyl) could display an η^2 complexation mode.

As η^2-binding of carbonylated ligands are typically known to occur around electron-deficient metal centers, most examples of this kind of coordination concern early d block metal complexes [26]. η^2-C(O)R (R = alkyl, NR_2, OR) complexes of Group 8 metals have however been described; they are generally stabilized by electron–donor phosphines [27]. The remarkable stability of bimetallic complexes of the type: $L(CO)_3M[\mu,\eta^2\text{-}C(O)R]M(CO)_3L$ (L = PR_3, CO; R = alkyl, aryl, NR_2 or OR; M = Fe, Ru) must be emphasized [27h,28]. However the η^2-C(O)R bridging ligands of these compounds seem very different from their homologues η^2-linked to a single metal center as they exhibit strong carbenoid characters. To our knowledge, complexes $Fe[\eta^2\text{-}C(O)N(i\text{-}Pr)_2](CF_3)(CO)_2(PPh_3)$ (**9**) [29] and $Fe[\eta^2\text{-}C(O)N(i\text{-}Pr)_2](I)(CO)_2(PPh_3)$ (**10**) [30] are the first η^2-carbamoyl iron compounds described in the literature. They present spectroscopic data very close to those displayed by **8c**. It is noteworthy that neither **8c** nor the structurally characterized complexes **9** and **10** display IR νC=O low frequencies or low field ^{13}C-NMR resonances for the carbonyl of their carbamoyl ligand. As such characteristics have often been considered as indicative of an η^2-coordination mode of a ligand [13a,26], our results confirm that these IR and NMR data are very dependent on the influence of ancillary ligands [31].

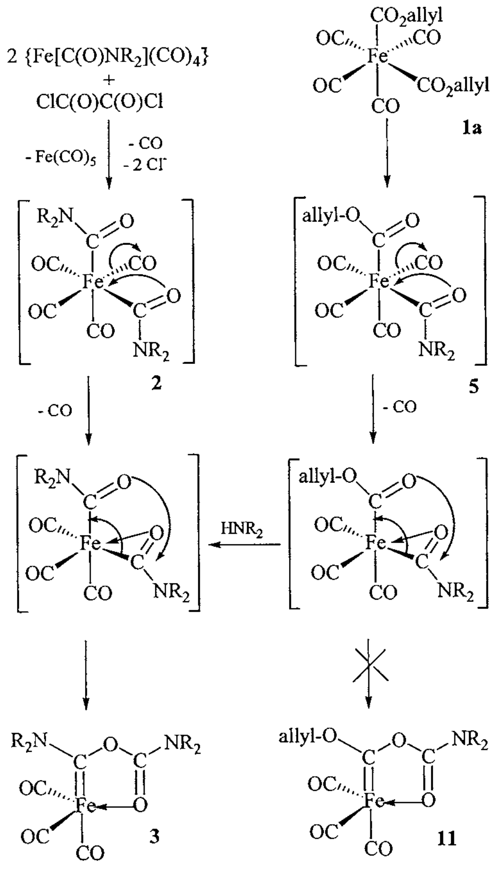
The presence of an oxygen atom bound to the metal centre (η^2-bonding mode of the carbamoyl ligand) induces in ^{13}C-NMR, as already quoted for the metallacyclic carbenes **3**, a shift of ca. 6 ppm toward the lower fields of the signals of the carbonyl ligands of **8c**. Thus, while the resonances of the terminal carbonyls of $Fe(CO)_3(PMe_3)(CO_2allyl)[\eta^1\text{-}C(O)NEt_2]$ (**7b**) and $Fe(CO)_4(CO_2allyl)[\eta^1\text{-}C(O)NEt_2]$ (**5b**) are detected between 205 and 201 ppm, those of the similar ligands of **8c** are found at 219 and 212 ppm. This observation also suggests that the more shifted signal (219 ppm) could be attributed to the terminal carbonyl in *trans* position from the iron–oxygen bond.

