Double carbonylation and beyond: systems at work and their organometallic models

Hervé des Abbayes and Jean-Yves Salaün

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 cedex, France

A quarter of a century after its (serendipitous) discovery, the catalytic sequential chaining of two carbon monoxides into an organic substrate (the so called double carbonylation reaction), is still not well understood. After a review of the most important experimental results, this Perspective proposes a critical survey of the main organometallic models and outlines some rather neglected tracks. Finally, the issue of the chaining of more than two carbon monoxides is also addressed.

Introduction, scope and limitations

Chemists have always been fascinated by recurring sequences constructed by regular repetition of simple motifs. An example (among many others) is given by perfectly alternating ethylene and carbon monoxide in polyketones **I** resulting from the transition metal catalyzed copolymerization of ethylene and carbon monoxide.[1] It is well known that ethylene alone polymerizes into polyethylene **II**,[1] but this is not the case for carbon monoxide and polymeric chainings such as **III** (Scheme 1) do not exist.

Meanwhile, at a very modest level for the value of *n*, chainings like **III** are found for *n* = 2 in very common 1–2 dicarbonyl compounds **IV** (Scheme 2) and for *n* > 2 in less
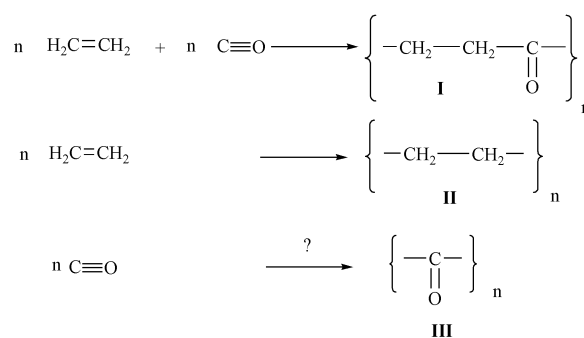
Scheme 1

common so-called vicinal polycarbonyl compounds (see examples **V**, **VI**, **VII**);[2] polycarbonyl anions such as **VIII** are closely related to this series.[3]

Although well documented, up to the middle of the seventies the carbonylation of organic substrates mediated by transition metals did not show any example of incorporation of more than one carbon monoxide into an organic substrate. For instance, carbonylation of organic halides **IX** only gave products of the general structure **X** (*n* = 1) (Scheme 3) and, at that time, mechanistic considerations on carbonylation
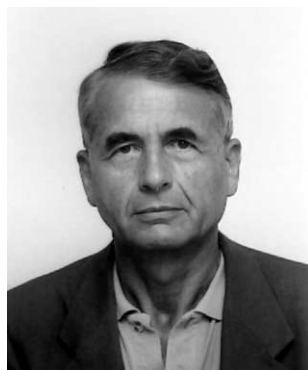
After a doctorate in organic chemistry devoted to some problems of ring–chain tautomerism in substituted succinaldehydic acids, H. des Abbayes took, in 1970, the opportunity of a position in Prof. Dabard's laboratory at Rennes (France) to be initiated into organotransition metal chemistry. Very soon interested by metal carbonyls and their applications, he spent around a year as a post doctoral fellow in Prof. Alper's laboratory at Ottawa University, in which he was free to develop, in collaboration with Prof. Alper, his own research proposal: the applications of phase transfer catalysis in metal carbonyl chemistry, which were almost unexplored at that time. He is now a full Professor at the University of Brest (France). His interests include the modelling of carbon–carbon coupling with octahedral iron complexes and ring–chain tautomerism in organometallic chemistry (in collaboration with Dr J. Y. Salaün), syntheses and evaluation of hemilabile ligands for homogeneous catalysis (in collaboration with Drs J. C. Clément, J. J. Yaouanc and P. Laurent); he also shares a strong interest with Drs J. J. Yaouanc and J. C. Clément on a very exciting field at the border of chemistry and biology: the problem of transfer of DNA with synthetic carriers.

Hervé des Abbayes

Jean-Yves Salaün studied chemistry at the Université de Bretagne Occidentale in Brest (France) and received his thesis in organic chemistry in 1979. In his thesis work, he investigated the validity of the Woodward–Hoffmann rules in photochemistry. He then moved toward organometallic chemistry, obtained a grant from the Royal Chemical Society and spent one year as a post-doctoral fellow in Gordon Stone's laboratory at the University of Bristol. During this year he studied the properties of clusters with bridging carbenes or carbynes. He then joined the Centre National de la Recherche Scientifique and started to study the influence of the geometry of organic bulky ligands on the properties of their Pt, Ti or Zr complexes. His actual main interest is the modelling, (carried out with Prof. H. des Abbayes) on iron compounds, of catalytic organic reactions such as carbon–carbon coupling processes (including the question of double carbonylation) or chain-cycle transformations induced by nucleophilic reagents.

Jean-Yves Salaün

IV   **V**   **VI**

VII   **VIII**

2^{-}

Scheme 2

RX → R[C(=O)—Nu]$_n$ via CO, [M], NuH

IX   **X**
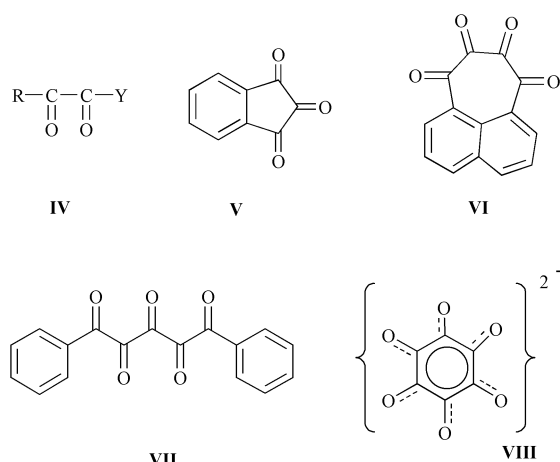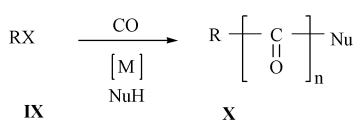
Scheme 3

processes were not in favour of supplementary sequential incorporations of carbon monoxide ($n = 2$ and beyond).[4]

Despite this, several examples of the thereafter so-called double carbonylation (Scheme 3, $n = 2$) were found fortuitously: the first one was the carbonylation of benzyl halides into phenylpyruvic acids (R = $C_6H_5CH_2$, X = Cl, $n = 2$, Nu = OH) with the cobalt carbonyl anion $[Co(CO)_4]^-$ as catalyst under basic conditions.[5–7] It was found later that aryl halides ArX could be directly converted into α-ketoamides (R = Ar, X = Br, Nu = NR_2', $n = 2$) with a palladium complex as the transition metal catalyst.[8,9]

To our knowledge, the last review dedicated to these systems is the article of J. Collin which appeared in 1988.[10] Our first aim here will be to give a timely factual survey of the most significant results in double carbonylation mediated by transition metals; although essentially focussing on catalytic systems, this review will also present a selection of stoichiometric double carbonylations as far as they seem relevant or affording original views; furthermore, several examples of transition metal mediated sequential incorporation of more than two carbon monoxides will be given. Our second aim will be to review monometallic complexes or reactions which have been proposed as models to support some of the elementary steps of double carbonylation with transition metals; thereafter we will have a look to other ways of sequential chainings of carbon monoxide. In this review, the meaning of the keyword *double carbonylation* will be restricted to formal sequential *double insertion* of carbon monoxide such as illustrated in Scheme 3 ($n = 2$) and therefore classical monocarbonylation (Scheme 3, $n = 1$) occurring at two different parts of the same substrate (for example transformation of α,α′-dibromo *p*-xylene into 1,4-phenylenediacetic acid) will not be considered.

Systems at work: factual survey of transition metal mediated double carbonylation and beyond

In this section we will give a selection of the most significant results on transition metal mediated double carbonylation, whatever the mechanism. It appears that long known efficient metals in traditional monocarbonylation (Fe, Ni, Co, Pd. . .)[11,12] are also operative in double carbonylation, although very few of them are efficient catalysts (essentially Co and Pd). Factual evidence for oligomerization of carbon monoxide will also be presented.

