2680 *Organometallics* **1998,** *17,* 2680−2682

Formation of Metallacyclic Iron Carbene Complexes via C−O Coupling between the Two Ligands of Bis(carbamoyl) Intermediates

Denis Luart,[†] Nathalie le Gall,[†] Jean-Yves Salaün,*[,†] Loïc Toupet,[‡] and Hervé des Abbayes[†]

Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521, UFR Sciences et Techniques, Université de Bretagne Occidentale, 6, avenue le Gorgeu, BP 809, 29285 Brest Cédex, France, and Groupe Matière Condensée et Matériaux, UMR CNRS 6626, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cédex, France

Received March 9, 1998

Summary: The bis(carbamoyl)iron complexes $Fe[C(O)NR_2]_2(CO)_4$*, prepared either by reaction of carbamoyl anions* $[Fe(C(O)NR_2)(CO)_4]^-$ *with 0.5 equiv of oxalyl chloride or by alkoxy/amine exchange from* $Fe(CO_2Me)_2(CO)_4$*, undergo, even at low temperature, a rapid carbon−oxygen coupling of their two carbamoyl ligands to afford, after decarbonylation, stable metallacyclic carbenes of the general formula* $\overline{Fe[C(NR_2)OC(O})NR_2](CO)_3$*. A mechanism of the reaction is proposed.*

Acyl, alkoxycarbonyl, or carbamoyl transition-metal complexes have been extensively studied because of their essential role in the nucleophilic activation of carbon monoxide.[1] Alkoxycarbonyl compounds are thus recognized as intermediates in important catalytic processes such as carbonylation of alcohols, alkyl halides, and olefins to saturated esters.

Bis(alkoxycarbonyl) complexes have also been the subject of intensive investigations,[2] as they are considered as key intermediates of oxalate ester formation in the process of oxidative carbonylation of alcohols; so far, though, no well-characterized *cis*-bis(alkoxycarbonyl) complex has been found to thermolyze into oxalate[3] by C−C coupling of its two ligands.

Surprisingly, to our knowledge, only three examples of their bis(carbamoyl) homologues have been described: the mercury complex $Hg[C(O)NEt_2]_2$,[4] the ruthenium diphosphine compound $Ru[C(O)N(i\text{-}Pr)_2]_2(CO)_2$(bis(diphenylphosphino)ethane),[5] and very recently the dianion $[W\{C(O)N(i\text{-}Pr)_2\}_2(CO)_4]^{2-}$.[6] It is noteworthy that these last two complexes are stabilized by high electron densities of their metal center.

To study further evolutions of two carbamoyl ligands in *cis* positions on a metal center, we have undertaken the synthesis of iron complexes of the general formula *cis*-$Fe[C(O)NR_2]_2(CO)_4$. Two different routes were followed to prepare these amino homologues of the well-known series of *cis*-bis(alkoxycarbonyl) complexes $Fe(CO_2R)_2(CO)_4$[3] (Scheme 1).

According to the first one (path a) 0.5 equiv of oxalyl chloride was added at low temperature to the carbamoyl anions $[Fe\{C(O)NR_2\}(CO)_4]^-$, themselves obtained by nucleophilic addition of $LiNR_2$ on one carbonyl of $Fe(CO)_5$. This process probably occurs, as already proposed for the analogous preparation of $Fe(CO_2R)_2(CO)_4$,[2b,3] *via* the formation of the monobridged, unstable complex $(CO)_4\{C(O)NR_2\}Fe\{C(O)C(O)\}Fe\{C(O)NR_2\}(CO)_4$, which after decarbonylation affords the monocarbonyl monobridged intermediate $(CO)_4\{C(O)NR_2\}Fe\{C(O)\}Fe\{C(O)NR_2\}(CO)_4$, which rearranges into $Fe\{C(O)NR_2\}_2(CO)_4$ and $Fe(CO)_5$. Path b consists of an alkoxy/amine exchange on complex **1**.