When the alkoxy–amine exchange in the presence of PPh_3 was performed with $HNEt_2$, it was known to react faster with $Fe(CO_2allyl)_2(CO)_4$: (**2a**) (see above), a mixture of 60% of the η^2-carbamoyl complex **8b** analogous to **8c** and (40%) of the *trans* tricarbonyl triphenylphosphinocarbene **6b** was obtained.

The methyl homologue of **6b**: the *trans* $Fe(PPh_3)(CO)_3[=C(NMe_2)OC(O)NMe_2]$ (**6a**) was found to be the only product of the reaction achieved with $HNMe_2$.

As we have already shown that $HNMe_2$ gives rapid exchanges with **1**, this result clearly establishes that PPh_3 is only able to react with (alkoxycarbonyl)(carbamoyl) intermediates when a fast second alkoxy–amine exchange does not lead to a rapid formation of bis carbamoyl intermediates. It also confirms that these bis-carbamoyl species are not trapped by phosphines as they very rapidly give rise to metallacyclic carbenes **3** which, by reaction with PPh_3, afford *trans* phosphino carbenes (**6**).

The formation of complexes **7** and **8** by reaction of **1** with amines in the presence of phosphines could result from a fast alkoxy–amine exchange affording $Fe(CO_2R)[C(O)NR_2](CO)_4$ (**5**). A fast departure of an axial carbonyl of these intermediates **5**, probably induced by the carbamoyl ligand [27h] followed by the coordination of the phosphine could then give rise to *fac* $Fe(CO_2R)[C(O)NR_2](PR_3)(CO)_3$ complexes **7**. As shown for bis alkoxycarbonyl complexes [12], the presence of a strong electron donor phosphine (PMe_3) on the complex could prevent any *fac–mer* isomerization of **7**. Steric interactions between the phosphine in the axial position and the carbamoyl ligand could make more difficult the achievement of a η^2-bonding mode of this last ligand. Contrary to the PMe_3 *fac* complexes **7** which are stable, their homologues bearing a less electron donor phosphine: PPh_3 could evolve, as observed



Scheme 6.

for bis alkoxycarbonyl complexes, toward their *mer* isomers. This isomerization which suppresses the steric hindrance preventing the η^2-carbamoyl formation, combined with a reduced electron density of the metal center could make possible the formation of η^2-complexes **8** by a decoordination of an axial CO induced by a new interaction of this ligand with the carbamoyl. The formation of **8** then confirms the easy formation of iron η^2-carbamoyl complexes.

Monitoring experiments and the formation of complexes **7** and **8** by alkoxy–amines exchanges performed from **1a** in presence of phosphines clearly show (Scheme 6) the occurrence of a rapid exchange affording $Fe(CO_2R)[C(O)NR_2](CO)_4$ (**5**). A fast decarbonylation of this intermediate would then give rise to a second intermediate: $Fe(CO_2allyl)[\eta^2\text{-}C(O)NR_2](CO)_3$. From this second intermediate, two reaction pathways could explain the formation of metallacyclic carbenes **3** (Scheme 6): the first one considers a carbon–oxygen coupling between the allyloxycarbonyl and the η^2-carbamoyl ligands, it could give rise to the allyloxycarbamato carbenes $(CO)_3Fe[=C(Oallyl)OC(O)NR_2]$ (**11**). An aminolysis [32] of these carbenes would then afford **3**. This assumption is however improbable as neither exchange reactions of **1a** with 1 mol of amine nor addition of one equivalent of $LiNR_2$ to the cation $[Fe(CO_2allyl)(CO)_5]^+$ [12,33] were found to induce the formation of **11** but to give rise to $Fe(CO)_5$ together with unextractible organic mixtures.