Double carbonylation with cobalt

Benzyl halides. Although monocarbonylation of benzyl halides into arylacetic acids (Scheme 4, R = $PhCH_2$, $n = 0$) with cobalt carbonyls has been known for a long time,[12] the first observation of double carbonylation of benzyl chlorides into arylpyruvic acids (R = $PhCH_2$, $n = 1$) was only described in an industrial patent which appeared in 1976.[5] This reaction was independently rediscovered soon after by one of us under phase transfer conditions.[6,7] In these processes, the ratio between mono- and di-carbonylation was found to be dependent on the nature of the substituents on the aromatic rings and on the experimental conditions. Further publications or patents came out soon after, extending the scope of the reaction to other benzylic compounds under similar conditions.[13–16]

RX $\xrightarrow[\text{CO, Base}]{Co_2(CO)_8}$ $R(CO)_nCO_2H$

IX   **XI**: $n = 0$; **XII**: $n = 1$
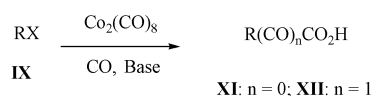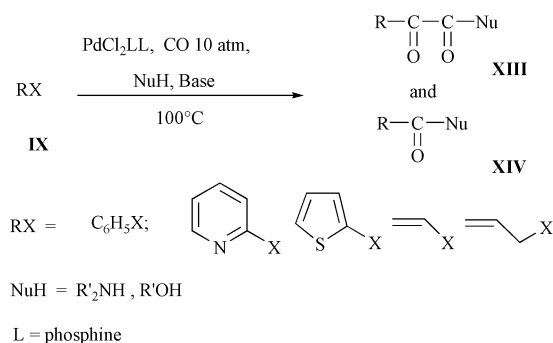
Scheme 4

Aryl halides. Although more reluctant to monocarbonylation with cobalt carbonyl than benzyl halides, aryl halides (Scheme 4, **IX** R = Ph) can be converted into benzoic acids (**XI**, $n = 0$).[17–20] Not too surprisingly, their conversion into α-keto acids **XII** ($n = 1$) was described soon after under special conditions: presence of methyl iodide or sulfate[20–24] or irradiation.[25]

Other substrates. Double carbonylation was also observed with cobalt carbonyl under conditions similar to those described above, namely with styrene oxides,[26] alkyl bromides or iodides[27] and phenetyl bromide.[28] Other results are also relevant in this context: they concern a supplementary CO insertion in a strained cyclobutanone[29] and sequential chaining of CO on acetylenic substrates.[30]

Double carbonylation with palladium

The discovery of double carbonylation with palladium came later than with cobalt. The main organic substrates are aryl, vinyl or allyl halides (mostly bromides and iodides), amines or alcohols.

Aryl, vinyl and allyl halides. A general sketch of the double carbonylation of halides with palladium is given in Scheme 5.

RX $\xrightarrow[\text{100°C}]{\substack{PdCl_2LL, \ CO \ 10 \ atm, \\ NuH, Base}}$

R—C(=O)—C(=O)—Nu   **XIII**

and

R—C(=O)—Nu   **XIV**

IX

RX = C_6H_5X; (pyridyl-X); (thienyl-X); =\—X; =\—X

NuH = $R_2'NH$, R'OH

L = phosphine

Scheme 5

The first mention of double carbonylation with palladium was made by Yamamoto and Ozawa in 1982. They described the stoichiometric transformation of *trans*-Pd(R)(X)(PMePh$_2$)$_2$ complexes into α-ketoamides **XIII** (Nu = NR_2') after attack, under a CO atmosphere, of an excess of secondary amine (NuH = NH(R′)$_2$).[31] Simultaneously, they gave a preliminary account on the catalytic double carbonylation of organic halides (mostly aryl bromides and iodides, and vinyl bromides) into α-ketoamides **XIII** in the presence of proper secondary amines.[8]

Very similar results were presented at the same time by Tanaka and Kobayashi.[9] Both works mentioned the critical role played by several factors such as: the nature of the amine (a secondary amine such as diethyl amine is generally convenient but the use of a mixture of n-butylamine and DABCO (1,4 diaza-bicyclo[2.2.2]octane) was recently reported to give α-keto-amides with a good selectivity under an atmospheric pressure of carbon monoxide),[32] the nature of the phosphine ligand L (PMePh$_2$ generally giving better yields than PPh$_3$), the pressure of carbon monoxide, the nature of the solvent, the temperature, *etc.*. . . These papers were followed by several others from different authors, which, for most of them, were extensions to similar substrates of these basic publications to give α-ketoamides,[33] α-ketoesters or their reduced form α-hydroxyesters (see refs. 34–38). It was also found that chlorobenzene, normally reluctant to double carbonylation under conditions of Scheme 5, could be partly converted into α-ketoamide (52% yield) after prior activation as its chromium tricarbonyl complex.[39] A paper entirely devoted to double carbonylation of vinyl bromides or iodides into α-ketoamides came out in 1988.[40] In some cases, α-diketones were obtained.[41] More recently it was found that allylic chlorides could be successfully doubly-carbonylated to give α-ketoamides.[42]

Amines and alcohols. Double carbonylation has also been observed for amines, alcohols,[43,44] aminoalcohols and diols.[45] Double carbonylation of alcohols into oxalate **XV** is of special interest since it is an important industrial process; its particular experimental conditions are summarized in Scheme 6; note the presence of dioxygen: thus, the reaction is an oxidative carbonylation.[46]
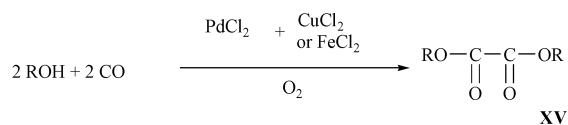
Scheme 6

Alkenes. The reaction shown in Scheme 7, although stoichiometric with palladium, is a rare example of double carbonylation of an alkene substrate.[47] It goes through intermediates **1**, which, after carbonyl insertion and further attack by piperidine, gives ketoamides **XVI**. Complexes of type **1** may also be directly synthesized by reaction of [PdCl$_4$]$^{2-}$ with the appropriate γ-aminoaldehydes.[48]
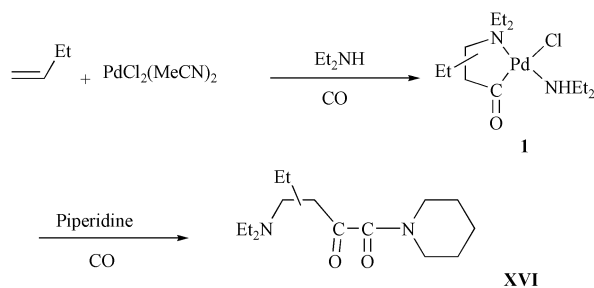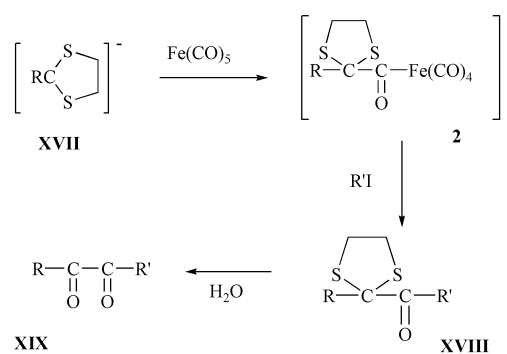
Scheme 7

Double carbonylation with other metals

Nickel. There are very few examples of catalytic double carbonylation with nickel; one of them is given in refs. 49 and 50.

Iron. As far as we are aware, there are only stoichiometric examples of double carbonylation with iron. A selection is given below.

The sequence in Scheme 8, proposed by Yamashita and Suemitsu,[51] shows the creation of a C(O)C(O) chaining by addition of the thioacetal anion **XVII** (which is a masked equivalent of an acylate) on one terminal CO of iron penta-
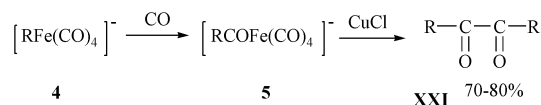
Scheme 8

carbonyl. Further oxidative addition of an alkyl or an aryl iodide, followed by hydrolysis gives the diketone **XIX**, probably through intermediates **2** and **XVIII**.

