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Recent developments in the activation of carbon dioxide by metal complexes

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Contents

Abstract

World leaders are negotiating a new global treaty that will lead to the reduction of global greenhouse gas emissions to legal commitments. Carbon dioxide is the largest single source

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of greenhouse gas, and emissions of carbon dioxide are increasing continuously. Utilization of carbon dioxide as a possible starting material for the synthesis of fine chemicals provides an attractive alternative to compounds presently derived from coal and petroleum. The effective conversion of carbon dioxide to useful chemicals will inevitably rely on transition metal catalysts. This review covers the recent progress in the direct activation of carbon dioxide by organo-transition metal complexes, with emphasis on insertion reactions and oxidative coupling reactions of carbon dioxide.

Keywords: Activation; Carbon dioxide; Coordination; Insertion; Oxidative coupling; Transition metal complex

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1. Introduction

Global warming, caused by increasing emissions of greenhouse gases such as carbon dioxide, methane and others, has been recognized as a serious environmental problem [1–9]. An obvious solution has been to reduce emissions of CO_2 [1–9], and other options are available [5–8]. These include reducing the use of energy derived from fossil fuels. Another option is the recovery of CO_2 from energy conversion processes, which is then stored in the ocean. An alternative approach is using CO_2 as a renewable resource, i.e. the reuse of existing CO_2 as a source of carbon for producing chemicals. The latter option has received much attention recently [9–34]. This is because the utilization of CO_2 as an alternative source of carbon has several advantages, such as:

1. alleviating global climate change caused in part by the increasing CO_2 emissions;
2. extending the present limited carbon resources (coal, petroleum and natural gas) into an environmentally friendly and easily obtainable carbon source, i.e. CO_2; and
3. simulating photosynthesis and enzyme-catalyzed reactions in the laboratory would be helpful in understanding the photosynthetic process in Nature and in utilizing enzyme-analogous reactions for chemical syntheses.

In spite of these advantages, the chemistry of CO_2 activation is still underdeveloped. This is due to the fact that CO_2 is highly thermodynamically stable and kinetically inert. The problem of CO_2 activation is a permanent challenge to the art of the chemist to ‘force’ this molecule into selective reactions under mild conditions.

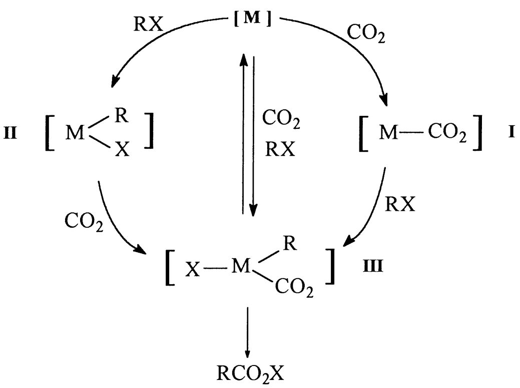
CO_2 has been used in the synthesis of urea, cyclic carbonates, salicylic acid and methanol. An increased use of CO_2 would only be possible if the relatively inert CO_2 molecule could be activated. Numerous ways for CO_2 activation are currently under investigation [9–34]. These include bioconversion [9], photochemical reduction [9,10,13–15], electrochemical reduction [9,10,13–15,23], thermal heterogeneous and homogeneous reductions [7,9,16–21] and coordination to transition metals [9,10,13–15,22–34], as well as some combinations of two or more methods described above [9,10]. All these methods have one feature in common, which is the activation of CO_2 by the coordination of CO_2 to a transition-metal centre. This coordination lowers the activation energy required in further reactions involving the CO_2 molecule, thus increasing the rates of these reactions, as in most cases this step is the rate-determining step for reactions involving CO_2. The coordination of CO_2 makes it possible to convert this inert molecule with suitable reactants into useful products.

The conversion of CO_2 and a substrate RX (RX might be alkyl halides, alkenes, alkynes, etc.) to the product RCO_2X at a transition metal centre is illustrated schematically in Scheme 1.

There are three possible routes (see Scheme 1) for the combination of CO_2 and a substrate RX at a transition metal centre to give the product RCO_2X:

1. coordination of CO_2 to the metal, providing a metal–CO_2 complex [**I**], followed by reaction of the metal–CO_2 complex [**I**] with the substrate RX to give [**III**]. Subsequent elimination would provide the product RCO_2X and reform the starting complex [M];
2. simultaneously coordinate both CO_2 and the substrate at the metal centre to afford [**III**], followed by reductive elimination to give the product RCO_2X and to reform the starting complex [M]; and
3. coordinate the substrate to the metal first, forming the substrate–metal complex [**II**] which could then react with CO_2. Subsequent elimination would provide the desired product RCO_2X.

Binding the CO_2 molecule and the substrate at the same transition-metal centre (structure [**III**]) would be a crucial step in both the stoichiometric and catalytic reactions of CO_2. The conversion of CO_2 by the above-mentioned three routes will be discussed in detail in Sections 2–4.



Scheme 1.

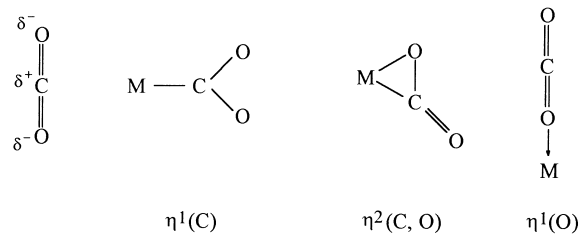


Fig. 1. CO_2 and its possible coordination modes at a transition metal centre.