The second way of evolution of the intermediate $(CO_2allyl)(\eta^2\text{-carbamoyl})$ into **3** requires a second exchange affording $Fe[\eta^1\text{-}C(O)NR_2][\eta^2\text{-}C(O)NR_2](CO)_3$. This entity is also very likely formed by decarbonylation of $Fe(CO)_4[C(O)NR_2]_2$ (**2**) complexes readily obtained by reaction of ClC(O)C(O)Cl with carbamoyl ferrates $\{Fe(CO)_4[C(O)NR_2]\}^-$. The formation of the amino carbamato metallacyclocarbene **3** would then result from an oxygen–carbon coupling between the oxygen of the η^1 and the sp_2 carbon of the carbonyl of the η^2-carbamoyl ligands of this intermediate. Such reactions are not so common; they have been described for the coupling between an η^2-carbamoyl and a CF_2 carbenic carbon of an iron complex [34] and between an aroyl and a CH_2 of ruthenium compounds [35]. The same couplings have also been suggested between the two thiocarbamoyl of the cation $\{Cl(CO)_2Ni\text{-}[C(S)NMe_2][\eta^2\text{-}C(S)NMe_2]\}^+$ [22] and between the two carbamoyls of the anion $\{IW(CO)_4[C(O)N(i\text{-}Pr)_2]_2\}^-$ [19]. For our counterpart we have already observed such an oxygen–carbon coupling between the pyruvoyl and the alkoxycarbonyl of $Fe[C(O)C(O)CH_3]\text{-}(CO_2R)(CO)_4$. This reaction was found to give rise to alkoxy metallalactones [36]. Some other works dealing with oxygen–carbon coupling between two organic ligands are currently under progress in our laboratory.

3. Conclusions

This work establishes the fast evolution at low temperature of bis-carbamoyl intermediates: *cis* $Fe[C(O)NR_2]_2(CO)_4$ (**2**) formed by reaction of oxalyl chloride with $\{Fe[C(O)NR_2](CO)_4\}^-$ into a second intermediate: $Fe[\eta^1\text{-}C(O)NR_2][\eta^2\text{-}C(O)NR_2](CO)_3$ also formed by alkoxy–amine exchanges from **1a**. This intermediate could give rise to metallacyclic carbenes $(CO)_3Fe[=C(NR_2)OC(O)NR_2]$ (**3**) by an oxygen–carbon coupling between the oxygen of the η^1-carbamoyl and the carbon of the carbonyl of the η^2-carbamoyl. The complexation of a carbamoyl via a η^2-mode is revealed by the easy formation, even at low temperature, of the phosphine derivatives **7** and **8**. To our knowledge the formation of **3** is the first C–O coupling affording a neutral metallacyclic carbene. Further experiments will be done to investigate the possible intervention in the reaction of formation of **3** of the trifunctionalized anions $\{Fe[C(O)NR_2]_x(CO_2allyl)_{3-x}(CO)_3\}^-$ shown by a recent study performed in our laboratory to be intermediates in exchange processes observed between **1** and amines [12,37].

4. Experimental

All reagents and solvents were transferred using techniques designed to eliminate contact with air. All solvents were distilled from the appropriate drying agent: THF and diethyl ether from sodium–benzophenone, hexane and dichloromethane from calcium hydride. ^{1}H- and ^{13}C-NMR were obtained using Brucker AC 300 and AMX 3-400 spectrometers. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane (^{1}H, ^{13}C) or from 87% H_3PO_4 as external standard (^{31}P). IR spectra were recorded on a Perkin–Elmer 1430 spectrometer. Elemental analyses were performed by the Service Central d'analyses du CNRS.

4.1. Preparation of the metalla-carbenes **3** $(CO)_3Fe[=C(NR_2)OC(O)NR_2]$

4.1.1. By reaction of ClC(O)C(O)Cl with $\{Fe[C(O)NR_2](CO)_4\}^-$ (R = Et, n-Pr)

A solution of $Fe(CO)_5$ (1.176 g, 790 μl, 6 mmol) in 30 ml of THF at −20°C was treated with 4 mmol of $LiNR_2$ (prepared by reaction of 4 mmol of BuLi with 0.293 g, 0.42 ml of $HNEt_2$: R = Et, or with 0.40 g, 0.555 ml of $HN(n\text{-}PR)_2$: R = *n*-Pr) in solution in THF. The mixture was stirred for 30 min at −20°C and 2 mmol of ClC(O)C(O)Cl (175 μl) were then added to the solution which instantaneously turned brown. The solvent was evaporated and the brown oily residue washed at −30°C with two portions of 20 ml of hexane and finally extracted with 2 × 20 ml of 1:1 dichloromethane–hexane. After filtration and concentration of the solution, **3b** (R = Et) and **3c** (R = *n*-Pr) were obtained as red powders: **3b**: 185 mg, yield: 27%; **3c**: 174 mg, yield: 22%.