Even at low temperatures (path a, −20 °C; path b, −5 °C), these two pathways did not afford the bis(carbamoyl) complexes **2** but orange-red products characterized as the metallacyclic carbenes **3**.[7] Yields obtained for **3** depend on the reaction affording these

---

* To whom correspondence should be addressed. E-mail: jean-yves.salaun@univ-brest.fr. Fax: (33) 0298016594.

[†] Université de Bretagne Occidentale.

[‡] Université de Rennes I.

(1) Ford, P. C.; Rockiki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139.

(2) (a) des Abbayes, H.; Laurent, P.; le Gall, G.; Salaün, J. Y. *Trends Organomet. Chem.* **1994**, *1*, 179. (b) Salaün, J. Y.; Laurent, P.; des Abbayes, H. *Coord. Chem. Rev.*, in press.

(3) Salaün, J. Y.; le Gall, G.; Laurent, P.; des Abbayes, H. *J. Organomet. Chem.* **1992**, *441*, 99.

(4) (a) Schöllkopf, U.; Gerhart, F. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 664. (b) Toman, K.; Hess, G. G. *Z. Kristallogr.* **1975**, *142*, 35.

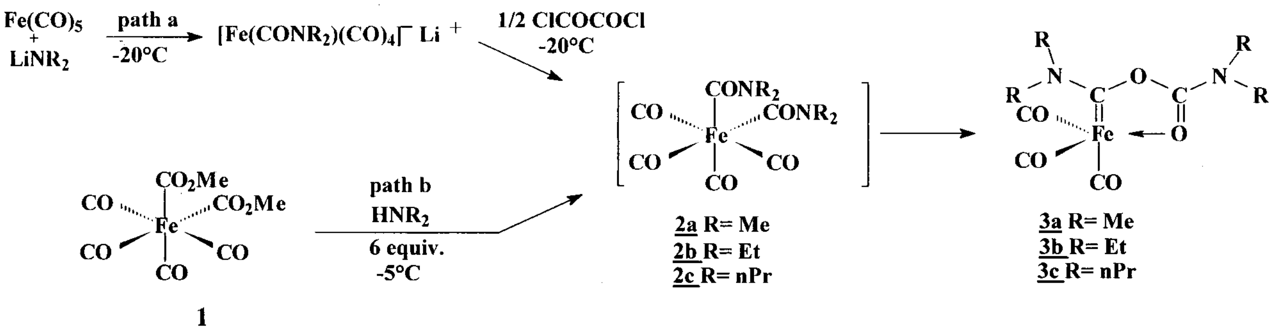
(5) Gargulak, J. D.; Gladfelter, W. L. *Inorg. Chem.* **1994**, *33*, 253.

(6) Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **1997**, *16*, 5595.