Yamagushi and co-workers observed that strained acyl iron carbonyl complex **3** could be oxidized into α-diketone **XX**[52] (Scheme 9).
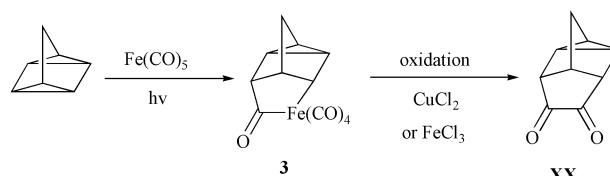
Scheme 9

Periasamy and co-workers showed that, by treatment of acyl ferrates **5** with CuCl, diketones **XXI** were obtained in good yields; since these acyl ferrates may be produced by CO insertion in alkyl ferrates **4**, this reaction is formally a double carbonylation[53–55] (Scheme 10).

Scheme 10

Appreciable amounts of the same diketone **XXI** was also obtained by thermolysis of a bis(μ-acyl or aryl) binuclear iron complex (CO)$_6$Fe$_2$[μ,η^2-RC(O)]$_2$ (**6**).[56]

It was shown later that a stoichiometric reaction of alkynes on the hydrido tetracarbonyliron anion **7** in the presence of iodine, iodomethane or trimethylchlorosilane and CuCl$_2$ gave cyclobutenedione **XXII** in good yields (Scheme 11).[57]
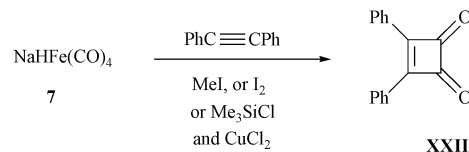
Scheme 11

Beyond double carbonylation

The example of Scheme 12 shows that on complex **8** three CO, which were previously coordinated to iron in pentacarbonyl-iron, have been sequentially linked.[58]
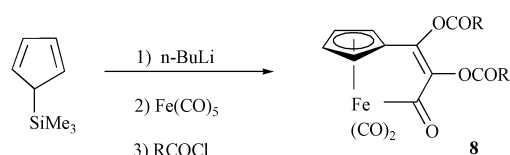
Scheme 12

So far, except the Fischer–Tropsch process[1] (nCO + $2n$H$_2$ → –(CH$_2$)$_n$– + nH$_2$O), there is no example of polymeric carbon–carbon chaining issued from carbon monoxide only.

It is worth pointing out that in this reaction the C–C bonds are created under reducing conditions; then a clue for oligomerization of carbon monoxide might be to explore other reducing agents than dihydrogen. This idea was at work in the recent example of catalytic reduction of carbon monoxide with hydrosilanes induced by rhodium complexes which produced adducts resulting from dimerization (**XXIII**) and trimerization (**XXIV**) of carbon monoxide, with traces of more oligomerized products[59] (Scheme 13). However, none of these oligomeric chainings of carbon monoxide are of the polycarbonyl type **III** of Scheme 1.

Scheme 13

How do they work? A review of organometallic models

Most reactions mentioned above may look rather tricky and puzzling and indeed serious mechanistic studies are generally lacking, except for the catalytic double carbonylation of benzyl halides with cobalt (Scheme 4) or of aryl halides with p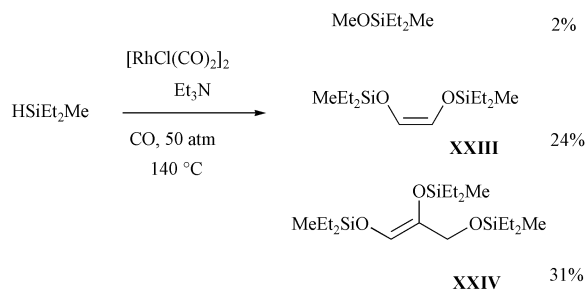alladium (Scheme 5), which thus will deserve special comments. The former has been mainly studied by Cassar and Foa; the latter separately by two groups: Yamamoto's group on the one hand and Chen's group on the other. Leading references from these authors will be quoted in the following text. Here, we will draw attention to well identified organometallic models (all of them being monometallic) which have been put forward to support mechanistic propositions. For a good understanding, some elementary processes of organotransition metal chemistry will be recalled along the discussion; a clear introduction to these topics is available from the book by Collman and Hegedus.[4]

Two basic routes, A and B, proposed for the double carbonylation of aryl halides[60] may also be considered for a general discussion of the catalytic double carbonylation of organic halides (Scheme 14).

The first step of the reaction is the oxidative addition on transition metal complexes (step a); it is quite well documented[4] and will not be discussed further here. The examples shown in Scheme 15 are of special interest as they are the first
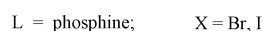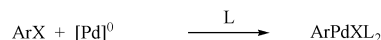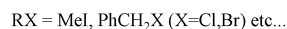
Scheme 15

steps of double carbonylation performed with cobalt or palladium.

This oxidative addition may occur *via* a two- or a one-electron mechanism. The latter, which may be photochemically initiated, involves radicals and it may be interesting to note that this point has never been taken into consideration in mechanistic propositions on double carbonylation performed with transition metals.

Step a of Scheme 14 is followed by the so-called migratory insertion of CO (step b). Then, two routes may be possible. Route A supposes a further migratory insertion of CO to create the C(O)C(O) chaining (step c), followed by a nucleophilic attack on the α-carbonyl of the so formed ligand to liberate the double carbonylated product (step d). Route B supposes a nucleophilic attack on a terminal CO (step f); then, a carbon-carbon coupling would afford the C(O)C(O) chaining (step g). These different steps will be discussed in the light of pertinent available organometallic models.

The sequential CO migratory insertion affording COCO chaining

Most carbonylation processes go through the so-called migratory insertion of carbon monoxide into a [M]–R bond affording [M]–C(O)–R.[4] Despite its very simple aspect, this essential step is far from being so. From many careful studies on well identified complexes, it results that, in fact, the reaction consists of a migration of the alkyl group on a terminal carbonyl in a *cis* position. Whatever they are, ancillary ligands L (CO, phosphines, amines or coordinated solvent) play an important role in this process. Changes in the oxidation state of the metal can also considerably accelerate the migratory insertion. The most important examples for our discussion are found for cobalt and palladium complexes.[4] The reaction, which is reversible, is in favour of the acyl form if R is electron-donating, and of the alkyl form if R is electron-withdrawing. It results from these electronic requirements of R that a migration of an acyl group (in which the carbon atom of the carbonyl is electron poor) on a carbonyl (formation of the C(O)C(O) chaining) is very unlikely (Scheme 16).

Indeed there are many examples of the reverse facile decarbonylation of α,β-dicarbonylated ligands. A classical example is given in Scheme 17:[61] complex **9**, which is kinetically reasonably stable, readily decarbonylates into **10**, which in turn, after a new decarbonylation, affords **11**.
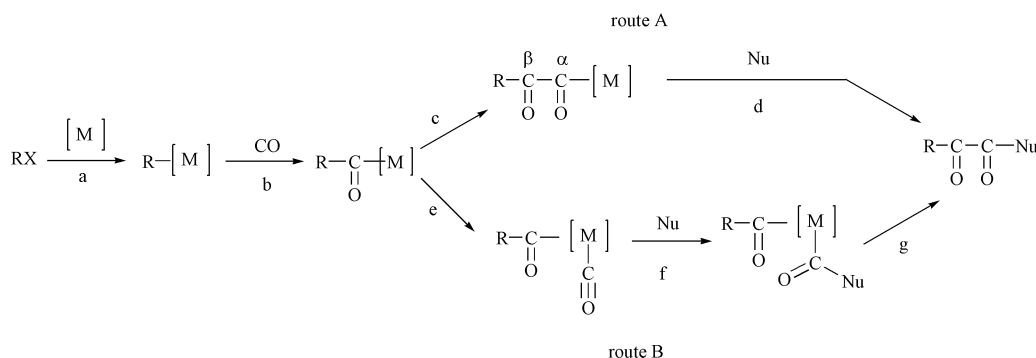
Scheme 14

Scheme 16

9 **10** **11**
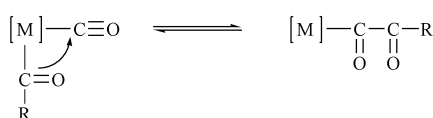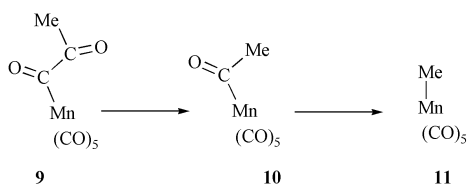
Scheme 17

Several other examples of complexes with a C(O)C(O) chaining and behaving similarly will be given below. Then, there is strong evidence that the sequence shown in Scheme 16 is not operative *as such* in double carbonylations. We should however not conclude from this that there is no hope to observe the occurrence of this C(O)C(O) chaining formation on well identified complexes under particular conditions. A nice example was found by Geoffroy and co-workers[62] (Scheme 18).