Table 2
Data collection and processing parameters for **3b**

Formula	$C_{13}H_{20}FeN_2O_5$
Molecular weight	340.16
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.774(7)
b (Å)	10.477(7)
c (Å)	16.929(5)
α (°)	81.33(3)
β (°)	84.54(3)
γ (°)	68.61(4)
V (Å^3)	1584(2)
Z	4
$D_{calc.}$ (g cm^{-3})	1.426
F(000)	712
μ(Mo–K$_\alpha$) (cm^{-1})	9.694
Temperature (K)	120
Crystal size (mm)	0.15 × 0.22 × 0.25
Radiation	Mo–K$_\alpha$
Max 2θ (°)	50
Scan	$\omega/2\theta = 1$
T_{max} (for one measure) (s)	60
Variance of standards	0.3%
Range of h,k,l	0.11; −12.12; −20.20
Reflections measured	5917
Reflections observed ($I > \sigma(I)$)	2961 (3σ)
R_{int} (from merging equivalent reflections)	0.023
R (isotropic)	0.120
R (anisotropic)	0.085
Fourier difference	0.72−0.46
N (obs)/N (var)	2961/500
R	0.039
R_w [a]	0.035
S_w	1.47
Max residual, (e Å^3)	0.32
Δ/σ	0.57

[a] $\omega = 1/\sigma^2(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$.

4.1.2. By exchange reactions from **1a**

Solutions of HNR_2 (R = Me: 4 mmol, 2 ml of a 2M solution in THF; R = Et: 24 mmol, 1.75 g, 2.50 ml; R = *n*-Pr: 24 mmol, 2.43 g, 3.33 ml) were added at −20°C to a solution of 2 mmol (0.675 g) of $Fe(CO_2allyl)_2(CO)_4$ **1a** in 20 ml of THF or CH_2Cl_2. The pale yellow solution turned red as evolution of CO was observed. After 3 h stirring at −5°C, the solvent was removed and the red residue treated as above to give 400 mg yield: 70% of **3a** (R = Me). IR: (hexane) cm^{-1} 1995 (m), 1890 (m), 1860 (s) (νC≡O); 1692 (m) (νC=O). ^{13}C-NMR (δ, CD_2Cl_2): 243.5 (Fe=*C*), 222.3 (C≡O), 157.3 (C=O), 45.1, 38.6, 37.9, 36.8 (CH_3). ^{1}H-NMR (δ, CD_2Cl_2): 3.63 (s, 3 H), 3.27 (s, 3 H), 3.25 (s, 3 H) 3.15 (s, 3 H) (CH_3). **3b** (R = Et) 428 mg yield: 63%. IR: (hexane) cm^{-1} 1992 (m), 1892 (m), 1860 (s) (νC≡O); 1682 (m) (νC=O). ^{13}C-NMR (δ, CD_2Cl_2): 243.5 (Fe=C); 222.7 (C≡O); 157.1 (C=O); 50.8, 43.8, 43.6, 42.7 (CH_2); 13.8 (2), 13.0, 12.6 (CH_3). ^{1}H-NMR (δ, CD_2Cl_2): 3.91 (q, J = 7.2 Hz, 2 H, CH_2), 3.54 (q, J = 7.3 Hz, 2 H, CH_2), 3.35 (m, 4 H, 2 CH_2), 1.35 (t, J = 7.3 Hz, 3 H, CH_3), 1.24 (t, J = 7.2 Hz, 3 H, CH_3), 1.14 (m, 6 H, 2 CH_3). **3c** (R = *n*-Pr) 356 mg yield: 45% IR: (hexane) cm^{-1} 2005 (m), 1902 (m), 1875 (s) (νC≡O); 1694 (m) (νC=O)). ^{13}C-NMR (δ, CD_2Cl_2): 244.0 (Fe=C); 222.4 (C≡O); 157.2 (C=O); 58.4, 52.0, 49.3, 49.2 (CH_2); 22.7, 21.6, 21.2 (2) (CH_2); 11.5 (2), 11.2 (2) (CH_3). ^{1}H-NMR (δ, CD_2Cl_2): 3.62 (m, 4 H, 2 CH_2); 3.58 (m, 2 H, CH_2); 3.32 (m, 2 H, CH_2); 1.45 (m, 8 H, 4 CH_2); 1.22 (t, 7.4 Hz, 3 H, CH_3); 1.15 (m, 9 H, 3 CH_3). These complexes were found to be too unstable to afford correct and reproducible analyses.

