Carbon dioxide and metal centres: from reactions inspired by nature to reactions in compressed carbon dioxide as solvent

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Abstract

Aspects of the chemistry of CO_2 at metal centres are reviewed with emphasis on the formation of metal carbamato complexes from CO_2 (an essential step in the activation of some enzymes containing carbamato groups as ligands), recent results of photochemical activation reactions of CO_2 and catalytic reactions at metal complexes in compressed CO_2 acting as reaction medium or as both solvent and substrate. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: CO_2 activation; Carbamato metal complexes; Enzyme models; Supercritical CO_2; Catalysis

1. Introduction

The chemistry of carbon dioxide at metal centres, i.e. the coordination of CO_2, its activation and conversion into organic compounds, is a rapidly increasing domain of coordination chemistry, organometallic chemistry and of catalysis. The fundamental challenge and motivation of this chemistry is based on the discrepancy between the highly advanced apparatus employed by nature to convert CO_2 into organic matter and the difficulties encountered by chemistry in converting this molecule via effective catalytic reactions into high quality products. In nature CO_2 is selectively transformed under mild conditions employing highly organised enzymatic systems in which metal centres are instrumental. In contrast, there are few catalytic syntheses known to use CO_2 as a building block.

The motivation of CO_2 chemistry, inspired by nature is not only to understand the fundamental processes of nature and to mimic them in artificial systems but also to look for key steps useful in chemical synthesis.

This article deals with recent developments in CO_2 chemistry since 1992 in the following three areas:

- Synthesis and reactions of carbamato metal complexes modelled on *rubisco*, *biotin*-dependent enzymes, *urease* and *phosphotriesterase*. The carbamato groups in the active centres have different modes of coordination to the metal ions involved (Mg, Mn, Ni, Zn) and accomplish various functions.
- Activation reactions of CO_2 at metal centres with the aid of light energy, mimicking the photosynthesis of green plants.
- Metal catalysed reactions with CO_2 either as a reaction medium or both as solvent and reagent.

An important motivation for these investigations is the question of whether supercritical or liquid CO_2 can be employed as an environmentally friendly, nontoxic solvent instead of organic reaction media. A list of publications about other relevant results in CO_2 chemistry in the recent past is presented [1–11].

2. Structure and function of enzymes, activated by CO_2 (carbamato groups containing systems)

2.1. Ribulose-1,5-biphosphatecarboxylase/oxygenase (rubisco)

The *rubisco* enzyme is probably the most abundant enzyme of the biosphere. The fixation of CO_2 and its transfer to organic substrates in the Calvin cycle leads by way of starch to an annual production of 10^{11} tons of biomass. The first structural elucidation of an enzyme deactivated by an inhibiting substrate (2-carboxy-D-arabitinol-1,5-bisphosphate) was accomplished in 1989 [12]. X-ray structures of the enzyme with embedded substrate ribulose-1,5-bisphosphate and without any substrate have recently been published [13,17]. Surprisingly, the single crystals of the enzyme possess no catalytic activity towards carboxylation. The reported X-ray structures (one example is given in Fig. 1) suggest that the active centre is pre-organised by carbamate formation.

The ε-NH_2 group of *lysine* reacts with CO_2 and Mg^{2+} resulting in a magnesium carbamat. The carbamato ligand was found to be monodentate according to recent crystal structures ([13]b, [15,17]). The magnesium ion seems to prefer penta-coordination in both substrate containing structures and octahedral coordination in a substrate free structure (Fig. 1 [13]b). The remaining ligands are provided by the substrate and the carboxylic group of the side chain of *Asp 203*. The first coordination sphere consists therefore solely of oxygen atoms. No nitrogen atoms of the peptide environment are directly involved in coordination.

The precise mechanism of carboxylation of the substrate is still uncertain since the structurally characterised single crystals of the enzyme do not possess any catalytic activity. Isotope labelling experiments show that the CO_2 of the carbamato
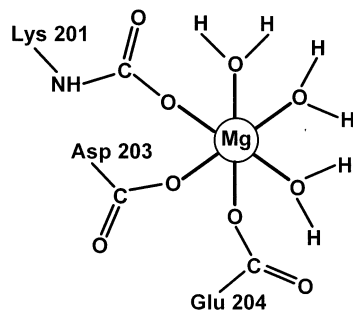
Fig. 1. X-ray structure of active the metal containing a unit of *rubisco* without substrate ([13]b).

group is not involved in carboxylation [14]. The essential role performed by the magnesium central atom has recently been confirmed [13,15]. It seems that the metal ion does not only induce a certain spatial orientation of the reacting compounds it also causes entatic states due to its positive charge. Mutation studies suggest that, in analogy to *urease*, the imidazole ring of a *histidine* acts as a proton acceptor in the initiating enolisation process [16]. The function of the carbamato ligand is not yet fully understood. Very recently, its role as a proton relay has been discussed in detail [17].

2.2. Biotin-dependent enzymes

The essential role of *biotin* as a prosthetic group in different carboxylating, *trans*- and decarboxylating enzymes is known. However, the structures of the species involved and the resulting mechanism are still the subject of discussions [18]. *N-Carboxybiotin* has been confirmed as an intermediate by chemical methods and NMR spectroscopy [19]. Model calculations support this observation [35]. However, there is no information about the nature of the stabilising cation available. Nutritional experiments suggest that Mg^{2+} might be of crucial importance [20]. In addition Mn^{2+} also possesses activating functions, although in the case of *rubisco* deactivating properties have been assigned to manganese [21].

The lively discussion about mechanistic aspects of the CO_2 fixation and transfer reactions is caused by the lack of structural information about the species involved. The suggested catalytic cycle, depicted in Fig. 2, is preceded by the formation of bicarbonate from CO_2 catalysed by *carbonic anhydrase*.

Bicarbonate is bound to *biotin* at the expense of ATP to form the key intermediate *N-carboxybiotin*. Since it is an inherently stable compound it has to be activated before the carboxylation of C–H acidic substrates can be accomplished. The activation might be achieved by protonation or rotation around the N–C bond. As a result of the carboxylation a proton is transferred to the *biotin*; thereby it becomes available for another catalytic cycle [22]. The mechanism of this transfer reaction and the role played by the metal ion are still not very well understood.
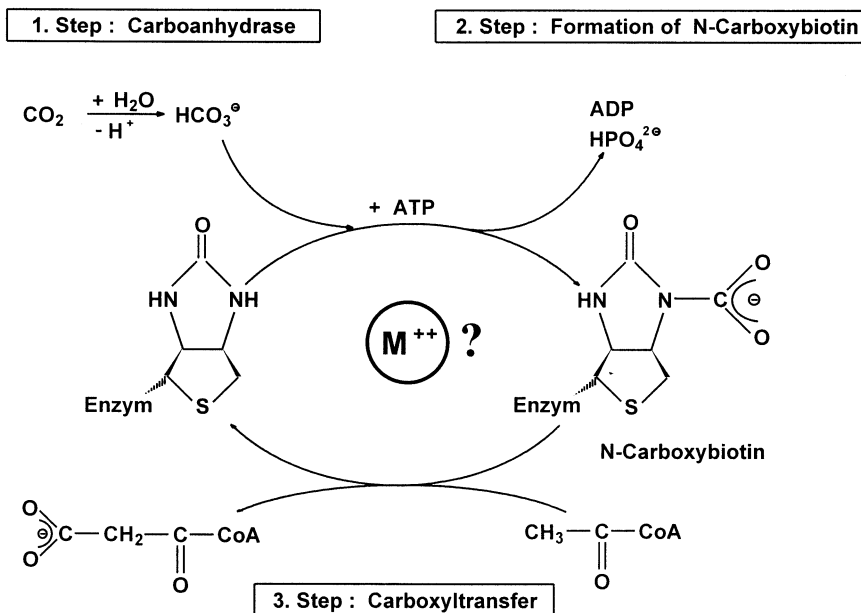
Fig. 2. Proposed catalytic cycle in *biotin*-depending CO_2 fixation and transfer.

2.3. Urease and phosphotriesterase

2.3.1. Structures

Both enzymes have a very similar structure of the active metal centres and catalyse the same type of reaction: the hydrolytic splitting of substrates.

Urease catalyses the hydrolysis of urea to ammonia and carbamic acid which rapidly decomposes into CO_2 and ammonia. This enzyme is historically important for two reasons: it was the first enzyme isolated [23], as well as the first enzyme in which nickel was identified as an essential metal [24].

The first crystal structures of *urease* were published by Karplus et al. in 1995 [25]. Refinement and comparison of 14 crystal structures up to now with a resolution of 2.2 Å and better reflect a quite precise picture of their structure. The active part consists of a binuclear Ni(II) unit whose coordination sphere is depicted in Fig. 3. The two nickel central atoms are connected via a carbamato bridge functioning as a bidentate ligand. Both metal centres are coordinated to two *histidine* nitrogen atoms. More recent interpretations indicate that each Ni centre is coordinated to one water molecule. A further molecule of water probably exists as a weakly bound bridging ligand. The coordination geometry of Ni-2 differs from that of Ni-1 since the latter is coordinated to an additional carboxylate group of *asparagat* [26].