2. Activation of carbon dioxide by the formation of metal CO_2 complexes

The formation of a transition metal–CO_2 complex via direct coordination is one of the most powerful and universal ways to induce the inert CO_2 molecule to undergo chemical reactions [31]. The synthesis and chemistry of transition metal–CO_2 complexes have been of continuous interest, and a number of reviews on this subject have appeared [9,10,13–15,22–34]. The latest review by Gibson, published in 1996, covered the most recent developments of the organometallic chemistry of metal–CO_2 complexes [32]. Thus, although metal–CO_2 complexes are central to CO_2 activation, they will not be discussed here in detail, other than to mention some particularly relevant aspects of CO_2 activation, and to comment on the most recent work.

2.1. Bonding of CO_2 at a transition metal centre

The CO_2 molecule is a linear triatomic molecule. The carbon atom possesses sp hybridization, and the C–O distance of 1.16 Å is shorter than a normal C=O double bond involving an sp^2 carbon atom. The different electronegativities of oxygen and carbon lead to a negative polarization on the oxygen atoms and a partial positive charge on the carbon atom. In its ground state, CO_2 also has two sets of π molecular orbitals which are orthogonal. Thus, the CO_2 molecule exhibits several distinct positions which could interact with a metal centre in different ways, as shown in Fig. 1.

The η^1(C) and η^2(C,O) side-on coordination modes have been confirmed by X-ray crystal structure determinations of known metal CO_2 complexes [35–37], e.g. $[Rh(diars)_2(Cl)(\eta^1\text{-}CO_2)]$ [35], $[Ni(\eta^2\text{-}CO_2)(PCy_3)_2]$ [36] and $[Cp'_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ [37]. No X-ray crystal structural data of the η^1(O) coordination mode in transition metal complexes are currently available.

Theoretical studies on the bonding of a CO_2 molecule to a metal centre have been reported [34,38–45]. The η^1(C) versus η^2(C,O) side-on coordination mode dichotomy is under both orbital and electrostatic control [45], as shown in Fig. 2. In the η^1(C) bonding mode there is a strong, two-electron stabilizing and charge transfer interaction between a d_z^2 type orbital (which is doubly occupied) and the π^* orbital of CO_2 (which is empty). In the η^2(C,O) side-on coordination mode the

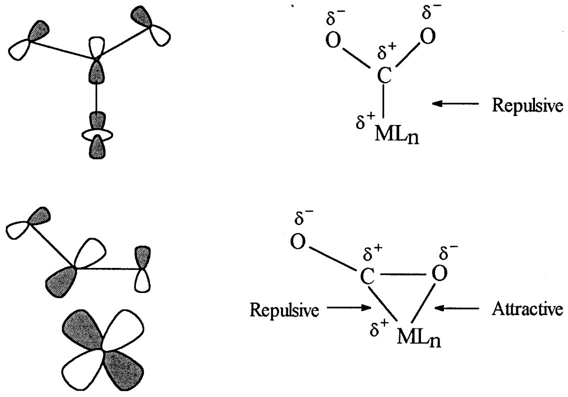


Fig. 2. Orbital overlapping and electrostatic interaction of the η^1(C) and η^2(C,O) side-on coordination modes of CO_2.

orbital interaction pattern is reversed. The dπ orbital interacts in a two-electron stabilizing interaction with the π^* orbital of CO_2. The η^1(C) bonding mode is most favoured when the transition metal fragment ML_n has a doubly occupied dσ type orbital that is relatively high in energy. This high energy will be best achieved if the metal is in a relatively low oxidation state which also reduces the repulsive electrostatic interaction. Examples of CO_2 complexes containing the η^1(C) bonding are [Rh(diars)$_2$(Cl)(η^1-CO_2)] [35] (Fig. 3) and [Co(salen)(η^1-CO_2)] [46–48]. The latter also has an alkali cation interacting with both oxygens (Fig. 4).

The η^2(C,O) side-on coordination mode is favoured by a high-energy dπ-type orbital. A stronger stabilization of the η^2(C,O) mode will be achieved if the dσ orbital which points towards the CO_2 ligand is empty. Many complexes with the η^2(C,O) mode have been reported in the literature, such as [Ni(PR$_3$)$_2$(η^2-CO_2)] (R = Cy, Ph, Bu, Et) [36,54], [Fe(PMe$_3$)$_4$(η^2-CO_2)] [55], [Cp$'_2$Nb(CH$_2$SiMe$_3$)(η^2-CO_2)] [37], *trans*-[Mo(PMe$_3$)$_4$(η^2-CO_2)$_2$] [56] and [Cp$_2$Mo(η^2-CO_2)] [57].

Very recently, Fujita et al. [58] found evidence for charge transfer in some cobalt–CO_2 complexes by X-ray absorption near-edge spectroscopy (XANES). The XANES study of the CO_2 adducts of [Co(HMD)] (HMD = 5,6,6,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) clearly indicates significant charge transfer from Co to the bound CO_2 in both five-coordinate [Co(III)(HMD)-

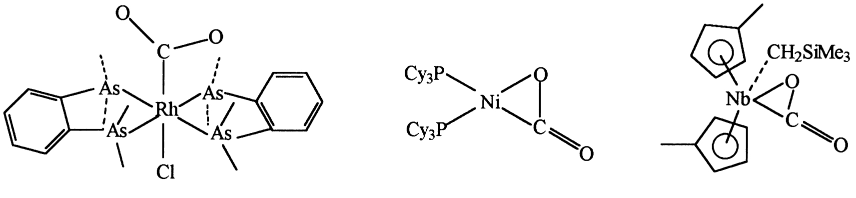


Fig. 3. Some representative examples of complexes with η^1(C) and η^2(C,O) side-on coordination modes.