4.1.3. Crystallographic study of **3b**

Suitable crystals for single-crystal X-ray diffraction studies were obtained from 2:1 hexane–dichloromethane mixture at −30°C. The crystal data and the structure refinement are collected in Table 2. Data were collected on a CAD-4 Enraf–Nonius diffractometer with graphite–monochromated Mo–K$_\alpha$ radiation.

Unit cell parameters were determined by least square fitting of 25 high θ reflexions. After Lorentz and polarization corrections, the structure was solved with direct methods, scale factor refinements and Fourier differences. After isotropic ($R = 0.120$) and anisotropic ($R = 0.085$) refinements, the hydrogens were located with a difference Fourier map. The entire structure was refined by full-matrix least-square techniques. Atomic scattering factors were taken from [38]. All calculations were performed on a digital microwax 3100 computer with the MOLEN package (Enraf–Nonius 1990).

4.2. Preparation of tetracarbonyl carbenes 4

Complex **3a** (1.70 g, 6 mmol) or **3b** (2.04 g) dissolved in 100 ml of CH_2Cl_2 was stirred for 3 days at 0°C under a CO atmosphere. The solvent was then removed and the brown residue washed with two portions of 20 ml of hexane at −20°C. After chromatography on alumina, (elution with a 9:1 hexane–dichloromethane mixture) **4** were obtained in 25% yield as white crystals. **4a** (R = Me) 468 mg; IR: (hexane) cm^{-1} 2060 (m), 1980 (m), 1984 (s) 1935 (s) (νC≡O); 1735 (m) (νC=O). ^{13}C-NMR (δ, CD_2Cl_2): 238.0 (Fe=C); 214.9 (C≡O); 149.4 (C=O); 46.7, 40.3, 36.4 and 36.3 (CH_3). ^1H-NMR (δ, CD_2Cl_2): 3.64 (s, 3 H, CH_3); 3.13 (s, 3 H, CH_3); 2.93 (s, 3 H, CH_3); 2.69 (s, 3 H, CH_3). Anal. Found: C, 38.62; H, 3.92; N, 8.99. $C_{10}FeH_{12}N_2O_6$. Calc.: C, 38.46; H, 3.85; N, 8.97%. **4b** (R = Et) 550 mg; IR: (hexane) cm^{-1} 2070 (m), 1975 (m), 1985 (s) 1930 (s) (νC≡O); 1750 (m) (νC=O) ^{13}C-NMR (δ, CD_2Cl_2) 237.7 ($Fe{=}\underline{C}$); 215.5 (C≡O); 149.6 (C=O); 51.8, 45.2, 42.3, 42.1 (CH_2); 14.1, 13.8, 12.9, 12.6 (CH_3). ^1H-NMR (δ, CD_2Cl_2): 3.70 (m 2 H, CH_2); 3.35 (m, 4 H, 2 CH_2); 2.75 (m, 2 H, CH_2); 1.3 (m, 12 H, 4 CH_3). Anal. Found: C, 45.72; H, 5.55; N, 7.54. $C_{14}FeH_{20}N_2O_6$ Calc.: C, 45.65; H, 5.43; N, 7.61%.