12 **13** **14**
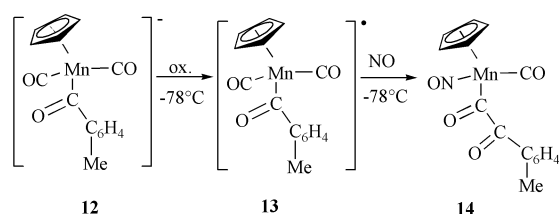
Scheme 18

Oxidation of anion **12** gives the rather stable (at −78 °C) radical **13**, which, on addition of NO, quantitatively affords a second CO insertion (complex **14**). It is worth pointing out here that a monoelectronic oxidation of the metal is obviously at work in this insertion reaction also favoured by the use of the suitable NO ligand which is also a radical.

An interesting explanation of double carbonylation, which only stands for benzyl halides, was proposed by Cassar:[63] it is well known in organic chemistry that enolizable ketones are readily deprotonated by a base; it is assumed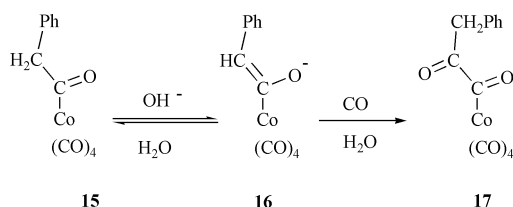 that such a reaction is also operative on the *in situ* characterized acyl organocobalt intermediate **15** (Scheme 19).

15 **16** **17**

Scheme 19

The carbon atom of the organic moiety linked to the cobalt, which was previously electron poor on **15**, becomes electron rich on the anionic organometallic enolate **16**; then it is assumed that the enolate group can migrate on a terminal CO to give complex **17**. Since complex **15** is quite fragile (and always in equilibrium with the alkyl form), there is very little hope to gain direct structural evidence of the existence of enolate **16**, and structural information about complex **17** is still lacking. Nevertheless, an indirect experimental support to this assumption was given:[15] a strong isotopic effect was observed for the double carbonylation of α-phenethyl bromide (Scheme 4, R = ArC(H)Me): when the hydrogen of the benzylic carbon was replaced by a deuterium, the yield of arylpyruvic acid was

significantly lowered. Then, the following question may be asked: do enolate anions similar to **16** exist; and, if so, is a further CO migratory insertion observable on these complexes? So far, if the deprotonation of acyl ligands on organotransition metal complexes to give stable enolates is well documented,[64,65] the so formed enolate groups do not show any tendency to migrate on terminal carbonyls of available models. What is not observable on enolate complexes might be so on a silyl enol ether derivative, which is structurally equivalent. This idea was beautifully illustrated by Cutler and Gregg[66] (Scheme 20): silylation of the acetyl complex **10** gives the siloxyvinyl **18** (which is formally equivalent to an acylate); then, under a carbon monoxide atmosphere, the second CO migratory insertion occurs; after acidification of complex **19**, the C(O)C(O) chaining is observable on complex **9**. All these complexes (**10**, **18**, **19**, **9**) were fully characterized.

10 **18** **19** **9**
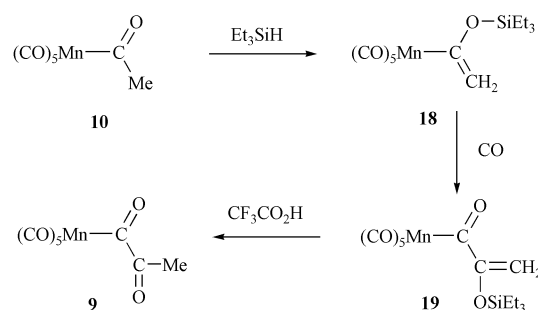
Scheme 20

So far, while there is no palladium model to support sequential migratory insertion of two carbon monoxide to give the COCO chaining (Scheme 16), some complexes bearing such a chaining, synthesized by other ways, were obtained and fully characterized (mostly by X-ray studies). Homologous platinum compounds which generally give similar but more stable complexes were also prepared. Their thermal behaviour has been studied and a facile thermal decarbonylation was systematically observed. Thus *trans*-[PhC(O)C(O)]Pd(PPh₃)₂Cl or *trans*-[PhC(O)C(O)]Pt(PPh₃)₂Cl (**20** or **21**) and *trans*-{[PhC(O)C(O)]Pt(PPh₃)₂(CO)}⁺ (**22**) are found to decarbonylate into respectively *trans*-[PhC(O)]Pd(PPh₃)₂Cl or *trans*-[PhC(O)]Pt(PPh₃)₂Cl (**23** or **24**)[67] and *trans*-{[PhC(O)]Pt-(PPh₃)₂(CO)}⁺ (**25**)[68] whereas *trans*-[PhC(O)C(O)]Pt(PPh₃)₂-(Et) (**26**) affords *trans*-[PhC(O)C(O)]Pt(PPh₃)₂[C(O)Et] (**27**).[69]

Nucleophilic addition and double carbonylation

As described in Scheme 14 nucleophilic additions can be involved in dicarbonylation processes according to two reaction paths: the first one concerns an addition on the α carbonyl of a RC(O)C(O) ligand formed by the sequential double CO insertion discussed above (step d) and the second involves an attack on a terminal carbonyl of a complex already substituted by an acyl, aryl, alkoxycarbonyl or carbamoyl ligand (step f). This last reaction would afford a complex bearing two mono-carbonylated ligands which, by a carbon–carbon coupling, would give rise to the C(O)C(O) chaining (step g). We will successively consider these two possibilities.

(a) Double carbonylation performed by nucleophilic addition on the α carbon of a RC(O)C(O) ligand

Despite the low probability of the efficiency of a sequential double insertion of CO in the double carbonylation process, the possibility of a nucleophilic attack on the α carbon of an α-ketoacyl ligand has been considered in some catalytic reactions. Thus in the following example (Scheme 21) of dicarbonylation of organic halides initiated by [Co(CO)₄]⁻,[7,15,16,63] together with a nucleophilic addition of an alcoholate on a
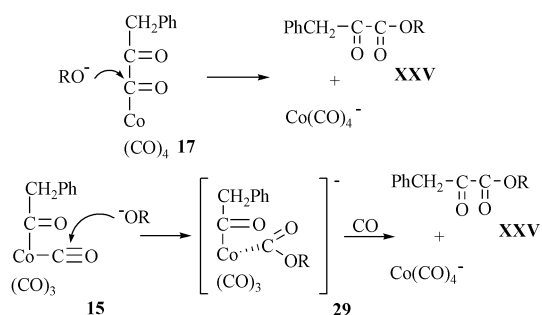
Scheme 21

terminal carbonyl of the acylated intermediate **15**, the possibility of an attack of the same nucleophile reagent on the α-carbon of a benzylglyoxyl ligand of the intermediate **17** has also been proposed to account for the formation of phenylpyruvic esters (or acids). As complexes PhCH₂Co(CO)₄ (**28**) and [PhCH₂C(O)]Co(CO)₄ (**15**) are always in equilibrium under CO, then, the formation of the intermediate **17** might arise from **15** *via* the acylate mechanism described in Scheme 19. The only experimental argument in favour of such a reaction path is the observation of a strong isotopic effect on the course of the process performed with α-phenethyl bromide.[15]

The essential part of mechanistic works on double carbonylation performed with palladium turns on aryl halides (see Scheme 5 for the general scope of this reaction). The most efficient system which works with a secondary amine (HN(Et)₂) as pronucleophile produces an α-ketoamide.[31] When the pronucleophile is an alcohol (activated by a tertiary amine), an α-ketoester is obtained in lower yield.[31b] As the reactions are performed with aryl halides, the "enolate route" affording the C(O)C(O) chaining is obviously not operative here and there is, to our knowledge, no palladium model of such a chaining formation by sequential insertion of two carbon monoxide ligands. These observations suggest that a nucleophilic addition on the α carbon of a RC(O)C(O) ligand (step d of Scheme 14) is not operative in the reaction of double carbonylation of aryl halides into α-ketoamides catalysed by palladium complexes. The following examples are in agreement with such an assertion: the phenylglyoxyl palladium complex **30** failed to afford the α-ketoamide **XXVII** which is surprisingly obtained in good yield from the benzoyl homologue **31**[70,71] (Scheme 22).
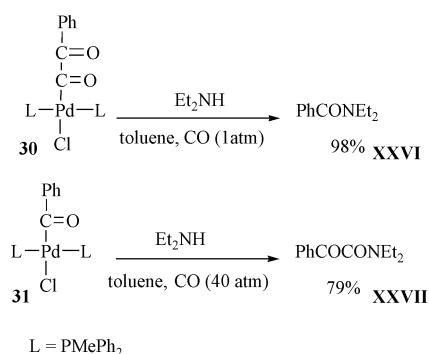
Scheme 22

However, it must be noticed that the second experiment is performed under high CO pressure (40 atm) and the first one at 1 atm.