There is an interesting structural resemblance to the active centre of *phosphotriesterase* where a carbamato ligand (formed from a *lysine*) connects the two essential metal ions (Zn in this case). Fig. 3 (right) shows the core of this enzyme.
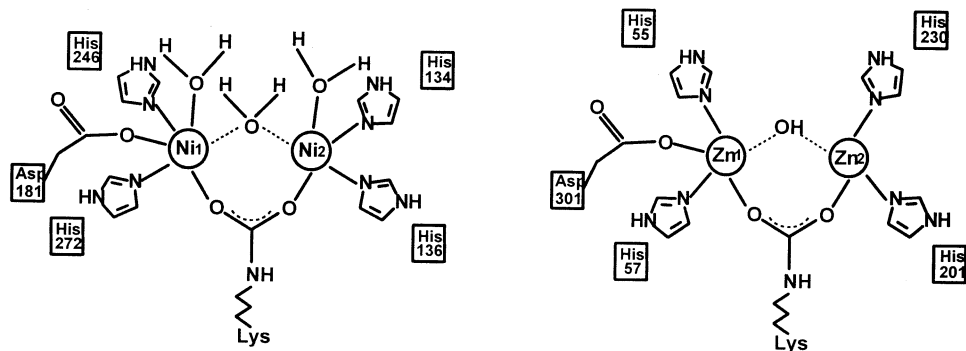
Fig. 3. Structures of the active centres in *urease* (left) and *phosphotriesterase* (right), according to the X-ray analyses [25–27].

2.3.2. Functions

The structures of both *urease* and *phosphotriesterase* provide an explanation for the fact that the enzymes are activated by CO_2 and the metal ions Ni^{2+} or Zn^{2+} [27]. The formation of the N–COOZn unit could be monitored by ^{13}C-NMR spectra in which a new signal at 164.9 ppm has been detected which is consistent with a carbamato group formed by CO_2, Mg^{2+} and the amino group of *lysine* in *rubisco* [33].

Neither the mechanism of the activation of both enzymes nor their function in hydrolytic reactions are completely understood yet. However, using the knowledge of the crystal structures it is possible to propose a feasible mechanism for the hydrolysis of urea depicted in Fig. 4 [28,29].

Fig. 4. Proposed mechanism of the hydrolytic splitting of urea by *urease* [28].

The displacement of water by the substrate urea insignificantly alters the coordination sphere of the nickel centre. Urea is coordinated via the carbonyl oxygen to the Ni-1 atom. Its four hydrogen atoms of the amino groups are probably bound to protein components via hydrogen bonds leading to an optimal sterical arrangement of the substrate.

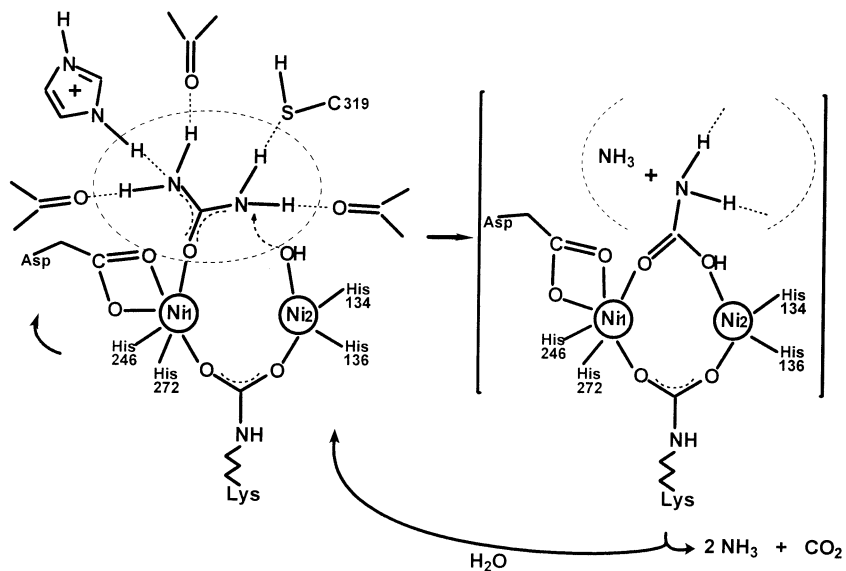A proton transfer from the Ni-2 coordinated water to the peripheral *histidine 320* could create a coordinated OH group. A nucleophilic attack at the C atom of the urea by the formed hydroxo ligand seems likely. NH_3 is split off and the carbamic acid so formed, fixed on two nickel centres, decomposes in a fast reaction into NH_3 and CO_2.

It is likely that the hydrolysis of triphosphates, catalysed by *phosphotriesterase*, follows a similar mechanism as that assumed for *urease* [25,30–32].

2.4. Comparison of carbamato group containing enzymes

Generally, the synthesis of the carbamato group in enzymes can be described as complex formation according to Fig. 5. However the mechanism of this activation reaction of the apoenzymes is not yet understood. The carbamato groups in enzymes act either as a monodendate ligand, e.g. in *rubisco* or as bridging ligand linking two metal centres in both *urease* and *phosphotriesterase*.

The function of the carbamato groups is quite distinct:
- It is the carrier of active CO_2 in *biotin*
- It activates the carboxylation of the substrate in *rubisco*, even though there is no evidence for a CO_2 transfer from the N–COO– group to the substrate
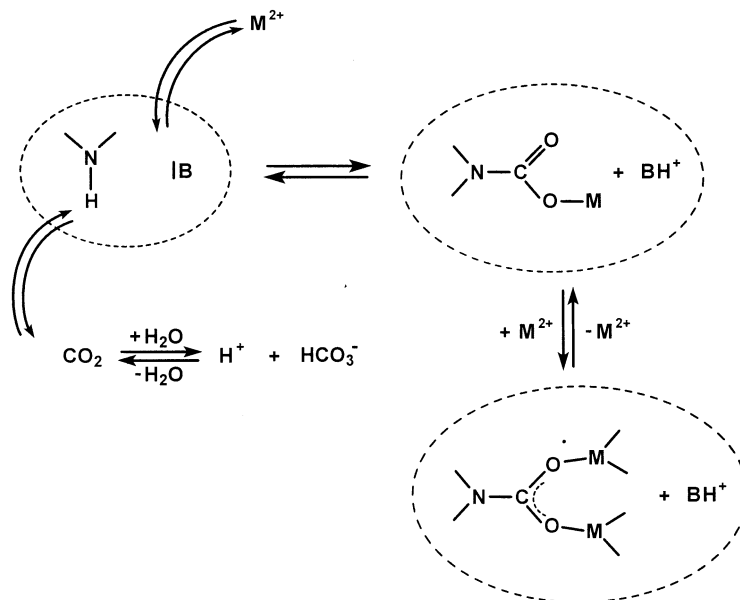

Fig. 5. Possible formation of the carbamato groups in *rubisco*, *urease* and *phosphotriesterase*.

● It positions two metals in both *urease* and phosphotriestrase at a distance which makes it possible to promote a hydrolytic splitting of urea or phosphates.

For synthetic chemistry a number of questions arise from these conclusions. Is it possible to construct structurally well characterised carbamato complexes capable of transferring CO_2 to C–H bonds? Why does nature need the N–COO–M group to promote hydrolytic reactions? A further problem may be to design artificial systems containing carbamato ligands that are not only stable towards water but also able to catalyse hydrolytic reactions, especially of urea. These fundamental issues provide reasons for the investigation of the coordination chemistry of carbamato complexes.

3. Carbamato complexes of biorelevant metals

3.1. Formation of carbamato complexes by CO_2 fixation

Carbamato complexes of main group and transition metals can be synthesised by following methods:

Reaction of CO_2 with secondary amines in the presence of metal halides:

$$2n R_2NH + n CO_2 + MX_n \rightarrow (R_2N-COO)_n M + n[R_2NH_2]^+ + nX^- \qquad \text{(A)}$$
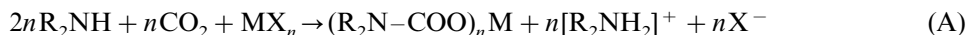
Insertion of CO_2 into metal amide bonds:

$$(R_2N)_n M + n CO_2 \rightarrow (R_2N-COO)_n M \qquad \text{(B)}$$

Oxidative coupling of CO_2 with Schiff bases:

$$R-CH=N-R + CO_2 + NiL_2 \rightarrow R-\underline{CH-N(R)-COO-Ni} + 2L \qquad \text{(C)}$$

Calderazzo's pioneering work resulted in a wide variety of homoleptic carbamato complexes prepared according to Reaction A [36,44,45]. Many of these compounds have been structurally elucidated by X-ray analysis.

Organometallic carbamato complexes especially of zinc and aluminium have been synthesised analogous to Reaction B [37,38]. In addition insertion reactions in complexes stabilised by additional ligands have also been reported.

Reaction C has been discovered in our research group. This reaction is limited to Ni(0) resulting in the formation of cyclic carbamato complexes possessing an additional Ni–C bond [1,39,40].

Various coordination modes of the carbamato ligands have been reported (Fig. 6) indicating that they might display a rich coordination chemistry. However their chemistry is still in their infancy considering the small number of structurally well characterised complexes and the lack of systematic investigations to prove the reactivity of the carbamato groups.

3.2. Carbamato complexes of magnesium and manganese

The first publications dealing with carbamates as structural models for CO_2
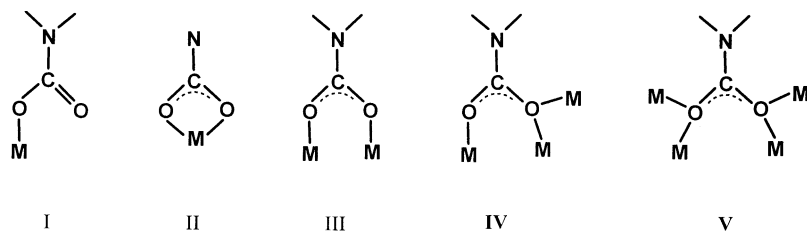
Fig. 6. Coordination modes in carbamato complexes.

fixation were published in the early 1970s by a Russian group. They investigated carbamates of substituted imidazolidon rings [34].

The structural characterisation of *N*-carbamates of imidazolidons has not been accomplished yet.

Only a few magnesium and manganese carbamates have been structurally characterised over the last 30 years. The great variety of possible coordination modes of the carbamato group in homoleptic compounds (monodentate, μ^2, μ^3, μ^4, chelate) seems to lead to polynuclear compounds of high complexity [36].