4.3. ^{13}C monitoring of reactions leading to 3b

4.3.1. Reaction of ClC(O)C(O)Cl with $\{Fe[C(O)NEt_2](CO)_4\}^-$

A solution of $Fe(CO)_5$ (39 mg; 26 μl, 0.2 mmol) was reacted with 0.1 mmol of $LiNEt_2$ (8 mg) in 0.6 ml of THF-d_8 at −20°C. The orange solution formed after 30 min was transferred into an NMR tube and cooled at −70°C. Oxalyl chloride was then added to the solution. (6.5 mg, 0.05 mmol, 4.5 μl). The NMR tube was introduced into the probe of the NMR machine at −70°C and spectra performed every 2 h.

4.3.2. Exchange reactions carried out with $HNEt_2$ or $HN(n\text{-}Pr)_2$

Compound **1a** (0.1 mmol, 34 mg) was dissolved in 0.6 ml of CD_2Cl_2 was introduced into a NMR tube. 0.2 mmol of $HNEt_2$ (15 mg, 21 μl) or of $HN(n\text{-}Pr)_2$ (20 mg, 28 μl) were added to this solution cooled at −70°C. ^{13}C-NMR spectra were achieved as above. **5b** ^{13}C-NMR (δ, CD_2Cl_2): 201.4 (2), 197.6, 194.3 C≡O); 187.6 (CO_2); 184.2 (C(O)N); 134.6, 117.0, 66.0 ($CH_2{=}CHCH_2$); 43.5, 43.4, 13.8, 13.6 (CH_2CH_3). **5c** ^{13}C-NMR (δ, CD_2Cl_2): 201.5 (2), 198.0, 194.4 (C≡O); 187.5 (CO_2); 185.0 (C(O)N); 134.7, 117.2, 66.1 ($CH_2{=}CHCH_2$); 48.2, 47.9, 22.0, 21.8, 11.2, 11.1 ($CH_2CH_2CH_3$).

4.4. Stabilization by complexation with PPh_3 or PMe_3 of the intermediates giving rise to 3

4.4.1. Reaction of ClC(O)C(O)Cl with $\{Fe[C(O)NEt_2](CO)_4\}^-$

A 1 M solution of BuLi (2 ml) in hexanes were added under argon to 2 mmol of $HNEt_2$ (147 mg, 0.210 ml) dissolved in 50 ml of dry THF at −20°C. The mixture was stirred for 15 min and 4 mmol of $Fe(CO)_5$ (784 mg, 0.525 ml) were added to the solution which rapidly turned orange. After 15 min stirring, successive additions of 2 mmol of PMe_3 (2 ml of a 1 M solution in THF) or PPh_3 (525 mg) and 1 mmol of ClC(O)C(O)Cl (130 mg, 90 μl) were then rapidly performed. The solution which turned brown was stirred for an additional hour at −20°C. The solvent was evaporated and the brown residue washed at −30°C with two portions of 15 ml of hexane and finally extracted at −5°C with 2 × 25 ml of a 5:1 hexane–CH_2Cl_2 mixture. After filtration and concentration of the solution at −50°C, **6b** and **6b′** were obtained as yellow crystals. Yields: **6b**: 65% (785 mg); **6b′**: 75% (620 mg).

4.4.2. Preparation of 6b and 6b′ by reaction of the appropriate phosphine with the metallacyclic carbene 3b.

To 3 mmol of **3b** (1.02 g) in solution in 30 ml of CH_2Cl_2 at −30°C was added one equivalent of PPh_3 (0.878 g) or PMe_3 (3 ml of a 1 M solution in THF). The solution which rapidly turned brown was stirred for 2 h at −5°C. Complexes **6b** and **6b′** were then obtained as above. **6b**: 1.45 g, yield: 80%; **6b′**: 1.06 g, 85%.