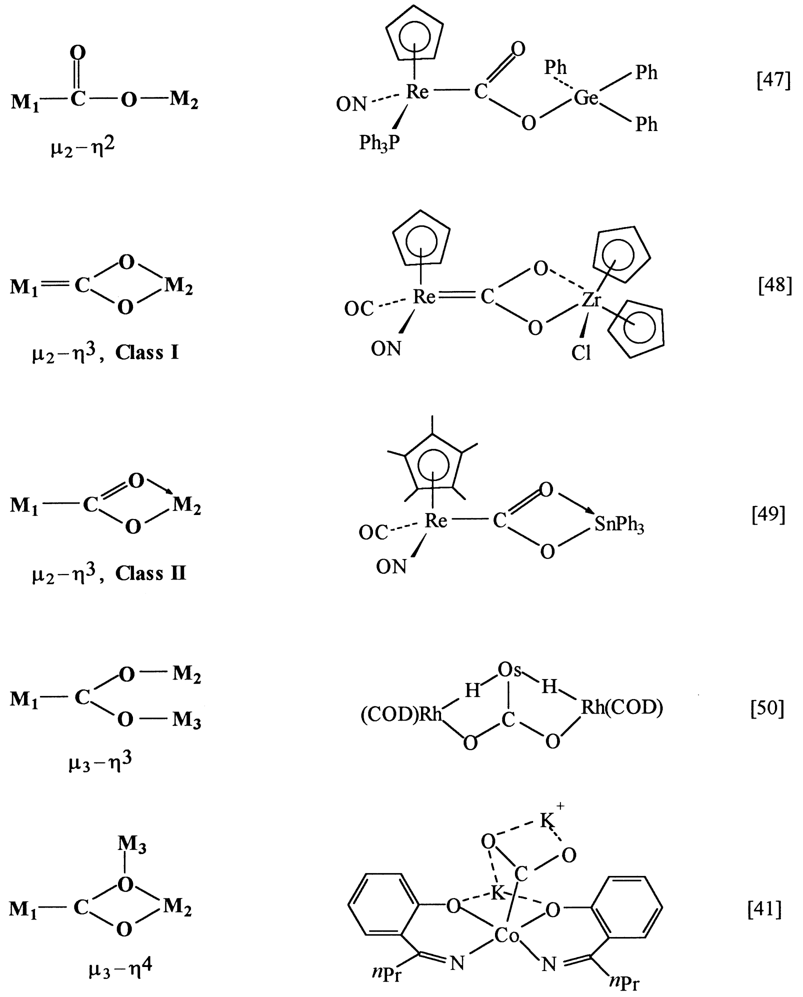
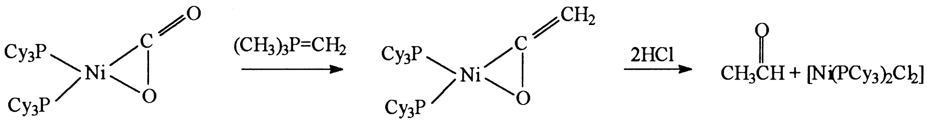


Fig. 4. Structural types and examples of CO_2 bridging complexes [46–53].

$(CO_2^{2-})]^+$ and six-coordinate $[Co(III)(HMD)(CO_2^{2-})(CH_3CN)]^+$ species. Binding of CO_2 to the cobalt through the electrophilic carbon, with the oxygens bending back in an η^1(C) bonding configuration, is the best model to account for the observed charge transfer [58].

2.2. Binding of CO_2 at two or more metal centres

CO_2 can be bound by two or more metal centres via the coordination of the carbon atom to one metal and either one or both of the oxygen atoms of the CO_2 to other metal(s). Thus, numerous complexes with bridging CO_2 ligand can be



Scheme 2.

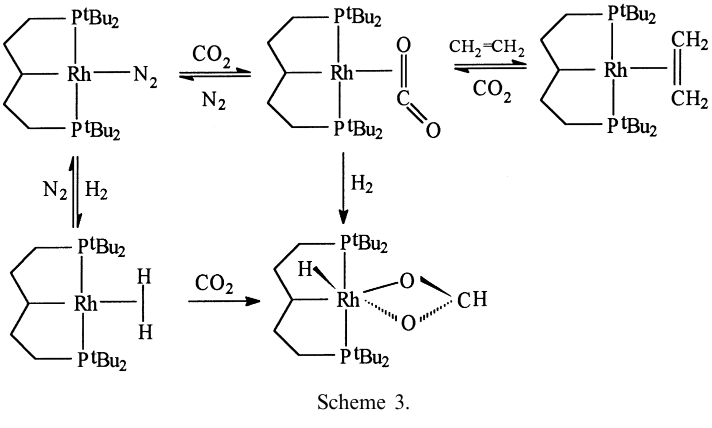
formed. The complexes with bridging CO_2 ligand can be classified according to their bonding modes [32,33], as shown in Fig. 4.

Since the synthesis and structural characterization of CO_2 bridging complexes have been comprehensively reviewed by Gibson very recently [32], this will not be repeated here. However, it is noteworthy that the activation of CO_2 by early–late transition metal complexes is of particular interest since this bifunctional activation of CO_2 by a combination of an early, oxophilic and a late, electron-rich transition metal might have great potential in successful activation of CO_2. The concept of activating CO_2 by bifunctional systems was first pioneered by Floriani and coworkers [46–48]. Some recent examples will be discussed in Section 4.6.

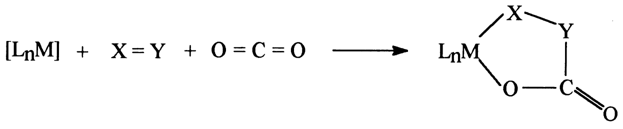
2.3. The reactivity of the coordinated CO_2 ligand

Although numerous metal–CO_2 complexes have been synthesized, the conversion of the CO_2 ligand in these complexes with suitable substrates to give organic products is much less well studied [32]. Recently, the reaction of the coordinated CO_2 ligand of the complex $[Ni(PCy_3)_2(CO_2)]$ with $(CH_3)_3P{=}CH_2$, leading to a nickel ketene complex, has been reported [59]. The reaction of the ketene complex with HCl provides $[Ni(PCy_3)_2Cl_2]$ and the organic product, acetaldehyde, as shown in Scheme 2.