This question about the possibility to perform a double carbonylation from a complex displaying a RC(O)C(O) pattern is not closed as the same authors reported later[72] that nucleophilic addition of alcohols in the presence of a tertiary amine on the cationic *trans* phenylglyoxyl palladium complex **32** afforded (no yield given) the ketoester **XXVIII** together with the monocarbonylated product **XXIX** (Scheme 23).
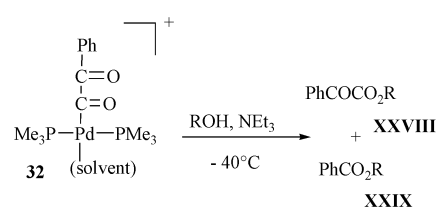
Scheme 23

Another argument against the occurrence of the intervention of a RC(O)C(O) ligand in the double carbonylation process has also been brought to the fore by the observation, on several models, that ligating carbons of RC(O)C(O) ligands (α carbon) are not the more electrophilic sites of the molecule (Scheme 24): on iron (**33**)[73] or platinum (**35**)[68] cationic complexes, additions of alcoholates or amines occur on terminal carbonyls while on a neutral iron compound (**37**), attack of a series of pronucleophiles takes place on the β carbonyl of the pyruvoyl ligand.[73]
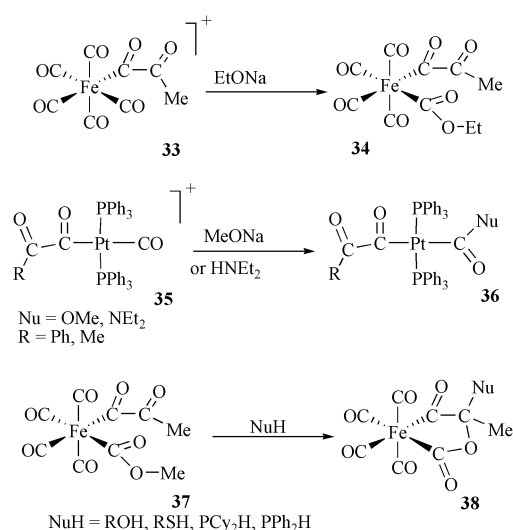
Scheme 24

The absence of firm experimental data concerning a possible nucleophilic addition on the α carbon of a C(O)C(O)R ligand leads to consideration of route B of Scheme 14 (a nucleophilic addition on a terminal carbonyl of a complex already bearing an acyl, aryl, alkoxycarbonyl or carbamoyl ligand followed by a carbon–carbon coupling between the two monocarbonylated ligands of the so obtained intermediate) as the more plausible mechanism that could account for the formation of bis carbonylated organic compounds. We will successively investigate the two steps of this reaction path.

(b) The nucleophilic addition to [M]–C(O)R complexes

Previous to the mechanistic work on double carbonylation, the number of clear-cut studies on the competitive attack of a nucleophile on an acyl RC(O) ligand or on a terminal carbonyl of the same organometallic complex was very limited. The historical example of Scheme 25 first established a preferential attack of a nucleophile on a terminal CO of a complex bearing an acyl ligand.[74] This complex was the first example of a series of Mn bis acyl anionic compounds.
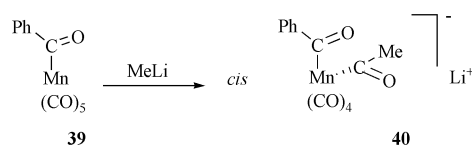
Scheme 25

This preferential addition on a terminal carbonyl, however, should not be considered as a paradigm. Thus preferential attacks of H^{−} on formyl ligands[75] have been observed and, an addition of methylmagnesium bromide on an alkoxycarbonyl ligand of a rhenium complex has also been reported; however, no other electrophilic site was available on this last complex.[76] Despite these results it remains largely true that nucleophiles add more easily on terminal carbonyl ligands.[4] The following examples confirm this assessment.

Concerning the already mentioned double carbonylation induced by $Co(CO)_4^-$ (see Scheme 21), together with the proposed nucleophilic addition on the α carbonyl of a phenylglyoxyl ligand of **17**, an attack of the nucleophile reagent on a terminal carbonyl of the acyl complex **15** affording the anion $\{[PhCH_2C(O)](CO_2R)Co(CO)_3\}^-$ (**29**) was also put forward.[7,15,16,63,77] Though not formally established in the above mentioned works, there is a good indirect experimental argument in favour of this addition on a terminal carbonyl. As shown in Scheme 26, due to the electron withdrawing character of the CH_2CO_2Me ligand, no CO insertion is detectable in complex **41**.[78] Meanwhile, in the presence of MeO[−] under a CO atmosphere, a reaction of monocarbonylation (formation of dimethyl malonate: **XXX**) is readily observed. This reaction takes place from the spectroscopically characterized alkyl-alkoxycarbonyl intermediate **42** whose formation results from an attack of MeO[−] on a terminal carbonyl of **41**.
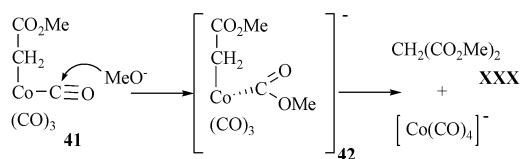
Scheme 26

The formation of a carbamoyl ligand by nucleophilic addition of an amine on a terminal CO of a cationic benzoyl palladium complex was clearly established by the full characterization of the intermediates *trans*-{Pd[PhC(O)](PMe_3)_2-(acetone)}[+] **43** and *trans*-{Pd[PhC(O)](PMe_3)_2(CO)}[+] **44** in the reaction of transformation of *trans*-Pd[PhC(O)](PMe_3)_2Cl (**45**) into *trans*-Pd[PhC(O)](PMe_3)_2[C(O)NR_2] (**46**).[79,80]

A quite similar scenario has been set up for *trans*-Pt[PhC-(O)](PPh_3)_2Cl (**24**), which, in the presence of a secondary amine under CO, affords the *trans*-Pt[PhC(O)](PPh_3)_2[C(O)NR_2] (**47**).[81] The achievement, by an analogous reaction, of the *cis*-Pt[PhC(O)](PPh_3)_2[C(O)NR_2] **49** from the cation *cis*-{Pt[PhC(O)](PPh_3)_2(CO)}[+] (**48**) is again a good example of an addition of an amine on a terminal carbonyl.[82]

Similarly, an addition of MeONa on the terminal carbonyl of the same cationic *cis* platinum complex **48** or of its *trans* isomer **25** afforded selectively the *cis*- or *trans*-Pt[PhC(O)]-(PPh_3)_2(CO_2Me) **50** and **51**.[67]

Except the Mn anionic diacyl compounds **40** described in Scheme 25, complexes of the prototype *cis*-[R(CO)][M]-[(CO)R′], where R and R′ are alkyl groups, are rare. The synthesis of the *cis*-diacyl platinum complex Pt[PhC(O)]_2-(PPh_3)_2 **52** by nucleophilic addition of PhLi on the *cis* cation **48** has, however, been reported. Note that on using MeLi instead of PhLi, an alkylation of the metal is additionally observed.[68,83]

The preceding examples show the possible formation of complexes displaying two carbonylated organic ligands by nucleophilic addition on terminal carbonyls of complexes already bearing an acyl, alkoxycarbonyl or a carbamoyl ligand. These compounds, by a carbon–carbon coupling, are then susceptible to produce bis carbonylated organic compounds. The next section will concern the study of these carbon–carbon coupling reactions.