In 1995 the structure of a mixed magnesium–aluminium carbamate was elucidated. This complex was isolated as a side product of the preparation of the pure aluminium complex. Its molecular structure is depicted in Fig. 7 [38].

Each magnesium ion possesses a tetrahedral coordination sphere consisting of four oxygen atoms originating from four distinct carbamato groups. Their bidentate character is retained by coordination to two aluminium centres.

Fig. 7. Structure of a mixed Al–Mg carbamato complex [38].

Fig. 8. X-ray structure of [(isoprop)$_2$N–COO–Mg(Br) (THF)$_2$]$_2$ [41] (bond lengths: Mg2-01 and Mg1-02, 2.36 Å; Mg1-01 and Mg2-02, 1.96 Å).
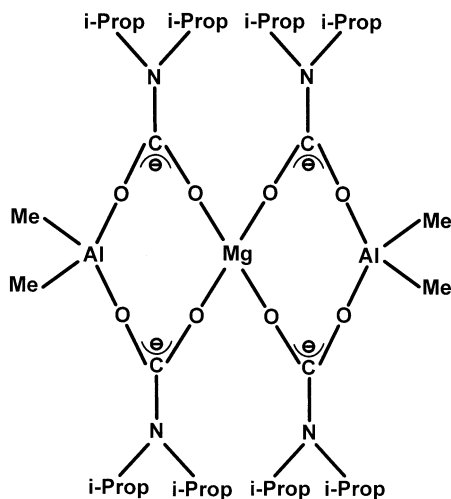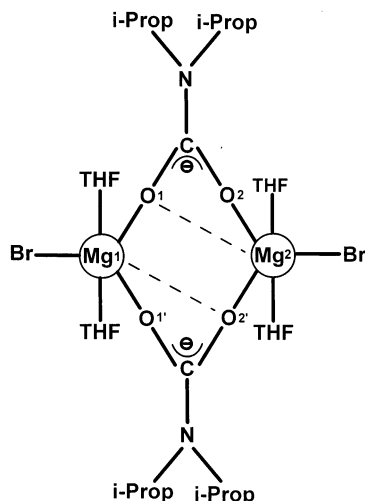
The complex [iso-prop)$_2$N–COO–Mg–(Br)$_2$(THF)$_2$]$_2$ is the first pure magnesium carbamate whose structure could be determined by X-ray analysis (Fig. 8) [41]. It is formed by insertion of CO_2 into the Mg–amide bonds prepared by reaction of the corresponding amine with CH_3MgBr.

The magnesium centres possess a distorted octahedral coordination sphere consisting of five oxygen donor atoms and one bromide ligand. Both carbamates coordinate as bridging ligands.

A further step on the way to nature's example, i.e. only μ^2 bridging carbamato ligands in the complex (as for example in *urease*) and solely oxygen donor atoms around the metal (as in *rubisco*), is represented by the trinuclear complex of the formal composition [Mg(CO$_2$)$_2$(TPOA)(THF)$_2$]$_3$, prepared by reaction of tetraphenyl-oxalamidinate-magnesium [(TPOA)Mg] with CO_2 in THF (Fig. 9) [42].

The core of the complex is basically of prismatic symmetry and the central magnesium ion is octahedrally coordinated by oxygen atoms of the surrounding carbamato groups. Each oxygen atom originates from a different carbamato function. The Mg^{2+} ions of the periphery are facially coordinated to three oxygen atoms of the carbamato groups and three THF molecules.

Only two carbamato complexes of manganese, a hexamer [43] and tetramer [44], have been structurally characterised. The manganese ions in both compounds are homoleptically coordinated by five oxygen atoms of the carbamato moieties. The manganese central atoms obtain an approximately trigonal bipyramidal coordination sphere, although the carbamates exhibit different modes of bridging (μ^2, μ^3, μ^4). To the best of our knowledge these manganese complexes have not been tested towards their capacities to simulate CO_2 transfer to organic substrates.
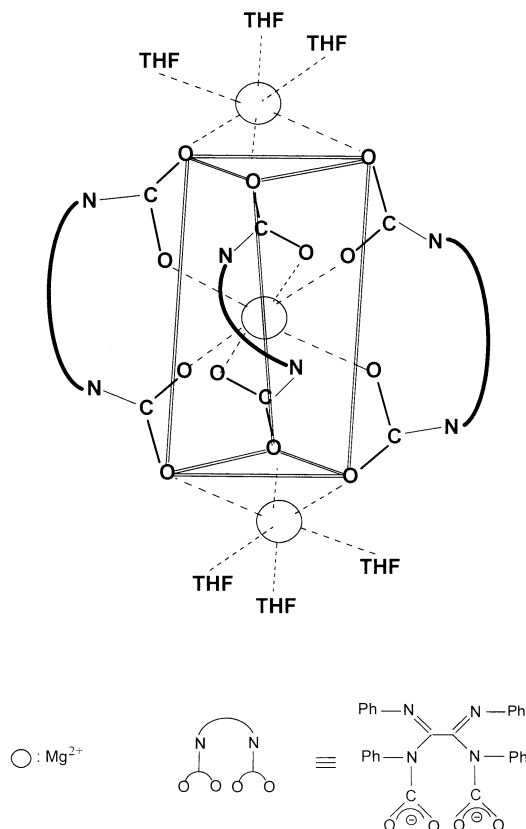
Fig. 9. Solid state structure of the trimeric homoleptic carbamato magnesium complex of the formal composition $[Mg_3(CO_2)_6(TPOA)_3(THF)_6]$ [42] (TPOA, tetraphenyl-oxalamidinate).

3.3. Carbamato complexes of nickel and zinc

Carbamato complexes of nickel whose structures are solved unequivocally are very scarce. Although Calderazzo et al. succeeded in synthesising the first homoleptic carbamato–Ni(II) complex of the type $[(R_2N–COO)_2Ni]_n$ from CO_2, diethylamine or diisopropylamine and Ni(II) ions, complete structural elucidation has not been accomplished [45].

The octanuclear carbamato complex $[Zn_2Ni_6(\mu_4\text{-}O)_2(OOC–N(isoprop)_2]$ was obtained as a side product of the reaction between $[Ni(acetonitrile)_6]ZnCl_4$, diisopropylamine and CO_2. After isolation, it was characterised in its solid state by X-ray analysis [45]. Accordingly, this complex consists of tetrahedral Zn centres and distorted trigonal bipyramidal nickel ions. The nickel and zinc central atoms are connected via the two μ_4-O atoms (probably formed from trace water) and bidentate carbamato ligands. The latter are acting both as bidentate ligands bridging the Zn- and Ni-centres and as tridentate ligands connecting the three Ni central atoms.
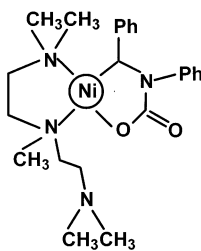
Fig. 10. X-ray structure of a nickelacycle containing a monodendate carbamato ligand [46].

Planar Ni(II) complexes containing cyclic carbamato ligands were described in a series of earlier papers [1,39,40]. In these compounds the carbamato group acts exclusively as a monodentate ligand. A novel example for this type of complex is depicted in Fig. 10 [46].

In the recent past the synthesis of a novel Ni(II) carbamato complex was accomplished wherein the carbamato moieties solely function as bidentate bridging ligands as in *urease*. The complex is formed in a surprisingly straight forward synthesis of $6CO_2$, 6Ni(0) centres and 12 furylidene-*N*-phenylimine ligands. Six of them form cyclic dianionic carbamates due to oxidative coupling of the imine and CO_2 at the Ni(0) centre, whereas the remaining six act as monodentate ligands (Fig. 11) [47].

The hexanuclear compound operates as a reversible CO_2 carrier. CO_2 is eliminated under heat or vacuum. As a result a tetranuclear carbamato complex can be formed wherein the carbamato groups function as tridentate bridging ligands under controlled conditions (Fig. 12) [47].
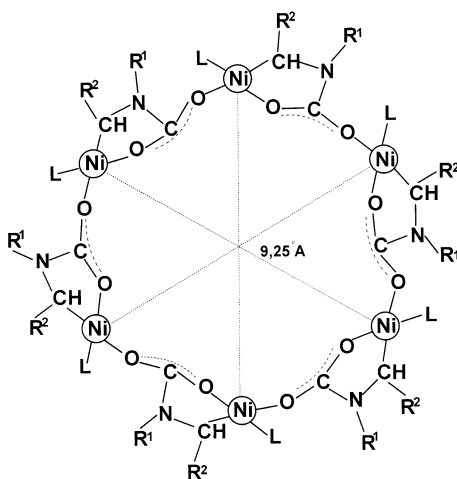
Fig. 11. The structure of a hexanuclear Ni(II)carbamato complex containing bidentate cyclic carbamato ligands [47] (L: furylidene-*N*-phenylimine, coordinated by the nitrogen of the Schiff base, see Fig. 12).

Fig. 12. Structure of a tetranuclear cyclic carbamato complex with tridentate carbamato groups [47] (R^1, furylidene; R^2, phenyl).

In tetrameric organometallic complexes of zinc the N–COO– groups act both as bidentate and tridentate bridges. However the octahedral monomeric complex (tmeda)Zn[(OOC–N(isoprop)$_2$] contains two bidentate chelating carbamato ligands [37].
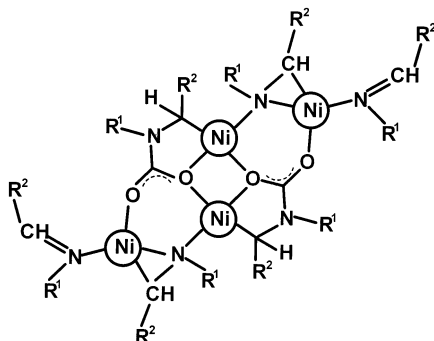
Hitherto there is obviously no carbamato Ni(II) complex synthesised which is capable of binding urea and catalysing its hydrolytic decomposition to carbamic acid and NH$_3$.