The newly reported rhodium CO_2 complex [60] (see Scheme 3), prepared from the rhodium dinitrogen or ethylene complexes, can react with H_2 to form the hydrido formate complex. The hydrido formate complex can also be obtained by the reaction of the dihydrogen complex with CO_2.



Scheme 3.



Scheme 4.

3. Oxidative coupling of CO_2 with unsaturated substrates

The second route for the conversion of CO_2 into organic products is the simultaneous oxidative coupling of CO_2 and an unsaturated compound at a transition metal centre. Several reviews discussing the oxidative coupling reactions of CO_2 with unsaturated substrates have been published [16,17,27,28,61]. Due to the importance of this reaction in the conversion of CO_2 into useful organic products, a brief summary of these results and comments on recent progress is presented.

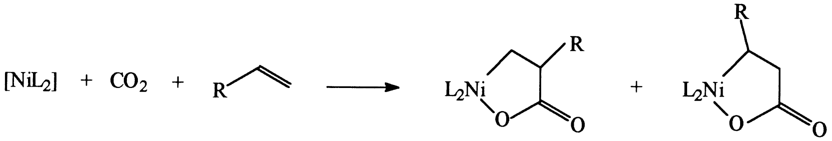
CO_2 undergoes oxidative coupling reactions with an unsaturated substrate X=Y at a metal centre [L_nM] to form the metallacycle as shown in Scheme 4.

The unsaturated compound X=Y can be a hydrocarbon (alkynes [62–65], alkenes [65–74], dienes and conjugated dienes [75–80], and cumulenes [81]), imines [27,82] or aldehydes [83,84]. The predominant transition metal complexes which mediate the coupling of CO_2 with unsaturated substrates are electron-rich Ni(0) complexes, but some other transition metals such as Ti [16,17], Mo [16,17,28], Fe [77], Pd [16,17,28] and Pt [82] are also reactive.

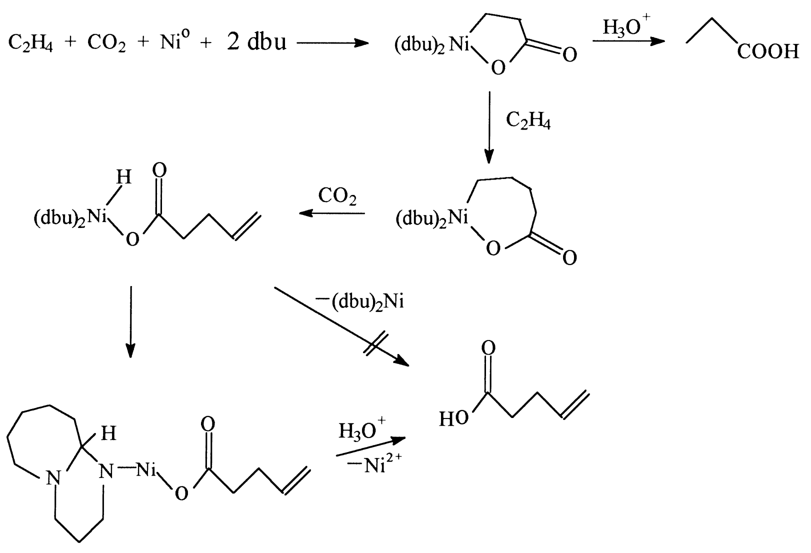
The formation of nickellacycles from CO_2 and alkenes has become the basis of an extensive organonickel-based chemistry for the carboxylation of alkenes, as shown in Schemes 5–8.

From the coupling reaction of ethylene and CO_2 with [$Ni(COD)_2$] in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (dbu), the complex [$(dbu)_2Ni\{\eta^2\text{-}CH_2CH_2C(O)O\}$] has been isolated and structurally characterized by Hoberg et al. [66]. This complex undergoes further ethylene insertion to give a seven-membered ring complex, which by subsequent β-H elimination and acid hydrolysis gives pentenoic acid, as shown in Scheme 6.

These authors [66] have also shown that the Ni–C bond in the bis-dbu complex is available for insertion reactions with compounds containing carbon–carbon double bonds: hence, various acid products could be obtained depending on the compounds and work-up conditions (see Scheme 7).

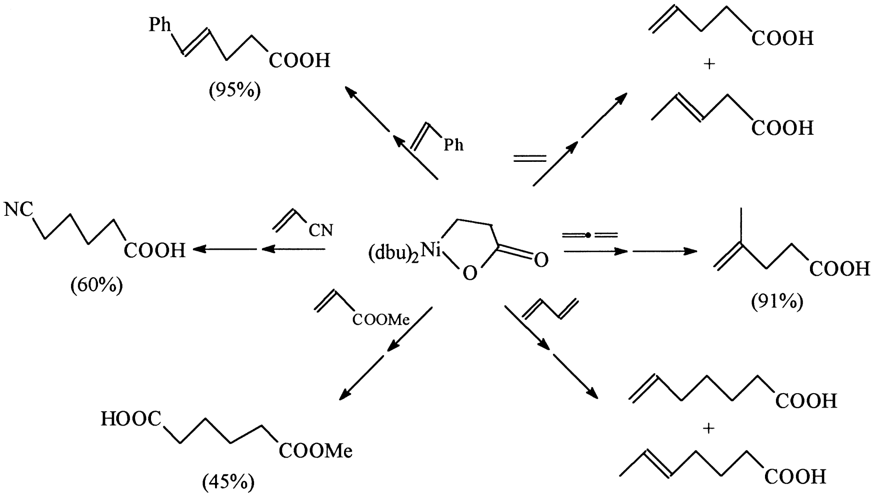


Scheme 5.