Complex **6b**: IR: (hexane) cm^{-1} 1880 (m), 1875 (m) (νC≡O); 1718 (m) (νC=O). ^{13}C-NMR (δ, CD_2Cl_2): 245.3 (d, $J = 19$ Hz, Fe=C); 216.4 (d, $J = 28$ Hz, C≡O); 150.0 (C=O); 134.1 (d, $J = 18$ Hz), 133.3 (d, $J = 11$ Hz), 131.2 (s), 129.2 (d, $J = 10$ Hz) (PPh_3); 51.2, 44.9, 41.9 (2) (CH_2); 14.2, 14.1, 13.0 (2) (CH_3). ^{31}P-NMR 83.3. ^1H-NMR: 7.2 (m, 15 H, PPh_3); 4.02 (m, 2 H, CH_2); 3.60 (m, 2 H, CH_2); 3.42 (m, 4 H, 2 CH_2) 1.39 (m, 3 H, CH_3); 1.24 (m, 6 H, 2 CH_3); 1.14 (m, 3 H, CH_3). Anal. Found C, 61.95; H, 5.90; N, 4.51. $C_{31}FeH_{35}N_2O_5P$. Calc.: C, 61.79; H, 5.81; N, 4.65%. **6b′**: IR (hexane) cm^{-1} 1875 (m), 1870 (m) (νC≡O); 1725 (m) (νC=O). ^{13}C-NMR (δ, CD_2Cl_2): 245.7 (d, $J = 17$ Hz, Fe=C); 216.7 (d, $J = 30$ Hz, C≡O); 150.1 (C=O); 50.8, 44.3, 41.7, 41.6 (CH_2); 17.1 (d, $J = 33$ Hz, PMe_3); 14.1, 13.9

(2), 12.9 (CH_3). ^{31}P-NMR 42.3. ^{1}H-NMR: 4.15 (m, 2 H), 3.45 (m, 2 H), 3.42 (m, 2 H), 3.37 (m, 2 H), (CH_2); 1.55 (m, 9 H, PMe_3); 1.38 (m, 3 H), 1.26 (m, 6 H), 1.15 (m, 3 H), (CH_3). Anal. Found: C, 46.27; H, 7.05; N, 6.65. $C_{16}FeH_{29}N_2O_5P$. Calc.: C, 46.15; H, 6.97; N, 6.73%.

*4.4.3. Alkoxy–amine exchanges performed from **1a** in presence of phosphines*

4.4.3.1. Reaction performed in presence of PMe_3. One equivalent of PMe_3 (2 ml of 1 M solution in THF) was added at −5°C to a solution of **1a** (2 mmol, 676 mg) in 30 ml of CH_2Cl_2. After 5 min stirring, the solution was cooled to −40°C and five equivalents of $HNEt_2$ were added (20 mmol, 1.46 g, 2.09 ml). The temperature was slowly raised to −5°C and the solution turned orange. After 30 min stirring the solvent was removed, the residue washed with 2 × 10 ml of hexane at −70°C and finally extracted with 2 × 15 ml of hexane at 0°C. The crude product obtained after evaporation of the solution was found composed of 40% of $Fe(CO)_4(PMe_3)$ and of 60% of **7b** which was purified by two fractional crystallizations in hexane at −30°C. Complex **7b** was obtained as an orange oily product. Yield: 10%, (80 mg): IR (hexane) cm^{-1} 2020 (m), 1965 (m) (νC≡O); 1640 (m) (νC=O). ^{13}C-NMR (δ, CD_2Cl_2): 208.9 (d, $J = 41$ Hz), 205.8 (d, $J = 16$ Hz), 203.8 (d, $J = 21$ Hz) (C≡O); 203.3 (d, $J = 31$ Hz, CO_2R); 197.2 (d, $J = 21$ Hz, C(O)N); 133.5, 116.5, 63.7, (CH_2=$CHCH_2$); 42.7, 42.5, 13.7, 13.5, (CH_2CH_3); 17.5, (d, $J = 30$ Hz, PMe_3). ^{31}P-NMR 16.2. ^{1}H-NMR: 5.8 (m, 1 H), 5.2(m, 2 H), 4.3 (m, 2 H), (CH_2=CH–CH_2); 3.4 (m, 1 H), 3.0 (m, 1 H), 2.8 (m, 1 H), 2.7 (m, 1 H), (CH_2); 1.50 (m, 15 H, CH_3). We were unable to get correct analyses of this product.