Carbon–carbon coupling and the double carbonylation

General nature of the carbon–carbon coupling reaction

Of utmost importance in organometallic chemistry (particularly for its involvement in catalysis) is the question of carbon–carbon coupling, which has been reviewed by Brown and Cooley.[84] It is difficult to draw general trends of the reaction since many factors are at work in the process. As a general rule a concerted carbon–carbon coupling will be favoured by the following parameters:

(i) The *cis* position of the two ligands involved in the process

(ii) The presence in the complex of a metal of small dimensions

(iii) A low electronic density of the metal centre (high oxidation state or possible initiation of the reaction by an oxidation process)

(iv) The easy formation of penta- or tri-coordinated intermediates (presence of easily dissociable ancillary ligands or easy addition on square planar compounds)

(v) The presence on the complex of electron withdrawing ancillary ligands

(vi) An electron donating ability of the ligands involved in the coupling.

However, one of the most important parameters governing the concerted carbon–carbon coupling occurring between two organic ligands is the hybridization of their ligating carbons. Complete series of complexes, with the same ancillary ligands, allowing an appraisal of the influence of this parameter are scarce and thus, even if these compounds are not true catalysts for carbon–carbon coupling reactions, the study of the thermal behaviour of the homogeneous series of iron complexes of general formula: cis-$(CO)_4Fe(R^1)(R^2)$ (**53**) is of particular interest (see Table 1).

This series clearly shows the great stability of a bis alkyl complex (**53a**) confirming that a coupling between two sp[3] carbons is not favoured. On the other hand, the ease of the coupling between an sp[3] carbon and an sp[2] carbon is shown by the low stability of complexes **53b–e** bearing an alkyl and a carbonylated ligand whose thermal evolution quantitatively affords, at low temperature, monocarbonylated organic compounds. The differences in stability of these complexes result from the electronic effects of the organic ligands involved in the reaction as electron withdrawing ligands make the reaction more difficult and then increase the stability of the complexes. The stability of complexes **53f–n**, whose organic ligands are linked to the metal by sp[2] carbonyl carbons, depends both on the decarbonylation ability of these ligands and on the easiness of a carbon–carbon coupling between the same ligands. The question of the occurrence of this reaction together with possible decarbonylations which take place under similar reaction conditions will be the topic of the next section.

Model complexes for double carbonylation by carbon–carbon coupling

Isomerization of model complexes. The first condition required for the achievement of carbon–carbon coupling is the mutual *cis* position of the two carbonylated ligands on the organometallic entity. The study of the geometries of the complexes described in the examples of the preceding section and the examination of their possible isomerizations is then quite important. On octahedral complexes, two acyl, alkoxycarbonyl or carbamoyl ligands are always observed in respective *cis* positions. On the other hand, it appears that square planar complexes bearing two of these ligands can selectively be obtained under *cis* or *trans* configurations. *Trans*-Pt[PhC(O)](PPh_3)_2-[C(O)NR_2] (**47**) is found to be stable in neat solution, however, in the presence of amine and under CO, a slow isomerization towards its *cis* isomer **49** is observed. The reaction, performed

Table 1 Thermolysis of *cis*-$(CO)_4Fe(R^1)(R^2)$ **53**[85]

Complex	R^1	R^2	Thermolysis temperature/°C	Product of thermolysis (yield, %)
53a[86]	CH_2CO_2Me	CH_2CO_2Me	30	No decomposition
53b[86]	CH_2CO_2Me	CO_2Me	20	$CH_2(CO_2Me)_2$ (100)
53c[87]	Me	CO_2Me	−30	$MeCO_2Me$ (100)
53d[86]	CH_2CO_2Me	$C(O)Me$	−30	$MeC(O)CH_2CO_2Me$ (100)
53e[88]	Me	$C(O)CO_2Me$	−10	$MeC(O)CO_2Me$ (50) + **53g** (50)
53f[89,90]	CO_2Me	CO_2Me	+20	Stable
53g[91,73]	CO_2Me	$C(O)Me$	+6	$MeCO_2Me$ + $Fe(CO)_5$
53h[92]	$C(O)Me$	$C(O)Me$	+6	$MeC(O)Me$ + $Fe(CO)_5$
53i[92]	$C(O)Me$	$C(O)C(O)Me$	+4	**53h** + $MeC(O)C(O)Me$ + $Fe(CO)_5$
53j[93]	CO_2Me	$C(O)CO_2Me$	+25	**53f** + $(CO_2Me)_2$ + $Fe(CO)_5$
53k[91]	$C(O)Me$	$C(O)CO_2Me$	−3	**53g** + $MeCO_2Me$ + $Fe(CO)_5$
53l[93]	$C(O)CO_2Me$	$C(O)CO_2Me$	+10	**53j**
53m[92]	$C(O)C(O)Me$	$C(O)C(O)Me$	+10	**53i**
53n[92]	$C(O)C(O)Me$	$C(O)CO_2Me$	+20	**37**

under a ^{13}CO atmosphere, shows the selective formation of *cis*-$Pt[C(O)Ph](PPh_3)_2[^{13}C(O)NR_2]$ (**54**) suggesting an intermolecular mechanism for this process.[81]

The replacement of the two PPh_3 ligands by the non-dissociating PMe_3 shows the importance of the ancillary ligands. Thus *trans*-$Pt[C(O)Ph](PMe_3)_2[C(O)NR_2]$ (**55**) is found to be stable towards isomerization, even in the presence of amine and under CO, suggesting dissociation of a phosphine as essential to the reaction. Under the same conditions, analogous results are observed for *trans*-$Pd[C(O)Ph](PMe_3)_2[C(O)NR_2]$ (**46**);[72,79] however, as a carbon–carbon coupling reaction is obtained in the presence of $NH_2R_2BF_4$, it is presumed that, for this palladium complex, a protonation of the carbamoyl ligand could induce the formation of the *cis* isomer.

Carbon–carbon coupling and the double carbonylation. Two kinds of carbon–carbon couplings may formally induce the formation of bis carbonylated organic compounds. The first one consists in a coupling between an alkyl and an RC(O)C(O) ligand and, in the second, (Scheme 14, step g) the reaction takes place between two RC(O) ligands: R = alkyl, OR′, $NR_2′$. As shown above, the low probability of formation of the RC(O)C(O) ligand makes the first process very unlikely in the dicarbonylation reaction. Two complexes which can be considered as models for this type of reaction have however been described. The first one, the platinum compound **56**, displays a *trans* configuration. It evolves thermally, probably *via* a decarbonylation followed by a CO insertion, into the *trans* bis acyl isomer **57** (Scheme 27).[68,94]

R or R' = Me, Et, Ph
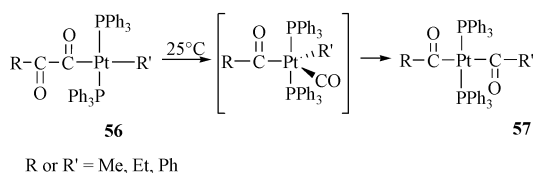
Scheme 27

A similar result is observed for the *cis* methyl methyloxalyl iron complex $(CO)_4Fe[C(O)CO_2Me](Me)$: **53e** (formation of *cis*-$(CO)_4Fe(CO_2Me)[C(O)Me]$: **53g**, see Table 1), however, in competition with this insertion reaction, a double carbonylating carbon–carbon coupling process is observed. The reaction affords methylpyruvate: $MeC(O)CO_2Me$ in 50% yields.[88]

Then, complexes displaying two monocarbonylated ligands in *cis* positions on the metal centre seem more likely better models for studying the double carbonylation process described in step g of Scheme 14.

We reported earlier (Scheme 25) the synthesis of the anion *cis*-$\{Mn[C(O)Me][C(O)Ph](CO)_4\}^-$ (**40**). Under thermolysis

conditions, this compound, due to the high electronic density of its metal centre, is only found to induce the formation of the monocarbonylated organic compound $PhC(O)Me$.