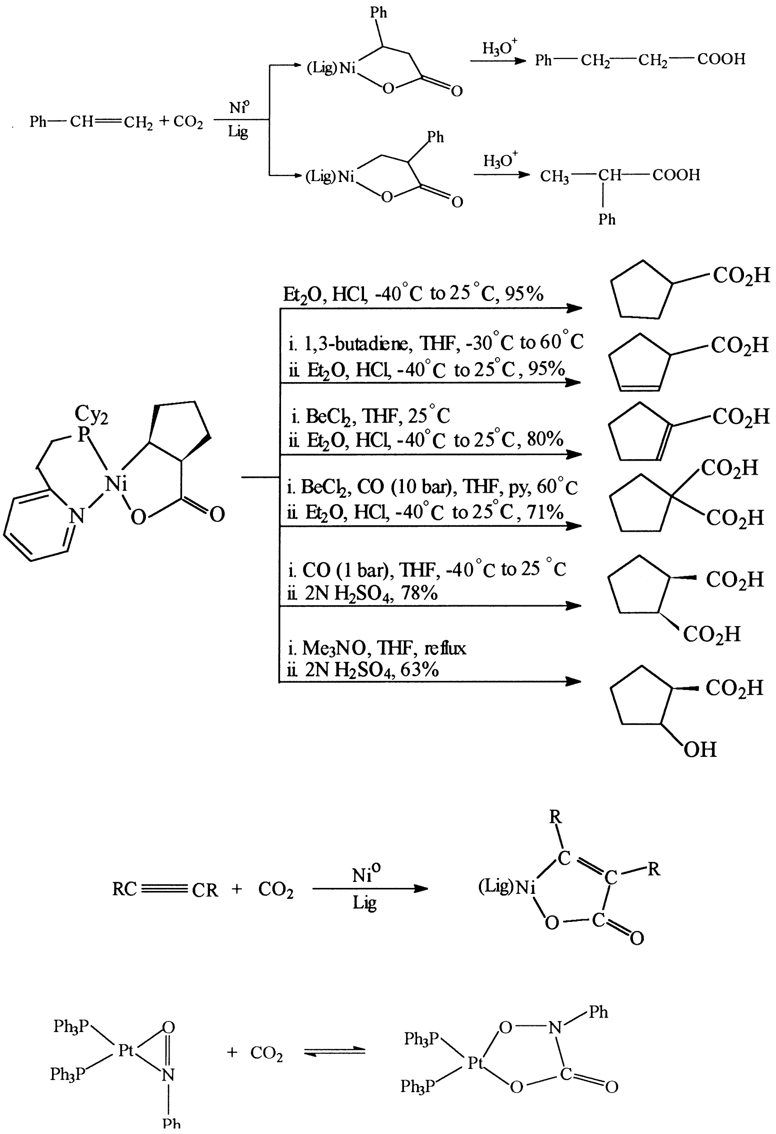


Scheme 6.

The starting nickel(0) complexes which have been used for the coupling reaction can also be [Ni(cdt)], [Ni(COD)(bipy)] or [Ni(TMEDA)(COD)]. The ligands used for stabilizing the Ni(0) species can be bipy, TMEDA, dcpe, dbu or dicyclohexyphosphinoethyl-2-pyridyl (dcpp). Depending on the starting organic substrates and work-up conditions, an extensive range of functionalized products can be obtained (see Scheme 8, for some examples [65,69,70,82]).

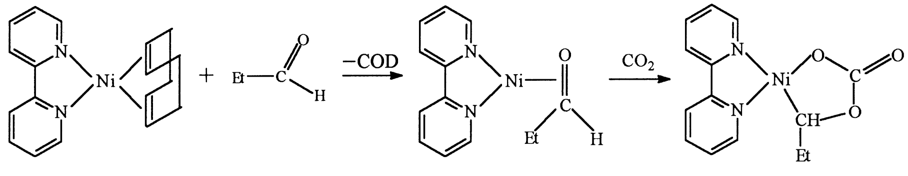


Scheme 7.

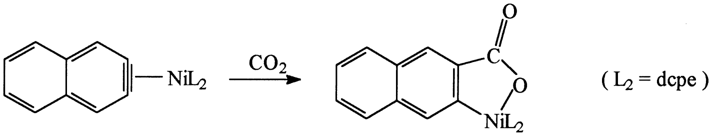


Scheme 8.

Reactions of aldehydes with CO_2 at Ni(0) centres have recently been studied by Geyer et al. [84]. A detailed kinetic analysis revealed that CO_2 does not react with [Ni(bipy)(COD)] directly but with the nickel propionaldehyde complex to form a five-membered cyclic nickel complex (Scheme 9). The reaction proceeds according to an associative mechanism, during which the CO_2 was inserted into a Ni–O bond by an oxidative coupling step.



Scheme 9.

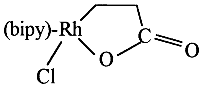


Scheme 10.

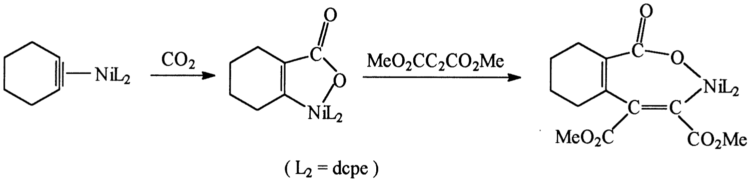
The reaction of the Ni(0) naphthalyne complex [Ni(η^2-$C_{10}H_6$)L_2] (L_2 = dcpe) with CO_2 gives the CO_2 inserted product as shown in Scheme 10 [85]. The analogous cyclohexyne complex [Ni(η^2-C_6H_8)L_2] (L_2 = dcpe) also reacts with CO_2 to give the five-membered metallacycle complex. Dimethylacetylenedicarboxylate inserts into the Ni–C σ bond of the metallacycle complex to give the seven-membered metallacycle, as shown in Scheme 11 [86].