Structural models for *urease* containing a binuclear Ni(II) unit which is connected via a carboxylato group of acetate are already known [48–54].

A binuclear Ni(II) complex in which a nickel binds urea was synthesised by Lippard et al. [52]. Krebs et al. reported binuclear nickel complexes containing alcoholato as well as acetate bridges [53]. They exhibit similar spectroscopic properties as the active centre of *urease* (of *Klebsiella aerogenes*). Although urea is not hydrolysed the hydrolysis of 4-nitrophenyl phosphate could be observed.

Recently Yamagachi et al. reported a functional model for *urease* containing two Ni(II) centres bridged by an acetato ligand. The urea is coordinated to one of the nickel centres via its C=O bond [54]. This compound is able to catalyse the ethanolysis of urea to ethyl carbamate (maximal turnover number: 4).

In 1997, kinetic investigations of the hydrolysis of urea on Pd(II) complexes containing aquo as well as *N*- or *S*-donating ligands were reported indicating that *N*-coordinated carbamic acid is the intermediate in these hydrolytic reactions [55].

In summary, it has been shown that there is a considerable need for further investigation in order to create catalytic binuclear nickel complexes capable of simulating the structure and function of *urease*. The question why especially in nature the carbamato metal units are used to catalyse hydrolytic cleavage of substrates remains open.

3.4. CO$_2$ transfer by carbamato metal complexes

Although, there are some examples for the first step of CO$_2$ fixation, there is little

known about the process of CO_2 transfer from the carbamates to the organic substrates and the role played by the metals involved [56]. Concerted and stepwise mechanisms have been proposed for the CO_2 transfer in imidazolidon derivatives [22]. However, all these investigations are uncertain since the structure of the carbamato complexes involved is unknown. The carboxylation of C–H acidic compounds imitates the *biotin*-dependent CO_2 transfer steps described for the enzyme catalysed reaction (e.g. *acetyl-CoA-carboxylase*):

$$R - COCH_3 \xrightarrow{\text{Carbamato} - M} R - COCH_2 - COOH$$
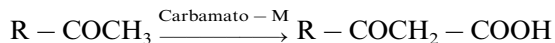
Only a few publications in classical organic chemistry deal with the carboxylation of organic substrates using in situ generated, not further characterised magnesium triethylamine compounds [57]. The applied transfer reagents are used in more than stoichiometric amounts in order to obtain reasonable yields. The reaction of cyclic ureas and related compounds with RMgX leads to magnesium amides which have been employed in the carboxylation of a variety of C–H acidic compounds [58].

The thermally reversible fixation of CO_2 and its transfer to acetophenone was accomplished by a number of nickel compounds with specific 1-azadiene-type ligands (Fig. 13) [59,60]. The structures of the carbamato complexes formed in this reactions are still unknown in contrast to the binuclear starting complexes containing bridging 1-azadienes.
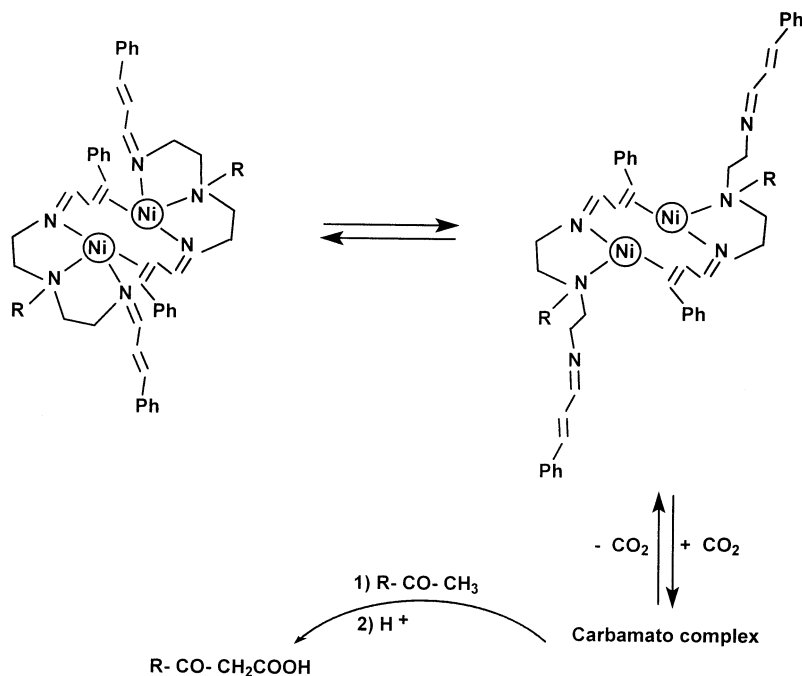

Fig. 13. CO_2 fixation by 1-azadiene–Ni(0) complexes and transfer of the activated CO_2 to C–H bonds [59].

The yields for this reaction are lower (15–20%) compared to the values obtained for magnesium and manganese complexes with diazadiene ligands [56]. This underlines the prominent position of these metals in transcarboxylation processes.

The first structural characterisation of a CO_2 transferring carbamato complex has been accomplished by the above described trinuclear magnesium complex $[Mg_3(CO_2)_6(TPOA)_3(THF)_6]$ (Fig. 9). This CO_2 carrier complex carboxylates acetophenone to the corresponding benzoylacetic acid [41].

4. Recent results in photoassisted and photocatalytical reductions of carbon dioxide in artificial systems

4.1. General principles

The process of natural photosynthesis can be subdivided into the light and dark reaction. The latter and a number of artificial systems simulating the step of CO_2 activation in the dark reaction have been described in Section 2.1.

A great deal of effort has been devoted in the last 15 years to mimic the mechanism of the light reaction, in which the energy of light is transformed into chemical energy, accomplished in the photosynthetic centres of green plants via a chain of electron carriers and chromophores. The structural elucidation of the photosynthetic centre of *Rhodopseudomonas viridis* by X-ray analysis provides support for this mechanism [61]. The transformed energy is stored in ATP and NADPH.

There are a number of publications dealing with artificial photosynthesis from the viewpoint of energy transfer and charge separation in inorganic multicomponent systems [62–65].

Another approach is to construct artificial photocatalytic systems which are able to use light energy for the reduction of CO_2.

In principle, such catalytic systems consist of (i) a photosensitive compound (photocatalyst), (ii) an electron relay (mediator) (M) (iii) a (sacrificial) electron donor (ED) according to Scheme 1. In some cases both the photocatalyst and the mediator are identical.

In Scheme 1, three possible photocatalytic cycles are described. Another pathway proceeding via a metal hydride has been discussed in the literature (see for example ref. [95]). However the formation of this intermediate is not yet well understood.

There are a number of unsolved problems in this very complex area of photocatalytic CO_2 activation:

● Knowledge about the mechanism of the photochemical CO_2 activation reaction is still underdeveloped.
● The tuning of the single components with respect of their redox potentials, life times and selectivities is still not well understood.
● The turnover numbers TON (mol reduction product of CO_2 mol^{-1} catalyst) of the photocatalytical reactions are low.
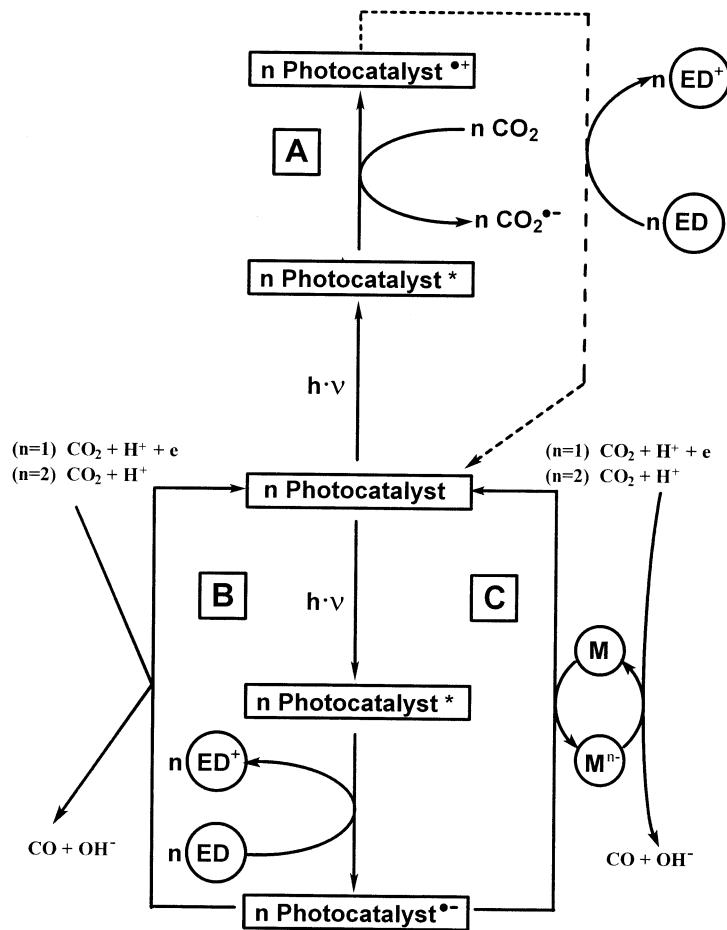
Scheme 1. Three principles of photocatalytic cycles in which CO_2 is reduced.

- The efficiency of these reactions is unsatisfactory with respect to both the value of the reduction products of CO_2 (usually C_1 products) and the oxidation products of the sacrificial electron donor.

4.2. Homogeneous photocatalytic or photoassisted reactions

An example for a new stoichiometric photochemically driven C–C bond forming process with $CO_2^{\bullet-}$ as reactive intermediate was discovered by Kubiak in 1993 [66–68] (Scheme 1A). The trinuclear nickel cluster (Fig. 14) which was characterised by X-ray analysis absorbs strongly in the visible region but does not emit.