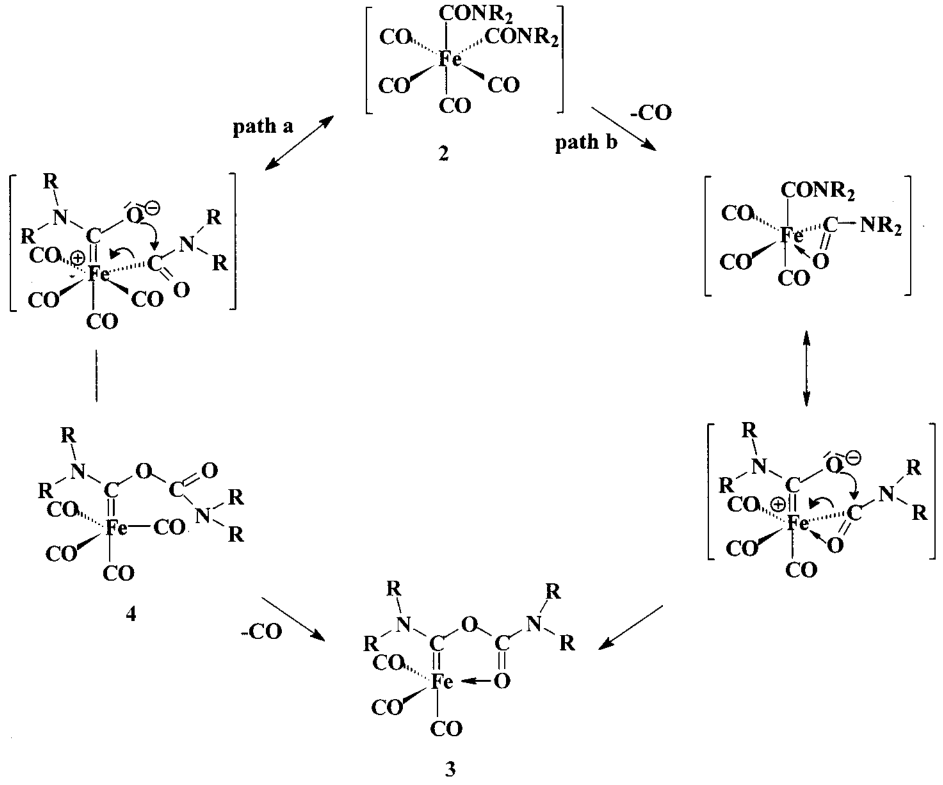
(7) In a typical procedure the following conditions were used for the synthesis of **3c**. Path a: 6 mmol of $Fe(CO)_5$ (1.176 g, 790 μL) in solution in 30 mL of THF at −20 °C was treated with 4 mmol of $LiN(n\text{-}Pr)_2$ in solution in THF. The mixture was stirred for 30 min, and 2 mmol of ClCOCOCl (175 μL) was then added to the solution, which immediately turned brown. The solvent was then evaporated, and the brown residue was extracted with two portions of 20 mL of dichloromethane−hexane (1/1). After filtration and concentration of the solution, the product precipitated as an orange-red powder. **3c** was recrystallized from hexane−dichloromethane (4/1); yield 25% (206 mg). Path b: 24 mmol of di-*n*-propylamine (2.4 g, 3.25 mL) was added to a solution of 2 mmol (572 mg) of $Fe(CO_2Me)_2(CO)_4$ (**1a**) in 10 mL of THF or CH_2Cl_2 at −5 °C. The pale yellow solution turned red as evolution of CO was observed. After 3 h the solvent was removed. The red residue was washed with two 10 mL portions of hexane. The red powder so obtained was recrystallized as detailed above to give 370 mg (yield 45%) of **3c**. Selected data for the new complexes **3** are as follows. **3a** (R = Me): IR (CH_2Cl_2) 1995 (m), 1890 (m), 1860 (s) (ν(CO)), 1692 cm^{-1} (w) (ν(NCO)); ^1H NMR (CD_2Cl_2, 0 °C) 3.63 (s, CH_3), 3.27 (s, CH_3), 3.25 (s, CH_3), 3.15 ppm (s, CH_3); $^{13}C\{^1H\}$ NMR 243.5 (Fe═C), 222.3 (CO), 157.3 (NCO), 45.1, 38.6, 37.9, 36.8 ppm (CH_3). **3b** (R = Et): IR (CH_2Cl_2) 1992 (m), 1892 (m), 1860 (s) (ν(CO)), 1682 cm^{-1} (w) (ν(NCO)); ^1H NMR (CD_2Cl_2, 0 °C) 3.91 (q, J_{H-H} = 7.2 Hz, CH_2), 3.54 (q, J_{H-H} = 7.3 Hz, CH_2), 3.35 (m, J_{H-H} = 7.3 and 7.1 Hz, $2CH_2$), 1.35 (t, J_{H-H} = 7.3 Hz, CH_3), 1.24 (t, J_{H-H} = 7.2 Hz, CH_3), 1.14 ppm (m, $2CH_3$); $^{13}C\{^1H\}$ NMR 243.5 (Fe═C), 222.7 (CO), 157.1 (NCO), 50.8, 43.8, 43.6, 42.7 (CH_2), 13.8 (2), 13.0, 12.6 ppm (CH_3). **3c** (R = n-Pr): IR (CH_2Cl_2) 2005 (m), 1902 (m), 1875 (s) (ν(CO)), 1694 cm^{-1} (w) (ν(NCO)); ^1H NMR (CD_2Cl_2, 0 °C) 3.62 (m, $2CH_2$), 3.58 (m, CH_2), 3.32 (m, CH_2), 1.45 (m, $4CH_2$), 1.22 (t, J_{H-H} = 7.4 Hz, CH_3), 1.15 ppm (m, $3CH_3$); $^{13}C\{^1H\}$ NMR 244.0 (Fe═C), 222.4 (CO), 157.2 (NCO), 58.4 (CH_2), 52.0 (CH_2), 49.3 (CH_2), 49.2 (CH_2), 22.7 (CH_2), 21.6 (CH_2), 21.2 ($2CH_2$), 11.5 ($2CH_3$), 11.2 ppm ($2CH_3$). Complexes **3** are too unstable to afford correct and reproducible analyses.