The tantalum–benzyne complex [Cp*Ta(η^4-buta-1,3-diene)(η^2-C_6H_4)] has similarly recently been reported to react with CO_2 to give a five-membered metallacycle complex [87].

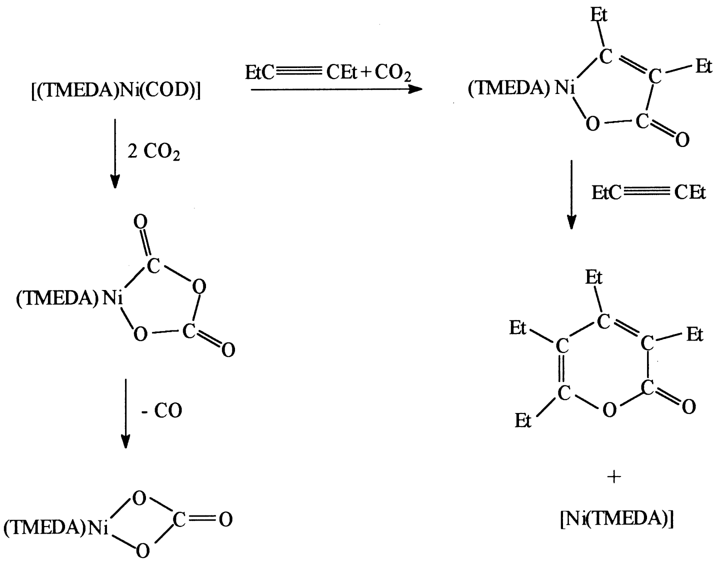
The rhodium ethylene complex [Rh(bipy)(C_2H_4)Cl] reacts slowly with CO_2 at r.t. in THF to give a brown solid, which has been postulated as the metallacycle shown below [88].



Immobilized palladium catalysts, prepared from [Pd(η^5-Cp)(η^3-C_3H_5)] and polymer-bound phosphines, are found to catalyze C–C coupling reactions of CO_2 and 1,3-butadiene to produce δ-lactone 2-ethylidene-6-heptene-5-olid. C_{17} carboxylic esters can also be obtained using catalysts with ligands prepared from chloromethylated polystyrene and $LiPPh_2$ [89].



Scheme 11.



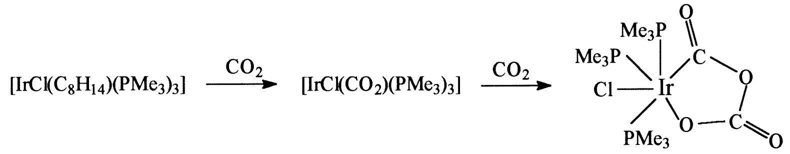
Scheme 12.

Recent studies of the reaction of hex-3-yne with CO_2 in the presence of [Ni(TMEDA)(COD)] have revealed that a competing reaction in the catalytic cyclo-oligomerization of hex-3-yne and CO_2 is the formation of carbon monoxide and [Ni(TMEDA)(CO_3)] [90]. These authors have suggested that the reduction of CO_2 to CO probably proceeds via an intermediate in which two molecules of CO_2 are coupled head-to-tail to form a metallacycle as shown in Scheme 12. The head-to-tail coupling of two molecules of CO_2 has been observed for an iridium complex, as shown in Scheme 13 [91].

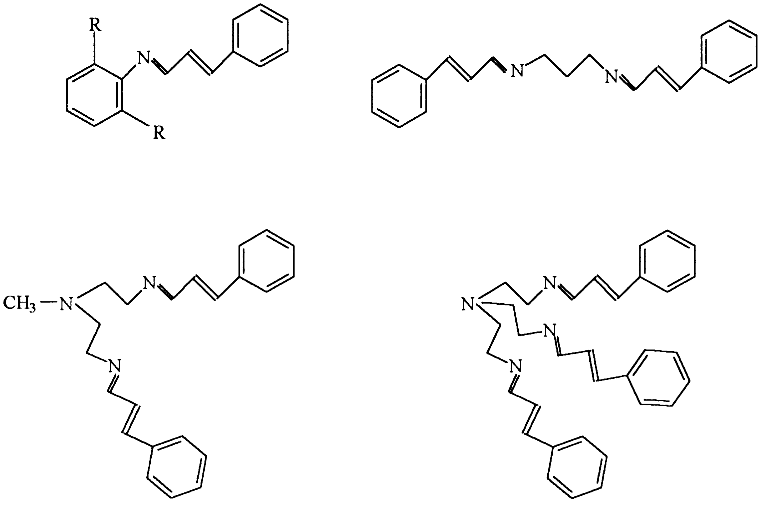
More recently, Walther et al. [92] have reported that the coupling of CO_2 with 1-azadiene type ligands (see Scheme 14) of the complexes $[Ni(1\text{-azadiene})_n]_2$ forms nickellacyclic carbamate complexes. In these carbamate complexes, CO_2 is activated and is able to carboxylate acetophenone to yield benzoylic acid upon protolysis.

The oxidative coupling of CO_2 with the metal carbon triple (M≡C) bond in some carbyne complexes has also been reported [93,94]. Either the carbon or one oxygen atom of a CO_2 molecule could bind to the metal depending on the nature of the metal of the carbyne complex. Fisher et al. [93] have reported the reaction of the anionic carbyne complexes with CO_2 to afford the oxygen-bound metallacycle as shown in Scheme 15.

The reaction of CO_2 with a ruthenium carbyne complex, however, affords the carbon-bound metallacycle as shown in Scheme 16 [94]. The above mentioned coupling reactions serve as unique examples for the oxidative coupling of CO_2 at a transition metal centre.