The reaction probably proceeds *via* a decarbonylation affording the intermediate *cis*-$\{Mn[C(O)Me](Ph)(CO)_4\}^-$ (**58**) followed by a rapid carbon–carbon coupling between the two organic ligands of this new complex, which, rapidly and quantitatively, gives rise to acetophenone.[95] On the other hand, under oxidation conditions, **40** is found to afford phenyl propanedione ($PhC(O)C(O)Me$) in 70% yield.[74]

Similarly a monocarbonylation reaction is observed when *cis*-$(CO)_4Fe[C(O)Me]_2$ (**53h**)[92] or *cis*-$(CO)_4Fe[C(O)Me](CO_2Me)$ (**53g**)[73,91] are thermolyzed at 6 °C. Acetone or methylacetate are then respectively formed (see Table 1). A ruthenium complex the *cis*-$Ru[C(O)Et][C(O)NEt_2](CO)(PMe_3)_2$ (**59**) also failed to produce by thermolysis at 100 °C any α-ketoamide $EtC(O)C(O)NEt_2$.[96]

A selection of carbon–carbon couplings between two carbonylated ligands of well identified palladium or platinum complexes is given in Table 2.

Trans-$Pd[C(O)Ph][C(O)NR_2](PMe_3)_2$ **46**, due to its disfavoured *trans* geometry is not found to induce a carbon–carbon coupling under CO and in the presence of amine. However, as shown above, when $H_2NR_2BF_4$ is added transformation of **46** into its *cis* isomer occurs and formation of α-ketoamide is then observed when the reaction is performed under CO (20% for $NR_2 = NMe_2$; 40% for NR_2 = pyrrolidine). The yield into dicarbonylated product can reach 80% (NMe_2) or 100% (pyrrolidine) when the reaction is carried out in the presence of 10 equiv. of the corresponding amine. However the reaction does not result from a simple intramolecular coupling since, when performed under an atmosphere of ^{13}CO, $PhC(O)^{13}$-$C(O)NR_2$ is almost selectively formed.[79,97]

Platinum models which present the favourable *cis* geometry clearly show the influence of the ligands involved in the coupling. The best results are obtained for bis-acyl complexes; for example *cis*-$Pt[C(O)Et]_2(PPh_3)_2$ **60** affords α-diketones in about 20% yield in neat solution. The reaction becomes quantitative when performed under CO;[94] however, as shown by crossover experiments, the reaction does not result from a simple intramolecular coupling. As shown for *cis*-$Pt[C(O)$-$Ph][C(O)NR_2](PPh_3)_2$ (**49**), when one of the ligands involved in the coupling is a carbamoyl, the yield of the reaction is lowered to 17% and when an alkoxycarbonyl is involved in the process (*cis*-$Pt[C(O)Ph](CO_2Me)(PPh_3)_2$ **50**), only traces of α-ketoesters are observed.[68]

These last results raise the question of the possibility of performing a carbon–carbon coupling between two alkoxycarbonyl ligands linked in *cis* positions on the same metal. Recall that this reaction might be envisioned as the key step of the important process of oxidative carbonylation of alcohols into oxalates (see Scheme 6).

Table 2 Thermolysis of palladium or platinum complexes

Complex	L	NR$_2$	Product of thermolysis (yield %)	Conditions of thermolysis
Trans-Pd[C(O)Ph][C(O)NR$_2$]L$_2$ **46**	PMe$_3$	Pyrrolidine	No coupling	CO, HNR$_2$, rt,[72,79]
Trans-Pd[C(O)Ph][C(O)NR$_2$]L$_2$ **46**	PMe$_3$	Pyrrolidine	Ph^{13}C(O)NR$_2$ (100)	^{13}CO, HNR$_2$, H$_2$NR$_2$BF$_4$[79,87]
Cis-Pt[C(O)Ph][C(O)NR$_2$]L$_2$ **49**	PPh$_3$	NEt$_2$	*Trans*-Pt[C(O)Ph]ClL$_2$ (79) PhC(O)NR$_2$ (17)	CDCl$_3$, 35 °C[68]
Cis-Pt[C(O)Ph](CO$_2$Me)L$_2$ **50**	PPh$_3$		PhC(O)CO$_2$Me (<1)	CDCl$_3$, 35 °C[68]
Cis-Pt[C(O)Et]$_2$L$_2$ **60**	PPh$_3$		EtC(O)C(O)Et (100)	C$_6$D$_6$, 50 °C, CO sat.[94]

Carbon–carbon coupling between two alkoxycarbonyl ligands: oxalate formation? The analogy between an alkoxycarbonyl ligand and its organic equivalent: an ester group, is rather misleading. The observed differences between these two C(O)OR patterns may be due to the importance of the mesomeric carbenic form and to the lability of the alkoxy group of the alkoxycarbonyl ligand. The mobility of such an alkoxy group is shown in Scheme 28 where the alkoxycarbonyl anion **61** which can also be written as its mesomeric carbenic form **62** is in equilibrium with pentacarbonyl iron and methylate.[98]

Scheme 28

Thus, depending on the reaction conditions, an alkoxycarbonyl ligand may evolve from a *cis* to a *trans* position (or the reverse) without real migration of the entire ligand. The principle of this isomerization is shown in Scheme 29.

Scheme 29

Such an intramolecular hopping of an alkoxy from a carbonyl to another situated in a *cis* position on the same metal has been suggested as the probable mechanism of isomerization of the ruthenium complex Ru(dppe)(CO)$_2$(CO$_2$Me)$_2$: **63**.[99]

As mentioned above, the oxidative carbonylation of alcohols is, in industry, an important route to oxalates and then to ethylene glycol. This reaction, performed under oxidative conditions in the presence of carbon monoxide and palladium salts as the catalyst (see Scheme 6),[46] is undoubtedly a complex process.

It has been claimed that thermolysis of (PPh$_3$)$_2$Pd(CO$_2$Me)$_2$ (**64**), whose *cis* structure was not clearly established, afforded dimethyl oxalate (**XXXI**)[100–102] (Scheme 30). However, no yield of oxalate was given and the authors admitted that the so obtained results did not conclusively confirm the formation of this product by a concerted carbon–carbon coupling occurring between the two alkoxycarbonyl ligands of the complex. Among the numerous *cis* bis-alkoxycarbonyl complexes described in the literature, not one was found to induce the formation of oxalate under thermolysis conditions.[85] Furthermore, complexes displaying a structure very close to **64**: *cis*-(L–L)Pd(CO$_2$Me)$_2$ (L–L = 1,10-phenanthroline;[103,104] (**65**) bipyridine[104,105] (**66**)) were thermally found to induce the formation of dimethyl carbonate (MeOC(O)OMe: **XXXII**), CO, MeOH

and metal residue. By reaction with aqueous HBF$_4$, a platinum complex: [Fe(CpPPh$_2$)$_2$]Pt(CO$_2$Me)$_2$ (**67**) affords traces of **XXXI**.[106] On the other hand, thermolysis of the bis-alkoxycarbonyl complex of the iron series displayed in Table 1: *cis*-(CO)$_4$Fe(CO$_2$Me)$_2$ (**53f**), stable until 20 °C, thermally evolves into the trinuclear complex [(CO)$_3$Fe(µ,η^2-CO$_2$Me)$_3$]$_2$Fe (**68**) whose formation probably results from the particular mobility of the alkoxy groups of **53f**.[107] Further thermolysis of **68** gives rise to dimethylcarbonate, CO and pentacarbonyl iron. Meanwhile, a very interesting observation was made on the complex (dppe)Pt(CO$_2$Me)$_2$ (**69**) whose thermal decomposition gave rise to MeOH, CO and MeC(O)H oligomers, but which, after oxidation with NOPF$_6$, AgBF$_4$ or AgPF$_6$ afforded a complex mixture containing **XXXI**.[108] Even better results were obtained by oxidation with iodine of the rhodium complex (C$_5$Me)$_5$Rh-(CO)(CO$_2$Me)$_2$ (**70**); 30 to 40% of oxalate were then produced.[109]

Models for the tri- or tetra-carbonylation

Though catalytic or stoichiometric triple carbonylation processes have never been observed, some complexes that might be considered as models for such reactions have been described in the literature. A series of platinum complexes of general formulae *cis*-Pt[C(O)C(O)R][C(O)R′](PPh$_3$)$_2$ (**71**) (R = Me, Et, Ph, OMe; R′ = Et, Ph) has been found to be thermally subjected to exclusive decarbonylation giving rise to *trans* diacyl or acyl alkoxycarbonyl complexes: Pt[RC(O)][C(O)R′](PPh$_3$)$_2$ (**57**).[94]

A similar series of iron compounds is reported in Table 1. By thermolysis these compounds *cis*-(CO)$_4$Fe[C(O)R][C(O)-C(O)R′] (R = R′ = Me **53i**;[92] R = R′ = OMe **53j**;[93] R = Me, R′ = OMe **53k**[91]) undergo a decarbonylation giving rise to diacyl (**53h**), dialkoxycarbonyl (**53f**) or acyl alkoxycarbonyl (**53g**) compounds together with a carbon–carbon coupling affording respectively butanedione (**XXXIII**, 30%); dimethyloxalate (**XXXI**, 15%) or methylpyruvate (**XXXIV**, 35%). On these complexes the substitution of a terminal carbonyl by PPh$_3$ precluded the decarbonylation and significantly improved the formation of bis-carbonylated organic compounds. Thus for (CO)$_3$(PPh$_3$)Fe[C(O)CO$_2$Me](CO$_2$Me) (**72**), the only observed thermal reaction is the carbon–carbon coupling giving rise quantitatively to **XXXI** (Scheme 31).[92] To our knowledge, **72** is the only complex inducing, in good yield, a double carbonylating carbon–carbon coupling into oxalate under thermolysis conditions.