S0276-7333(98)00173-3 CCC: $15.00
Publication on Web 06/06/1998

Scheme 1



Scheme 2



compounds (path a, 25%) and also on the nature of R (path b: R = Me, 66%; R = Et, 63%; R = n-Pr, 45%). These carbenes are stabilized by two heteroatoms on their carbenic carbon and by the presence of a metallacycle.

To our knowledge only one iron complex of this type has been described.[8] This compound, $Fe[C\{N(i\text{-}Pr)_2\}OC(O)Et](CO)_3$, was obtained in 6% yield as a side product of the preparation of $Fe[C(OEt)N(i\text{-}Pr)_2](CO)_4$, by the usual Fischer carbene synthesis method.

^{13}C NMR spectra of complexes **3** exhibit resonances at ~244 ppm for their carbenic carbon and at ~157 ppm for their carbamate carbonyl. In contrast to the observations made on $Fe[C\{N(i\text{-}Pr)_2\}OC(O)Et](CO)_3$,[8] the presence of a single resonance at 222 ppm for the three carbonyl ligands of complexes **3** is indicative of fast exchanges occurring, even at low temperature, between these ligands. As already observed for amino carbenes[9] or for organic amides,[10] the substituents of the nitrogen atoms all appear different in ^1H or ^{13}C NMR. This is the result of restricted rotations about the C−N bonds induced by delocalizations of the nitrogen electronic doublets along the carbene or carbamate double bonds. In IR spectroscopy, the presence of three bands in the υ(CO) area is indicative of a local C_s symmetry of the $Fe(CO)_3$ fragment resulting from a coordination of the carbene chelate in axial and equatorial positions on a trigonal bipyramid.

This geometry is confirmed by the X-ray molecular structure determination of **3b**[11] (Figure 1), which shows that the carbene carbon is in an axial position and

---

[8] Fischer, E. O.; Schneider, J.; Ackermann, K. *Z. Naturforsch.* **1984**, *39B*, 468.

[9] Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

[10] Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

[11] Crystal structure data for **3b**: $C_{13}H_{20}FeN_2O_5$, M_r = 340.16, triclinic, space group $P\bar{1}$, a = 9.774(7) Å, b = 10.477(7) Å, c = 16.929(5) Å, α = 81.33(3)°, β = 84.54(3)°, γ = 68.61(4)°, V = 1584(2) Å^3, D(calcd) = 1.426 g cm^{-3}, Z = 2, μ(Mo Kα) = 9.694 cm^{-1}, F(000) = 712, T = 120 K. A parallelepiped of dimensions 0.15 × 0.22 × 0.25 mm was selected and studied on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation. The structure was solved by the Patterson method. A total of 5917 reflections were collected, of which 2961 ($I > 3\sigma(I)$) were used to give R = 0.039 and R_w = 0.035.