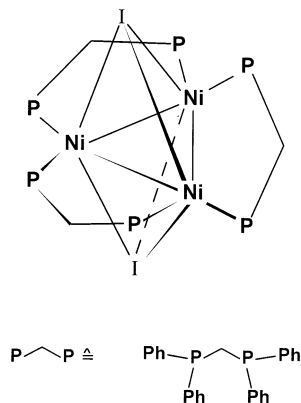The excited state formed upon irradiation ($\lambda < 300$ nm) is a strong reducing agent capable of reacting with CO_2.

Fig. 14. X-ray structure of a photochemically active Ni_3 cluster [66].

In the absence of any other substrate, CO_2 is transformed into CO and CO_3^{2-} possibly formed from $CO_2^{\bullet-}$, the primary product of the photoredoxreaction, by disproportionation. This assumption could be verified by employing cyclohexene as a radical scavenger which reacts with the radical anion of CO_2 in a thermal reaction to form the radical anion of cylohexanecarboxylic acid. This intermediate reacts in a reversible Kolbe reaction with CO_2 to yield the dicarboxylated species. Reduction of this species by the nickel cluster I (Fig. 14) results in the formation of the dianion of cyclohexanedicarboxylic acid. This reaction is non catalytic since the oxidised cationic nickel cluster could not be reduced to the starting compound (Scheme 2).

One of the highest turnover numbers (TON = 70) observed for a homogeneous photacatalytic CO_2 reduction was reported by Neta et al. using the iron porphyrin system as both photocatalyst and mediator, which is after reduction able to coordinate CO_2 (Scheme 1B) [69].

Several intermediates of the photoreduction of the iron centre could be identified by their photochemical properties. The proposed reaction mechanism starts with a ligand to metal charge transfer from axially bound triethylamine (TEA) which acts as sacrificial electron donor to the Fe(III) centre upon which a Fe(II)–porphyrin species could be detected ($\phi = 0.05$). Irradiation of the resulting solution leads to a second photoreduction possibly via a similar process ($\phi = 0.01$) to form the Fe(I) complex.

Although not observed, the authors claim a possible disproportionation of the Fe(I) complex yielding the active Fe(0)–porphyrin and the corresponding Fe(II) complex. The Fe(0)–porphyrin seems able to coordinate CO_2.

Under a CO_2 atmosphere a steady state concentration of the Fe(I)–porphyrin could be obtained and large amounts of a Fe(II)–porphyrin with an axially bound carbonyl ligand were detected. Photodissociation of this carbonyl complex [70] liberates CO ($\phi = 0.54$).

The photochemical CO_2 reduction employing cobalt tetraazamacrocles as electron relays is also possible if suitable organic photocatalyst like terphenyl (TP) and
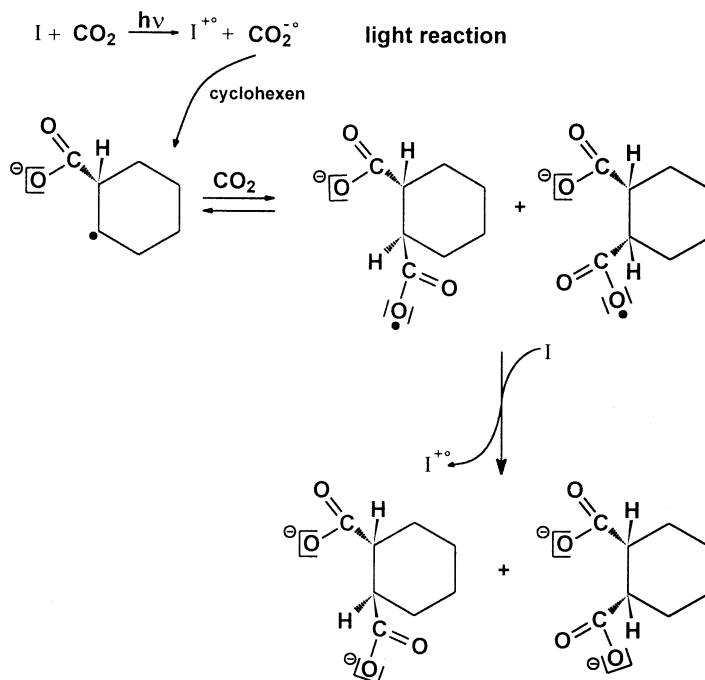
Scheme 2. Stoichiometric photochemical reaction and dark reaction of CO_2 activated by a Ni_3 cluster (structure see Fig. 14).

phenazine (PA) are used. Triethylamine (TEA) acts as a sacrificial electron donor [71–74].

In 1995, the mechanism of this photocatalytic reaction was investigated in detail [73]. Transient spectra taken during the actual photocatalysis indicate the formation of the radical anion $TP^{\bullet-}$ and the Co complexes [LCo(II)], [LCo(I)],[LCo(I)(CO$_2$)] and [(solvent)(L)Co(III)(CO$_2$)$^{2-}$]. This leads to a proposed photocatalytic cycle which is strongly supported by many experimental results (Scheme 3).

The radical anion $TP^{\bullet-}$ formed by photochemical reduction of TP in the presence of TEA as electron donor is able to reduce the Co(II) macrocycle to form the Co(I) complex which binds CO_2. Addition of a solvent molecule (DMF or acetonitrile) yields the Co(III) complex [(solvent)(L)Co(III)(CO$_2$)$^{2-}$] in which two electrons are transferred from the central atom to the coordinated CO_2. The suggested next reaction is the addition of protons resulting in the formation of a coordinated COOH group.

In the last step of the catalytic reaction CO and OH^- are produced. This step requires a second reducing equivalent. It is likely that the Co(I) tetraazamacrocycle [LCo(I)] acts as electron donor under the experimental conditions of the flash photolysis regenerating the Co(II) complex which can start a new catalytic cycle. This reaction is a special case of the catalytic cycle shown in Scheme 1 (C, $n = 1$).
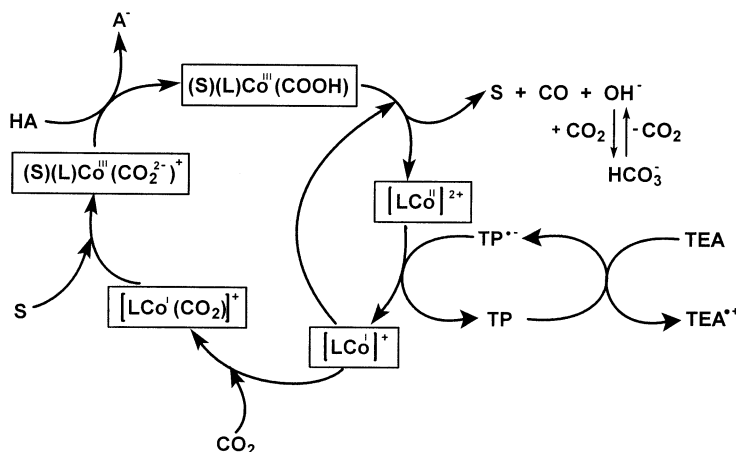
Scheme 3. Light driven catalytic cycle reducing CO_2. Light reaction: terphenyl (TP) as a photocatalyst, triethylamin (TEA) as reductive quencher (electron donor). Dark reaction: cyclam cobalt complex as electron relay (a) oxidising the terphenyl radical anion and (b) reducing CO_2.

The photocatalysed reduction of CO_2 by rhenium complexes of the type *fac*-[(bpy)(CO)$_3$ReX](X: Cl, Br) or *fac*-[(bpy)(CO)$_3$ReL]$^+$A$^-$ (A$^-$: PF$_6^-$, BF$_4^-$ and other non coordinating or weakly coordinating anions) has attracted much attention over the past 15 years [88–91]. Fig. 15 shows the structural principle.

The complexes exhibit intense absorption in the visible region. It was possible to assign a MLCT transition to these bands by investigating the change of IR stretching frequencies for the carbonyl ligands under irradiation [93]. Koike and Hori have found that the cationic complex with $L = P(OEt)_3$ has the highest photocatalytic activity among the related homogeneous photocatalysts reported so far [94]. Recently, they have investigated the mechanism and the influence of the nature of the ligand L on the catalytic CO_2 reduction with triethanolamin (TEOA) as sacrificial donor [92,94].