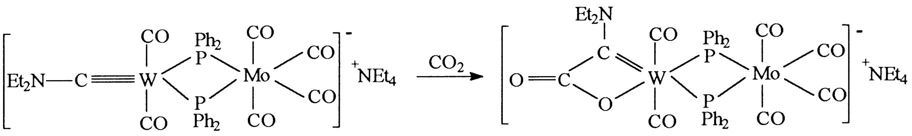
Scheme 13.



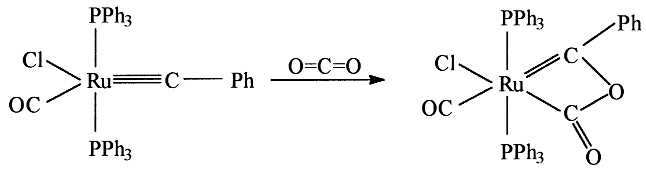
Scheme 14.

4. Insertion reactions of CO_2

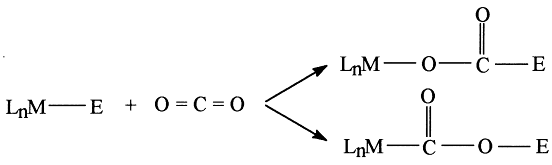
The insertion of CO_2 into a preformed metal–element (M–E) bond is of great industrial importance. There are mainly seven types of CO_2 insertion reactions reported so far, i.e. the insertion of CO_2 into the M–E bond (where E = C, H, N, O, P, Si or other metal). Two possible products could be obtained from the insertion of CO_2 into the M–E bond, as shown in Scheme 17.



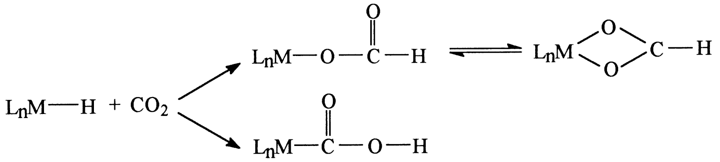
Scheme 15.



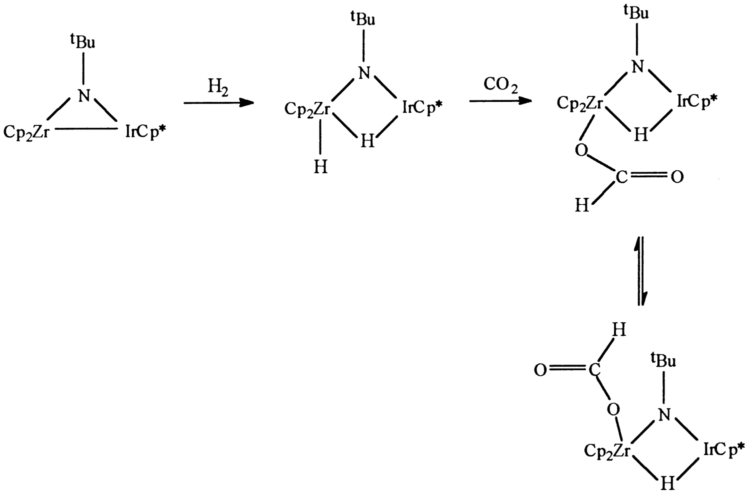
Scheme 16



Scheme 17

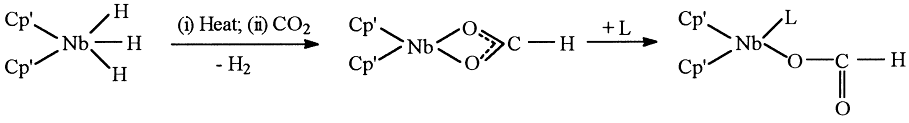


Scheme 18.



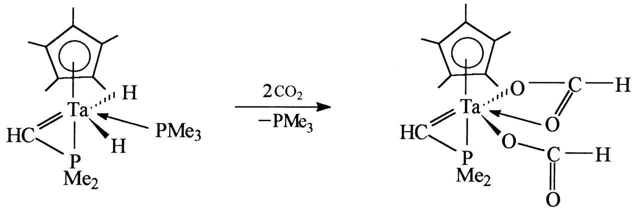
Scheme 19

There are several reviews on the insertion of CO_2 into the M–E bond in the literature [22,27–31], which have covered the results in this area up to 1994. Only the more recent developments in this area will be summarized. If there is no current example of a particular type of reaction, examples of earlier studies may be provided. This is to show the wide applications of the insertion reactions in

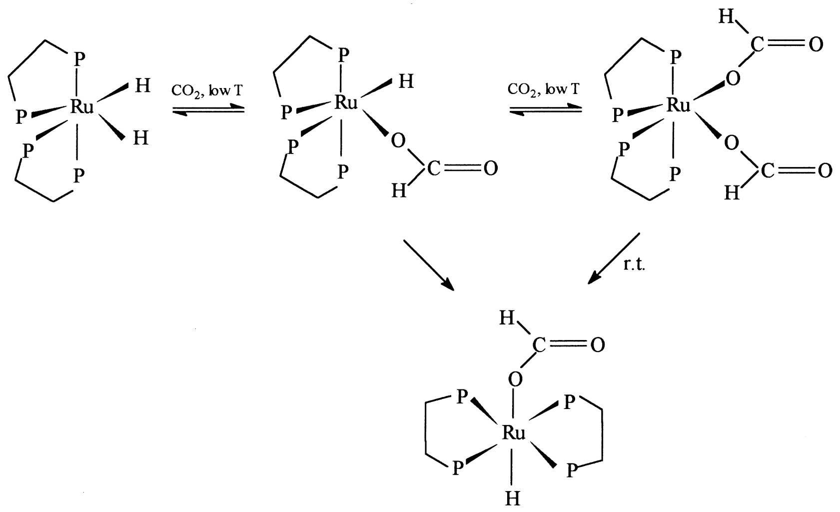


Cp' = η^5-$C_5H_4SiMe_3$

Scheme 20



Scheme 21



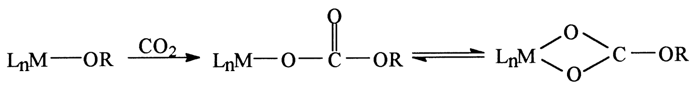
Scheme 22

activation of CO_2. Only the successfully demonstrated examples of CO_2 insertion reactions will be included and attempted, but unsuccessful results will be excluded except in cases where a comparison between the reactivity of related complexes is made.