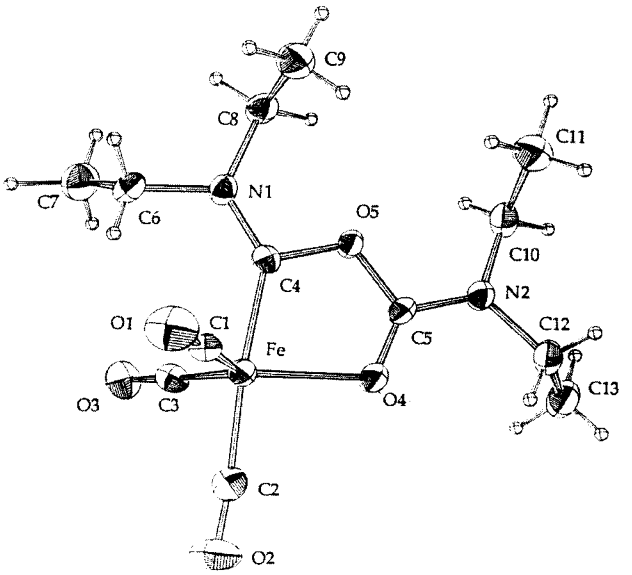


Figure 1. Molecular structure of the carbene **3b**. Important distances (Å): Fe−C1, 1.756(4); Fe−C2, 1.801(5); Fe−C3, 1.745(5); Fe−C4, 1.911(5); C4−N1, 1.314(6); C4−O5, 1.394(5); Fe−O4, 2.066(3). Selected angles (deg): O4−Fe−C4, 79.3(2); Fe−C4−O5, 115.0(3); C4−O5−C5, 113.3(3); O4−C5−O5, 120.0(3); Fe−O4−C5, 112.3(3); C1−Fe−C3, 121.5(5); C1−Fe−O4, 117.5(2); O4−Fe−C3, 120.5(2); C1−Fe−C2, 89.4(2); C2−Fe−C3, 91.6(2); O4−Fe−C2, 95.8(2).

confirms the presence on the complex of a metallacycle formed by a bond between the metal and the oxygen of the carbamate carbonyl.

Owing to the five-membered ring thus formed, the angle C4−Fe−O4 is reduced to 79.3(2)°, resulting in a distorted-trigonal-bipyramidal geometry. The metallacycle is essentially planar. The two NEt_2 substituents (N1, C6, C8 and N2, C10, C12 atoms) are also almost coplanar with the cycle (N1−C6 forms a torsion angle of −3.05 (0.67)° with the Fe−C4 bond and C10−N2 an angle of −8.95(0.58)° with C5−O5), confirming that the nitrogen doublets are in resonance with the carbene (N1) and the carbonyl of the carbamate (N2). Such planar geometries of carbenic metallacycles have already been observed for chromium complexes.[9] The Fe−C4 bond length is comparable with those of Fe−carbene bonds in a variety of iron carbene complexes. As expected, C4−N1 (1.314(6) Å) and C4−O5 (1.394(5) Å) bonds are shortened with respect to C−N and C−O single bonds.[12] The distance between the metal and the oxygen of the carbamate (Fe−O4) has a value (2.066(3) Å) comparable with that observed for $Fe[C\{N(i\text{-}Pr)_2\}\text{-}OC(O)Et](CO)_3$ (2.025(4) Å).[8]

The reactions affording **3** and the structure observed for these complexes strongly suggest that their formation could occur via the unstable bis(carbamoyl) $Fe[C(O)NR_2]_2(CO)_4$ (**2**) intermediates. Further evolution of these intermediates giving rise to the metallacyclic carbenes **3** may be rationalized in Scheme 2.

According to path a a carbamoyl oxygen of **2** could attack the carbon of the carbonyl of the second carbamoyl. This coupling between two carbamoyl ligands by formation of a C−O bond would induce the formation of the amino(carbamato)carbenes $Fe[C(NR_2)OC(O)NR_2](CO)_4$ (**4**), which after the loss of a carbonyl would afford **3**.