The excited state of the rhenium complexes is a strong oxidising agent which can be reductively quenched by TEOA. This results in the formation of the one electron reduced species [(bpy)(CO)$_3$ReL] (Scheme 4).
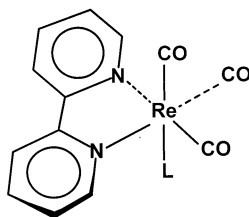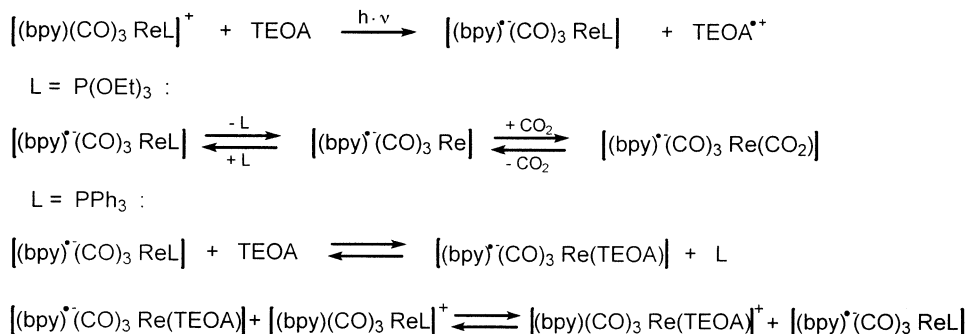

Fig. 15. Structure of (bipy)(phosphin)rheniumtricarbonyl complexes acting as photocatalyst in the photochemical CO_2 reduction [88–91].

$$[(bpy)(CO)_3 ReL]^+ \;+\; TEOA \;\xrightarrow{h \cdot \nu}\; [(bpy)^{\bullet -}(CO)_3 ReL] \;+\; TEOA^{\bullet +}$$

L = P(OEt)$_3$:

$$[(bpy)^{\bullet -}(CO)_3 ReL] \;\underset{+L}{\overset{-L}{\rightleftarrows}}\; [(bpy)^{\bullet -}(CO)_3 Re] \;\underset{-CO_2}{\overset{+CO_2}{\rightleftarrows}}\; [(bpy)^{\bullet -}(CO)_3 Re(CO_2)]$$

L = PPh$_3$:

$$[(bpy)^{\bullet -}(CO)_3 ReL] \;+\; TEOA \;\rightleftarrows\; [(bpy)^{\bullet -}(CO)_3 Re(TEOA)] \;+\; L$$

$$[(bpy)^{\bullet -}(CO)_3 Re(TEOA)] + [(bpy)(CO)_3 ReL]^+ \rightleftarrows [(bpy)(CO)_3 Re(TEOA)]^+ + [(bpy)^{\bullet -}(CO)_3 ReL]$$

Scheme 4. Light and dark reaction of (bipyridine) (phosphine)-rheniumtricarbonyls in the presence of triethanolamine (TEOA) and CO$_2$ if L = P(OEt)$_3$ or PPh$_3$.

Interestingly, variation of the ligand L, seems to open different reaction routes leading to CO as final product of the reduction of CO$_2$ [94,95].

In the case of L = P(OEt)$_3$, the exchange of L by CO$_2$ leads to the formation of a CO$_2$ complex which is further reduced by another electron donor of so far unknown origin and liberates thereafter CO [94].

In the case of PPh$_3$ as ligand L, the proposed reaction mechanism involves an unusual chain ligand substitution ($\phi = 16.9$!) yielding the rhenium CO$_2$ species (Scheme 4).

It has been suggested that the formation of a formato species as the insertion product of an intermediary produced rhenium hydride could also play a role [94]. Some other reaction intermediates were analysed by HPLC and electron spray MS [96,97].

These complex catalytic cycles are still under investigation, especially to obtain more information about the last steps of the reaction sequence in which the CO$_2$ complex produces CO.

The well-known photochemical properties of the Ru(bpy)$_3^{2+}$ complexes [75,76] have been used by Kimura et al. in a bifunctional supermolecule consisting of a light absorbing ruthenium moiety linked via a pyridinium unit to a nickel macrocycle which contains the cyclam ligand [77]. The former can also act as a electron reservoir whereas the latter is a known electron relay catalyst for the electrochemical reduction of CO$_2$ [78]. This complex supermolecule is depicted in Fig. 16.

The catalyst did show enhanced activity for the photochemical CO$_2$ reduction in solution, compared to the separated system Ru(bpy)$_3^{2+}$/Ni(cyclam), but was very labile to photocleavage.

4.3. Heterogeneous photocatalytic systems

It is also possible to employ nanosized semiconductor particles as heterogeneous photocatalysts [79–85]. Yanagida and co-workers recently discovered that nanocrystalline ZnS–DMF can act as a photocatalyst in a heterogeneous system
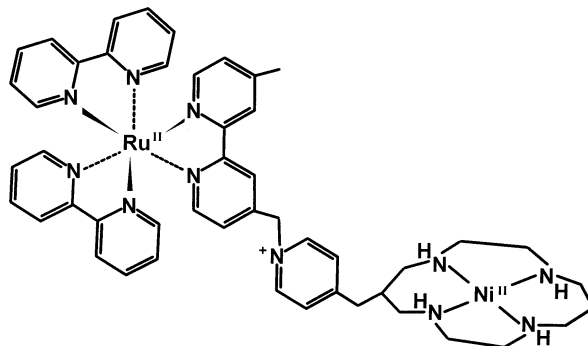
Fig. 16. Structure of a photochemically active supermolecule containing two metal centres (Ru^{II}, Ni^{II}) [77].

using Et_3N (TEA) as a sacrificial electron donor [86]. Formate and carbon monoxide were produced upon UV-irradiation under a CO_2 atmosphere ($HCOO^-$/ $CO = 76.7$) with a quantum yield for the formate formation of $\phi = 0.14$. The product ratio changed dramatically upon addition of excess Zn^{2+}. Less formate was produced with respect to CO ($HCOO^-/CO = 0.4$). A possible explanation for these interesting results lies in the coordination of zinc ions to vacant sulphur sites on the surface of the semiconductor which otherwise can be protonated. This may reduce the amount of available protons at the reduction site of CO_2 and therefore inhibit the formation of formate.

Watanabe described a system utilising ZnO as photocatalyst and employing CO_2 pressures of up to 40 bar which produced CH_4 and CH_3OH from CO_2 and H_2O with a quantum efficiency of 6% under irradiation with visible light ($\lambda > 490$ nm) [87]. The proposed mechanism is thought to involve formaldehyde.

Although the energy used in the described reactions is provided by light they involve degradation of sacrificial donors such as triethanolamine or triethylamine. Since the energy balance of the reaction is influenced unfavourably by this fact, it seems necessary to device systems which do not require any sacrificial donors.

Recently, Yoneyama et al. described the photochemical synthesis of malic acid from lactic acid and CO_2 without any sacrificial donors [98]. They employed a multicomponent system based on a cadmium sulphide suspension acting as a photocatalyst, methylviologen as electron relay, ferredoxin-$NADP^+$-reductase (FNR) and malic enzyme (ME). The proposed catalytic cycle is depicted in Scheme 5.

Under irradiation of an aqueous solution containing the above listed components photogenerated electrons are transferred from the CdS photocatalyst to methylviologen ion MV^{2+}. The reduced methylviologen provides the electrons needed for the reduction of $NADP^+$ and H^+.

The photogenerated electrons leave a hole in the conduction band of the semiconductor particles. The resulting potential is sufficient to oxidise lactic acid to
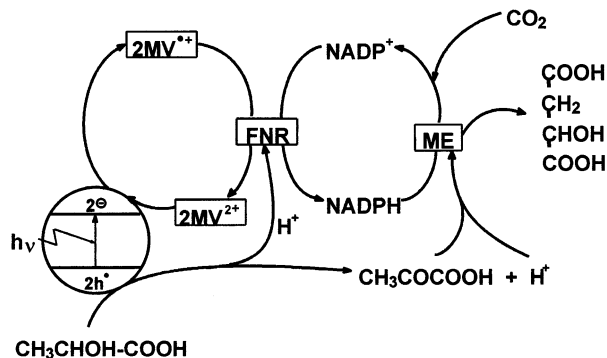
Scheme 5. Proposed catalytic cycle of the light driven carboxylation of lactic acid to form malic acid (MV^{2+}, methylviologen dication, FNR, ferredoxin-NADP-reductase; ME, malic enzyme).

pyruvic acid on one hand and restoring the photocatalyst on the other. This process produces the substrate for the ME catalysed production of malic acid from pyruvic acid, CO_2 and NADPH.

Malic acid can therefore be described as the product of two coupled photoredox-reactions, i.e. the reduction of MV^{2+} and the oxidation of lactic acid. The C–C bond formation between pyruvic acid and CO_2 takes place in the dark.

The above described reactions show that the photocatalytic reduction of CO_2 is possible. However relatively low turnover numbers and the use of sacrificial donors such as TEOA are serious drawbacks for a wider application. The system reported by Yoneyama and co-workers circumvents this problem by using the full potential of the activated photocatalyst, i.e. its strong reducing and oxidation capabilities, but it needs enzymatic systems in two steps of the catalytic cycle. A more general application of this principle might lead to a significant enhancement of performance in other systems.

5. Metal assisted and catalysed reactions in compressed carbon dioxide

This section provides an overview of the rapidly growing, innovative and challenging field of metal-assisted and -catalysed reactions using compressed CO_2 either as a reaction medium or as solvent and as substrate from 1992 onwards (for earlier results see [99]). An initial study was reported by Ibers et al. [100]. Table 1 lists both the advantages and disadvantages of compressed CO_2 as a reaction medium for reactions of metal complexes or organometallics.

The most important advantages are the environmentally benign nature of CO_2 and the possibility to adjust the properties of the solvent by changing the temperature and pressure. On the other hand it is necessary to carry out these reactions under pressure.

Table 1
Advantages and disadvantages of scCO$_2$ as reaction medium for metal assisted or metal catalysed reactions

Advantages	Disadvantages
Environmentally neutral	Reactions must be carried out under pressure
Nontoxic and nonflammable	Autoclave technique is necessary
Low viscosity and density, high diffusibility, easy adjustable by temperature and pressure	Low solubility of metal compounds and organometallics in scCO$_2$
Easy to recycle or to remove	Reactive M–H, M–C, M–N and M–O bonds react under insertion of CO$_2$
Supercritical region is easily accessible (31°C, 73 atm = 1071 psi)	The phase behaviour with reactants is not completely understood
High miscibility with other gases (e.g. H$_2$, CO, O$_2$)	Number of metal-directed reactions reported is small, synthetic processes have yet to be explored
Nonpolar, weak molecular association	Electrophilic properties limit the compatibility with some organic compounds (e.g. RNH$_2$, bases)
Thermodynamically stable, not oxidisable and often kinetically inert	
Inexpensive	

5.1. Solubility and reactivity of metal complexes and organometallics in compressed CO$_2$

5.1.1. The solubility of metal compounds in CO$_2$

Only a limited number of metal complexes, organometallics and organic compounds are soluble in CO$_2$ since CO$_2$ is a nonpolar solvent. In order to increase the solubility of metal compounds in compressed CO$_2$ a variety of different strategies have been developed which can be summarised in the following points:

- Substitution of hydrogen by fluoro substituents increases the solubility [101–103]. Generally, the solubility decreases in the order: fluorine-substitution > substitution by alkyl groups > substitution by aryl groups for a given complex. Introducing fluoralkyl-, fluorether or silicon tails as CO$_2$-philic groups into ligands increases the solubility of both ligands and metal complexes [104–106].
- Special counterions (e.g. F$_3$C–SO$_3^-$ and other fluoro group containing anions) improve the solubility of cationic complexes [107].
- Me$_3$P, CO and cyclopentadienyl ligands are also CO$_2$-philic and increase the solubility of the corresponding metal complexes.