Scheme 31

A series of models for the tetracarbonylation *cis*-(CO)$_4$Fe-[C(O)C(O)R][C(O)C(O)R′] (R = R′ = OMe **53l**; R = R′ = Me **53m**; R = Me, R′ = OMe **53n**) has also been depicted; the only reaction observed for these complexes is a decarbonylation affording respectively **53j**,[93] **53i**[92] and *cis*-(CO)$_4$Fe[C(O)C(O)-Me](CO$_2$Me): **37**[92] (see Table 1).

354

XXXI

Scheme 30

As the above studied examples were not efficient in performing the double carbonylation process, other mechanisms may be envisioned to justify the observed catalytic reactions.

Further prospects

Double carbonylation initiated by free radical formation

Free radical monocarbonylation is more and more acknowledged in organic chemistry (for a recent review see ref. 110). In the presence of a classical system (AIBN and Bu₃SnH), carbon monoxide is readily incorporated into organic substrates. An example of free radical carbonylation of organic halides, which does not require any transition metal catalyst, is given in Scheme 32.
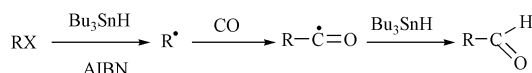
Scheme 32

So far as we are aware, there is no report of double carbonylation of organic compounds under such conditions. Concerning the double carbonylation induced by organometallic complexes, we have already mentioned the formation of oxalate by oxidation of bis alkoxycarbonyl complexes. These reactions could occur *via* the formation of $^{\bullet}CO_2R$ radicals. A clear-cut example of the construction of the COCO chaining starting from an organo-transition metal complex under radical formation conditions is reported in Scheme 33.[111]
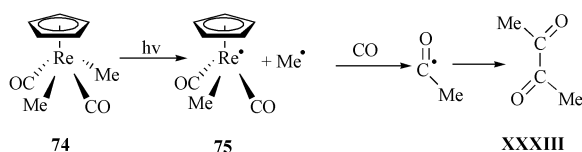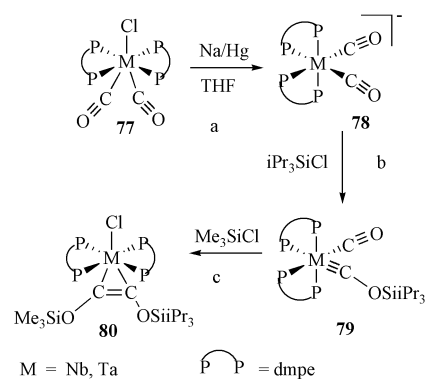

Scheme 33

It is also worth recalling here that some oxocarbon bis anions such as $^{-}OC{\equiv}CO^{-}$ may be generated *via* dimerization of the radical anion of carbon monoxide ($CO^{\bullet-}$) generated under strongly reducing conditions.[112] There is also fairly good evidence that oxidatively induced coupling of nickel acylates: $\{(CO)_3Ni[C(O)R]\}^{-}$ (**76**) into α-diketones $RC(O)C(O)R$ (**XXI**) goes through a radical mechanism.[113] In a recent example, the radical catalytic double carbonylation and cyclization of 4-allenyl iodides has been performed using a Pd/light system.[114]

The siloxycarbyne intermediate: a new mode of coupling of carbon monoxide?

We have already described the sequential double insertion of carbon monoxide induced by a rhodium complex under reducing conditions provided by a hydrosilane intermediate (Scheme 13). It was then suggested that this new type of coupling could occur *via* a siloxycarbyne intermediate.[59] Indeed, the occurrence of this intermediate and further carbon–carbon coupling has been nicely documented by Lippard and co-workers, on niobium and tantalum complexes.[115] As all the compounds of Scheme 34 were reasonably well characterized, step c of the reaction clearly demonstrates a carbon–carbon coupling between a siloxy carbyne ligand and a terminal carbonyl.

Organo-lanthanides or actinides and sequential chaining of carbon monoxide

Marks and Molloy contributed significantly to the development of carbon monoxide activation with organo-lanthanides or actinides.[116] Two examples of this series are displayed in Scheme 35. 35a shows the stoichiometric formation of a sequential
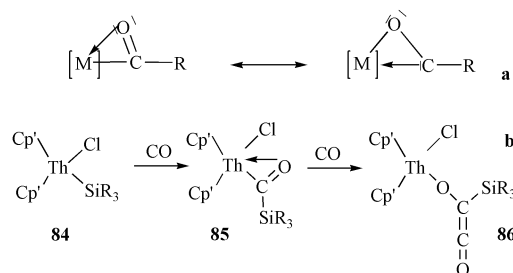

Scheme 34
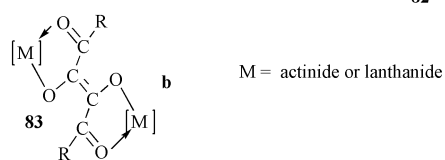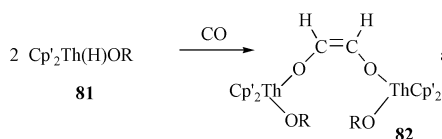
Scheme 35

chaining of two carbon monoxides while 35b shows a complex in which, formally, a sequential chaining of four carbon monoxide moieties has occurred.

It has also been suggested that carbon–carbon coupling could occur through the reaction of a carbon monoxide with an η²-acyl intermediate to give a ketene. This sequence was indeed established in the reaction displayed in Scheme 36b. Complexes **84** and **85** of Scheme 36b were reasonably well characterized by spectroscopy; complex **86** was isolated.[117]

Scheme 36

Concluding remarks

Our attempt in this review was to propose a rather broad outlook of the problem of sequential chaining of carbon monoxide. The least to be said is that the question is not closed. It may be noticed that the first examples of double carbonylation were discovered by chance, rather at variance with mechanistic beliefs of the time. Undoubtedly, there are several possible mechanistic routes at work. Some elementary steps are fairly well supported by pertinent models, as far as we believe that they are not too far from the real intermediates, which may be difficult or impossible to see. It seems well established that the classical migratory insertion of carbon monoxide cannot work sequentially without any amendment since, once an acyl ligand is produced, the electronic requirement for a further migratory insertion of carbon monoxide is at variance with the electron-poor character of the acyl ligand; we have already seen such possible amendments: the enolization or the reduction of

the acyl group. As we have seen, the question of nucleophilic attack is not closed, and the intriguing point of this issue is that a nucleophilic attack on a coordinated acyl ligand has never been clearly demonstrated on the pertinent above described models. Another important question is the carbon–carbon coupling giving rise to the COCO chaining; as we have seen, the results of the organometallic modelling are rather disappointing, and it must be said that except for one model (**60**, Table 2), coupling between two sp^2 hybridized carbons of carbonyls does not occur, or occurs in poor yields, or *via* a complex intermolecular process. Then, it seems that there are good reasons which mean that no carbonyl chaining beyond two has been performed so far under conditions of transition metal catalysis; if formal sequential CO insertions beyond two have been observed, they do not give rise to an authentic (CO)$_n$ chaining and their mechanistic machinery remains obscure. Finally it must be stressed that several mechanistic tracks such as radical processes have been so far almost completely neglected in the realm of double carbonylation and beyond.

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