However, this pathway is ruled out by the easy preparation and the full characterization of the intermediates **4**.[13] These complexes are indeed readily formed when species **3** are maintained under an atmosphere of carbon monoxide, but the reverse reaction (decarbonylation of **4** affording **3**) does not occur even under an inert atmosphere at room temperature.

Path b represents the most likely route for the evolution of the bis(carbamoyl) compounds **2** into the metallacarbenes **3**. This process requires the formation of the intermediate η^1-carbamoyl, η^2-carbamoyl compound $Fe[\eta^1\text{-}C(O)NR_2][\eta^2\text{-}C(O)NR_2](CO)_3$.[16] The oxygen of the η^1-carbamoyl group of this intermediate would attack the carbon of the carbonyl of the η^2-carbamoyl, affording **3** by a carbon−oxygen coupling between the two carbamoyl ligands. Such a coupling between two ligands via a C−O bond formation is rather unusual. It has, however, been observed in the coupling of carbamoyl and difluorocarbene ligands[19] and has very recently been suggested in the conversion of a bis(carbamoyl)-tungsten dianion into an aminomethylidyne complex.[6] This carbon−oxygen coupling also occurs in the process of formation of a platinum carbene by intramolecular coupling of two α-ketoacyl and carbamoyl ligands[20] and in the cyclization of two alkoxycarbonyl and alkyloxalyl ligands affording a ferraalkoxyketolactone complex.[21]

Further experiments to confirm the proposed mechanism of formation of **3** are currently in progress.

Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances and angles, and torsion angles for **3b** (16 pages). Ordering information is given on any current masthead page.

OM980173L

---

[12] Lide, D. R. *Tetrahedron* **1962**, *17*, 125.

[13] Example of preparation of complexes **4**. $Fe[C(NMe_2)OC(O)NMe_2](CO)_4$ (**4a**): 6 mmol of **3a** (1.704 g) in solution in 100 mL of CH_2Cl_2 was stirred for 3 days at 0 °C under an atmosphere of carbon monoxide. After evaporation of the solvent, the brown residue was extracted with two 10 mL portions of a hexane−dichloromethane mixture (9/1). After chromatography at room temperature on alumina, **4a** was obtained as pale yellow crystals (yield 50%; 936 mg). **4a**: IR (hexane) 2047 (m), 1963 (m), 1938 (s), 1925 (s) (ν(CO)), 1729 cm^{-1} (m) (ν(NCO)); ^1H NMR (CD_2Cl_2, 0 °C) 3.64 (s, CH_3), 3.13 (s, CH_3), 2.93 (s, CH_3), 2.98 ppm (s, CH_3); $^{13}C\{^1H\}$ NMR 238.0 (Fe=C), 214.9 (CO), 149.4 (NCO), 46.7, 40.3, 36.4, 36.3 ppm (CH_3). Anal. Calcd for $C_{10}H_{12}FeO_6N_2$ (mw 312.15): C, 38.49; H, 3.88; N, 8.98. Found: C, 38.35; H, 3.95; N, 8.92. These IR and NMR characteristics are very close to those observed for similar tetracarbonyliron carbene complexes.[8,14,15]

[14] Fisher, E. O.; Beck, H. J.; Kreiter, G. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

[15] (a) Petz, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 367. (b) Petz, W. *J. Organomet. Chem.* **1981**, *205*, 203.

[16] Such modes of complexation have already been observed for iron complexes (η^2-acyl[17] or η^2-carbamoyl[18]).

[17] Birk, H.; Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1988**, *121*, 1557.

[18] Anderson, S.; Hill, A. F.; Clark, G. R. *Organometallics* **1992**, *11*, 1988.

[19] Anderson, S.; Hill, A. F.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 266.

[20] Chen, J. T.; Tzeng, W. H.; Tsai, F. Y.; Cheng, M. C.; Wang, Y. *Organometallics* **1991**, *10*, 3954.

[21] Sellin, M.; Luart, D.; Salaün, J. Y.; Laurent, P.; Toupet, L.; des Abbayes, H. *J. Chem. Soc., Chem. Commun.* **1996**, 857.