Recently, Smart et al. published solubility data of a number of chelate complexes which are of interest in metal extraction processes [108].

Most of the information is available for 1,3-diketonates and their metal complexes [108–111].The substitution of hydrogen in the acetylacetonato complex of Yttrium by fluorine increased the solubility by a factor of 10^3 to 10^4.This is just one example illustrating the major influence of the CO$_2$-philic fluorine substituent on the solubility of compounds in scCO$_2$.

Systematic investigations have shown that all monomeric metal carbonyls and many other metal carbonyls including $Co_2(CO)_8$, $Ru_3(CO)_{12}$ and $CpMn(CO)_3$ are also soluble in CO_2. They are quite stable in this solvent and can therefore be used for a wide variety of organometallic reactions [112].

Metallocenes exhibit different solubilities and stabilities in $scCO_2$. Ferrocene derivatives are readily soluble and quite stable in both liquid and $scCO_2$ [108,112]. Surprisingly, the much more reactive nickelocene and cobaltocene complexes are both soluble and less reactive towards CO_2, even at 45°C [112]. Therefore, it can be concluded that they possess an interesting catalytic potential in compressed CO_2 as solvent.

Only a very limited number of alkyl metal compounds have been investigated in CO_2. The well-known oxidation catalyst CH_3ReO_3 [113] is highly soluble both in liquid and supercritical CO_2. It is noteworthy that even at 70°C it does not undergo any carboxylation reactions. It can be recrystallised and isolated in very pure form from CO_2 [112]. $Cp_2Ti(CH_3)_2$ can also be dissolved in CO_2. No reaction with the solvent has been observed. On the other hand $CpReO_3$ is only sparingly soluble.

Several complexes with Me_3P as ligand, e.g. $(Me_3P)_2Ni(cod)$ [112], $(Me_3P)_4RuCl_2$ [114] and $(hfacac)Cu(PMe_3)$ are soluble in $scCO_2$ and can therefore be employed as precatalysts for homogeneous reactions. $(hfacac)Cu(PMe_3)$ exhibits $scCO_2$ solubility of the order of 0.1 M. This compound is of practical importance in metal deposition on a hot surface [115].

5.1.2. Reactions of coordination compounds and organometallics in CO_2 as solvent

Some general aspects of reactions in supercritical fluids including reactions in $scCO_2$ were summarised in previous reviews [116–118].

In their initial studies, Poliakoff et al. investigated the photolysis of $CpMn(CO)_3$ in the presence of H_2 yielding the dihydrogen complex $CpMn(CO)_2(H_2)$ in which H_2 is η^2-coordinated [119,120]:

$$CpMn(CO)_3 + H_2 \rightarrow CpMn(CO)_2(H_2) + CO$$
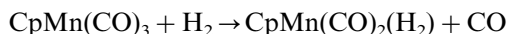
The activation of the C–H bonds in alkenes or alkanes could also be achieved by $Cp^*Ir(CO)_2$ [121].

The unique combination of the gas- and liquid-like properties of $scCO_2$ provides the perfect reaction medium for impregnation of organometallics into polyethylene. Poliakoff et al. succeeded in this field which is of growing interest for the investigation of unconventional organometallic species in a polymer matrix [118,122]. For example, if $Cp^*Ir(CO)_2$ in contact with polyethylene (PE) was irradiated with UV light in $scCO_2$ elimination of CO followed by the oxidative addition of a C–H bond of a polymer unit could be observed.

The photochemical reaction of $Fe(CO)_5$ in $scCO_2$ leading to $Fe_2(CO)_9$ followed by thermal formation of $Fe_3(CO)_{12}$ has been investigated by IR spectroscopy. It was found that the solvent CO_2 did not coordinate to the iron centre [112].

The extremely reactive organometallic compound (cyclododecatriene)Ni(0) [(cdt)Ni] is readily soluble in liquid CO_2. At 0°C, it neither decomposes nor reacts with CO_2. In $scCO_2$, the compound forms an orange solution which decomposes

thermally to finely dispersed, highly reactive nickel powder which can be used for special catalytic reactions [112]:

(cdt)Ni (dissolved in CO_2) → Ni + cdt (dissolved in CO_2)
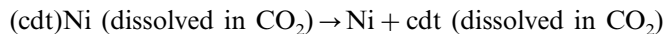
In contrast, $(cod)_2$Ni is only very sparingly soluble both in liquid and supercritical CO_2.

Recently a sol–gel process in $scCO_2$ was described in which iron containing heme proteins were encapsulated in a sol–gel formed by hydrolysis of tetramethylsilane in the presence of the corresponding protein. The electronic spectra of the immobilised protein sample gave evidence for the formation of a CO_2 adduct in $scCO_2$ [123]. This sol–gel methodology may offer an interesting general possibility for spectroscopic characterisation of other CO_2 adducts of low stability in supercritical CO_2.

5.2. Catalytic reactions in compressed CO_2 as a reaction medium

5.2.1. Hydroformylation

The first investigation of the hydroformylation of propene in $scCO_2$ by Rattke et al. in which $Co_2(CO)_8$ was used as a precatalyst has shown that the ratio between linear and branched aldehydes was slightly higher if the catalysis was carried out in $scCO_2$ instead of organic solvents [124,125]. However, the reaction rates and the nature of the active species were very similar compared with those observed in conventional nonpolar solvents.

The ratio of linear/branched butyraldehyde was 2.7 at 91.86 atm and 4.3 at 183.71 atm measured at 88°C [126].

Leitner et al. synthesised perfluoralkyl substituted aryl phosphine ligands to improve the solubility of their complexes L_3RhCl acting as precatalysts for the hydroformylation of 1-olefins in $scCO_2$. In a preliminary investigation they observed that the hydroformylation of 1-octene resulted in the formation of aldehydes in high yields. The molar ratio of linear/branched aldehydes was found to be 4:1 at 60°C and an overall pressure of 220 atm [127].

The hydroformylation/hydrogenation of 3,3-dimethyl-1,2-diphenylcyclopropene using $HMn(CO)_5$ was described by Noyori et al. [128]. They found no evidence for a radical mechanism of the hydroformylation reaction.

5.2.2. Catalytic hydrogenation in supercritical CO_2

The heterogeneous catalytic hydrogenation of unsaturated ketones is possible if Pd supported on alumina is used as catalyst [129]. The hydrogenation of fatty acids on a Pd fixed-bed catalyst at 140°C could be utilised for the selective hardening of edible oils and fatty acids [130–132]. In contrast Pt was found to be inactivated if the hydrogenation of ethylpyruvate was carried out in $scCO_2$ [129].

The first asymmetric catalysis in $scCO_2$ reported by Burk and Tumas et al. in 1995 [107] was the catalytic hydrogenation of enamides with cationic phosphine rhodium complexes. The solubility of the catalyst in $scCO_2$ was improved by using highly lipophilic counterions such as [3,5-bis(trifluoromethyl)phenyl-borate]
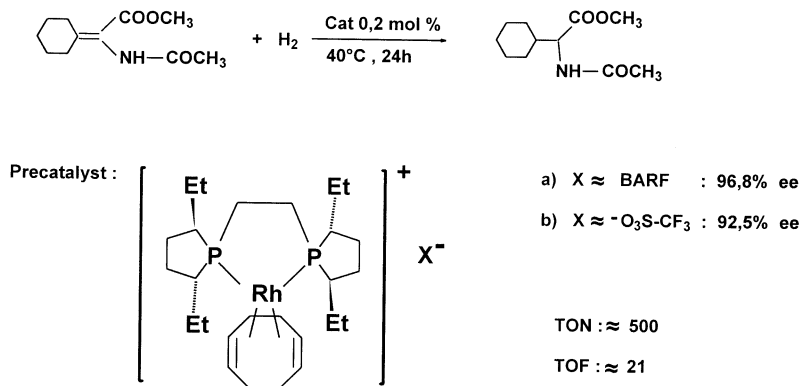
Fig. 17. Asymmetric hydrogenation of enamides in scCO$_2$ catalysed by Rh complexes [107].

(BARF) or trifluormethane-sulphonate (triflat). Comparison of the results with those obtained in methanol or hexane established that high enantioselectivities could be achieved in all three solvents. In some cases significantly higher selectivities were reported if scCO$_2$ was used as a solvent (Fig. 17).

The yield of (*S*)-2-methylbutanoic acid in scCO$_2$ was lower than in methanol for the asymmetric hydrogenation of tiglic acid with Ru complexes stabilised by a D-BINAP derivative. However, using CF$_3$(CF$_2$)$_6$OH as an additive, it was possible to improve the ee value of the product [116,133] (Fig. 18).