4.4.3.2. Reaction performed in presence of PPh_3. Complex **1a** (676 mg, 2 mmol) in solution in 30 ml of CH_2Cl_2 at −5°C was treated with 1.25 equivalents of PPh_3 (2.5 mmol; 0.655 g) in solution in 5 ml of CH_2Cl_2. The mixture was stirred for 5 min and cooled to −40°C. Five equivalents of HN(n-Pr)$_2$ (20 mmol, 2.02 g, 2.77 ml) were then added to the solution which was stirred for 1 h as the temperature was raised to −5°C. The reaction mixture turned yellow. The solvent was removed at −30°C and the residue washed with two portions of 15 ml of hexane to afford **8c** as a yellow powder which was recrystallized in a 5:1 hexane–dichloromethane mixture at −5°C. Yield: 52% (0.610 g). Complex **8c**: IR (hexane) cm^{-1} 2007 (m), 1938 (m), (νC≡O); 1608 (m), 1635 (m), (νC=O). ^{13}C-NMR: (δ, CD_2Cl_2) 219.4 (d, $J = 16$ Hz), 212.1 (d, $J = 15$ Hz), (C≡O); 205.6 (d, $J = 58$ Hz, CO_2R); 203.4 (d, $J = 14$ Hz, C(O)N); 134.3, 115.7, 63.7 (CH_2=$CHCH_2$); 132.5 (d, $J = 16$ Hz), 132.3 (d, $J = 12$ Hz), 130.6 (s), 129.2 (d, $J = 10$ Hz) (PPh_3); 53.0, 50.6, 21.6, 20.5, 11.1, 11.0 ($CH_2CH_2CH_3$). ^{31}P-NMR 50.5. ^{1}H-NMR: 7.25 (m, 15 H, PPh_3); 5.84 (m, 1 H), 5.23 (d, $J = 17$ Hz,1 H), 5.07 (d, $J = 9$ Hz, 1H), 4.35 (dd, $J = 5.4$, 13.8 Hz, 1H), 4.3 (dd, $J = 5.0$, 13.8 Hz, 1 H), (CH_2=$CHCH_2$); 3.83 (m, 1 H, CH_2); 3.05 (m, 1 H, CH_2); 2.9 (m, 1 H, CH_2), 2.75 (m, 1 H, CH_2) 1.55 (m, 4 H, CH_2) 0.85 (m, 6 H, CH_3). Anal. Found: C, 63.58; H, 6.05; N, 2.15. $C_{31}FeH_{34}NO_5P$. Anal. Calc.: C, 63.37; H, 5.84; N, 2.38%.

The reaction with $HNEt_2$ was performed as above; five equivalents of amine (20 mmol, 1.46 g, 2.09 ml) were used. After evaporation of the solvent a yellow oil was obtained. The ^{13}C-NMR showed that this oil was composed of **8b** (60%) and of the triphenylphosphino carbene **6b** (40%). Complex **8b** was not isolated but its ^{13}C-NMR spectrum was obtained after removal of the signals of **6b** from those of the crude product. Complex **8b**:^{13}C-NMR: 219.3 (d, $J = 13$ Hz), 212.2 (d, $J = 15$ Hz), (C≡O); 205.4 (d, $J = 58$ Hz, CO_2R); 202.9 (d, $J = 13$ Hz, C(O)N); 134.3, 115.8, 63.9, (CH_2=CH–CH_2); 131.7 (d, $J = 15$ Hz), 131.3 (d, $J = 14$ Hz), 131.2 (s), 129.5 (d, $J = 10$ Hz) (PPh_3); 44.9, 41.8, 13.0, 12.5, (CH_2CH_3).

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC no. 149329. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk)

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