5.2.3. The catalytic Pauson–Khand reaction

The cyclisation of olefins with alkynes and CO (Pauson–Khand reaction) can be achieved catalytically employing Co$_2$(CO)$_8$ as precatalyst [134]. The yields obtained in scCO$_2$ vary between 50 and 91% depending on temperature, pressure and the nature of the substrates used. The reaction is relatively slow. The turnover
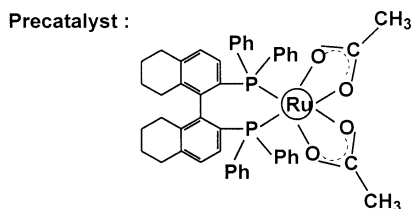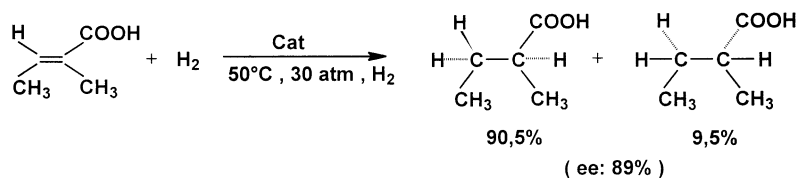

Fig. 18. Enantioselective hydrogenation of tiglic acid catalysed by a Ru complex [116,133].
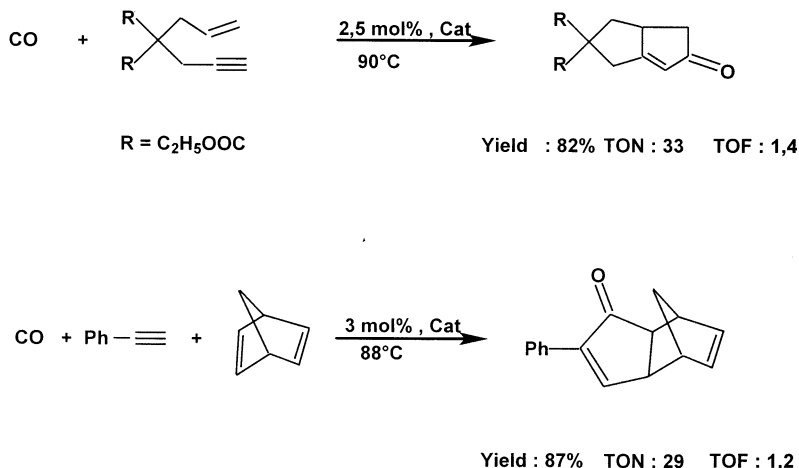
R = C$_2$H$_5$OOC

Yield : 82% TON : 33   TOF : 1,4

Yield : 87%   TON : 29   TOF : 1,2

Fig. 19. Catalytic Pauson–Khand reaction in supercritical CO$_2$ [134].

frequency is less then two catalytic cycles/h (TONs ca. 30). Typical examples are depicted in Fig. 19.

5.2.4. Catalytic polymerisation

The cationic polymerisation of unsaturated substrates is feasible in liquid and in supercritical CO$_2$. Thus, bismethoxymethyloxetane and vinyl ether can be polymerised employing R$_n$AlCl$_m$ ($n + m = 3$) [135,136]. The product precipitating from supercritical CO$_2$ does not incorporate CO$_2$.

Isobutylene polymerised to polyisobutylene, with a molar weight of 2000–2300 g mol^{-1} which is higher than the molar weight obtained in conventional solvents (molar weight of ca. 1800 g mol^{-1}) [136,137].

Radically initiated polymerisation's are also possible with good yields, as demonstrated by deSimone et al. [138].

Very recently, Fürstner and Leitner described the ring opening polymerisation of norbornene or cyclooctene using the well-known metathesis catalyst [(Cy$_3$P)$_2$Ru(CHR)Cl$_2$] [139]. The activity of this catalyst was higher than those of the complex [Ru(H$_2$O)$_6$(Otos)$_2$] [140].

The ring closure metathesis of α,ω-dienes catalysed by a molybdenum carben complex was also successful if compressed CO$_2$ was used as solvent [140].

5.2.5. Catalytic oxidation reactions

Only a limited number of oxidation reactions in compressed CO$_2$ have been reported. Toluene could be partly oxidised to benzoic acid as main product employing CoO as catalyst [141].

Ethanol reacts with oxygen to yield acetaldehyde using Pt/TiO$_2$ as heterogeneous catalyst. The aldehyde is further oxidised with O$_2$ with formation of CO [142].

The oxidation of olefins to oxiranes with H$_2$O$_2$ or t-BuOOH could be achieved if CH$_3$ReO$_3$, Mo(CO)$_6$ or Ti(OR)$_4$ were used as precatalyst [112].

A few complete oxidation reactions of aromatic systems to CO_2 and water on Pt supported on alumina have been described [143].

The oxidation of alcohols to aldehydes catalysed by (phenantroline)CuX/K_2CO_3 as a catalyst precursor system is possible. In toluene the reaction proceeds quantitatively [144]. In $scCO_2$ the catalysis does not occur. However, after addition of 1% toluene to the heterogeneous catalytic system the catalysis works well yielding aldehydes in high yields [145]. This clearly demonstrates the influence of modifiers on reactions in $scCO_2$.

5.3. Catalytic reactions using CO_2 as both solvent and substrate

5.3.1. Catalytic hydrogenation of CO_2 in $scCO_2$ to formic acid derivatives

Noyoris pioneering work concerning the catalytic synthesis of formic acid derivatives by hydrogenation of CO_2 in $scCO_2$ in the presence of an additional substrate influencing the reaction thermodynamically favourable is summarised in Fig. 20 [117,146–149].

In these reactions, the remarkable strength of $scCO_2$ to merge with hydrogen and therefore to enable a rapid flow of matter is used to develop efficient catalysis. An excellent example is the very economical synthesis of dimethylformamide in $scCO_2$ which is superior to the conventional system by high turnover numbers and high selectivity (Fig. 20).

The utilisation of complexes of the type $(Me_3P)_4RuX_2$ as catalyst precursors was essential for success: these complexes are adequately soluble in supercritical CO_2 and will not be deactivated by side reactions.

5.3.2. 2-Pyrones derived from alkynes and carbon dioxide in compressed CO_2

The hitherto solely highly selective catalytic C–C coupling reaction using CO_2 as substrate [150,151] can also be realised in compressed CO_2. Chelating phosphines have only a moderate influence on the selectivity of this Ni(0) catalysed cooligomerisation [152]. However, the application of trimethylphosphine or tri-
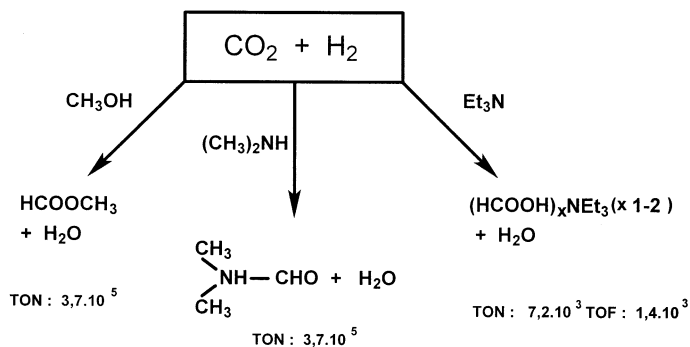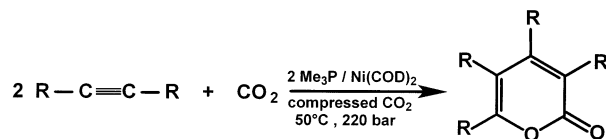

Fig. 20. Catalytic hydrogenation of CO_2 in supercritical CO_2 in the presence of additional substrates [117,146–148].

$$2 \; R-C\equiv C-R \;+\; CO_2 \;\xrightarrow[\substack{\text{compressed } CO_2 \\ 50°C \,,\, 220 \text{ bar}}]{2 \, Me_3P \,/\, Ni(COD)_2}$$

R = C_2H_5 :   TON = 20-40   Selectivity : 98,5%
R = C_4H_9 :   TON = 2   Selectivity : 93%

Fig. 21. Ni(0) catalysed cycloco-oligomerisation of CO_2 and alkynes in compressed CO_2 [153,154].

ethylphosphine as controlling ligand results in reactions with high selectivity (e.g. for hex-3-yne up to 99%) [153,154] (Fig. 21).

IR-spectroscopic investigations of the deactivation of the catalyst employed lead to the conclusion that the Ni(0) species decomposes upon reaction with CO_2 to form carbonyl-phosphine-Ni(0) species [112]:

$$(Et_3P)_2Ni(CO_2) \rightarrow Et_3PO + (Et_3P)Ni(CO) \; (\rightarrow \text{disproportionation})$$
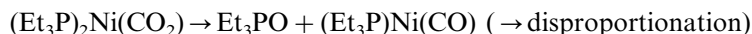
Other alkynes can also be converted to 2-pyrones.

5.3.3. Ring opening polymerisation of oxiranes with carbon dioxide in scCO$_2$

The formation of polymeric organic carbonates from oxiranes and CO_2 in scCO$_2$ as solvent has been investigated by Dahrensbourg et al. [155,156]. The authors discovered that zinc–phenolato complexes, used previously in conventional solvents, can act as catalyst in the co-polymerisation of cyclohexene oxide and CO_2 yielding polymers with molecular weights of 3800 g mol^{-1} if the reaction is carried out in CO_2 at 80°C. The most active precatalyst for this type of co-polymerisation discovered up to now is (6-diphenylphenoxide)$_2$Zn(diethylether)$_2$.

5.3.4. Cyclic carbonates from olefins, hydroperoxides and CO$_2$

The formation of cyclic carbonates was observed if styrene or cyclooctene react in a catalytic system permitting the epoxidation as well as the reaction to cyclic carbonates. However, the latter reaction proceeds in a heterogeneous-catalytic manner [112,157].

The potential of this types of catalytic reaction is by no means yet explored. Therefore the field of homogeneous catalysis in compressed CO_2 will attract major interest in future. The development of new CO_2 soluble catalysts, understanding how to prevent deactivation reactions with CO_2 as well as the control of the fine tuning of the reaction parameters in scCO$_2$ are starting points to discover new selective catalysis in scCO$_2$

Acknowledgements

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