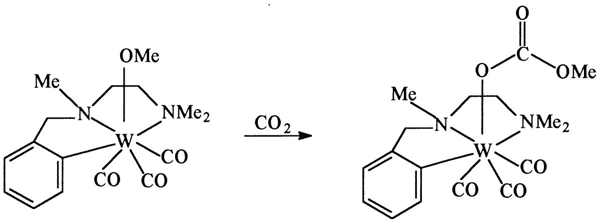
4.1. Insertion of CO_2 into the M–H bond

The insertion of CO_2 into the M–H bond can lead either to a formate complex or a metallocarboxylic acid complex as shown in Scheme 18.

The first step in the reaction is the nucleophilic attack of the $L_nM^{\delta+}-H^{\delta-}$ at the electrophilic carbon of CO_2 to form the polar transition states **IV** and **V**. This process requires a rather polar $M^{\delta+}-H^{\delta-}$ bond [95].

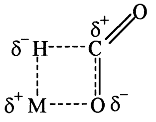


Scheme 23

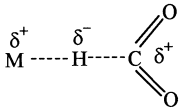


VI **VII**

Scheme 24



IV

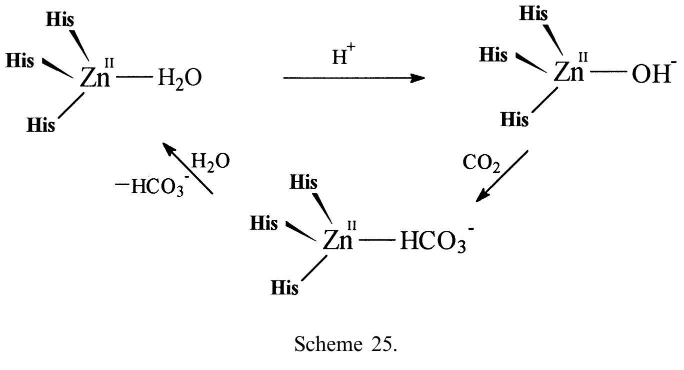


V

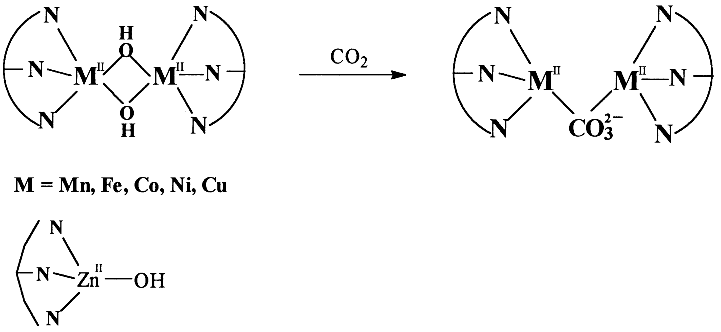
Rearrangement of the intermediates **IV** and **V** generally affords the formate complex, while the metallocarboxylic acid complex is a much less common product. In fact, to the best of our knowledge, there are no examples of stable metallacarboxylic acids obtained directly from CO_2 insertion into M–H bonds. A new cobaloxime carboxylic acid complex $[Co(dmgH)_2(H_2O)(CO_2H)]$ ($dmgH_2 =$ dimethylglyoxime) with a Co–C bond, however, has been prepared by the reaction of $[Co(dmgH)_2(H_2O)_2]$ with CO_2 [96].

Earlier studies have shown that the rates of insertion of CO_2 into the M–H bond of the anionic complexes $[MH(CO)_4L]^-$ (M = Cr, Mo, W; L = CO, PR_3) are dependent on the nucleophilicity of these species, which is affected by the donating ability of the ligand L [97].

The reaction of $[\{CpTi(\mu\text{-}H)\}_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]$ with CO_2 in toluene leads to the formation of the bis(formato) complex $[\{CpTi(\mu\text{-}\eta^1\text{-}OC(O)H)\}_2(C_{10}H_8)]$, which has been characterized by X-ray structural analysis to contain two monodendate bridging formates [98].



Scheme 25.



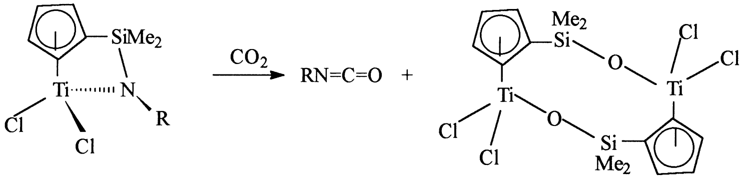
Scheme 26.

The heterobinuclear complex [$Cp_2Zr(H)(\mu\text{-}H)(\mu\text{-}N^tBu)IrCp^*$] reacts rapidly with CO_2, leading to the formation of two diastereomeric heterobimetallic formate complexes, as shown in Scheme 19 [99]. It has also been found that CO_2 inserts selectively into the terminal Zr–H bond to afford the terminal formate complex, with no evidence of insertion into the bridging hydride. The reaction of the formate complex with PhLi leads to lithium formate in 30% yield and regenerates [$Cp_2Zr(\mu\text{-}N^tBu)IrCp^*$].

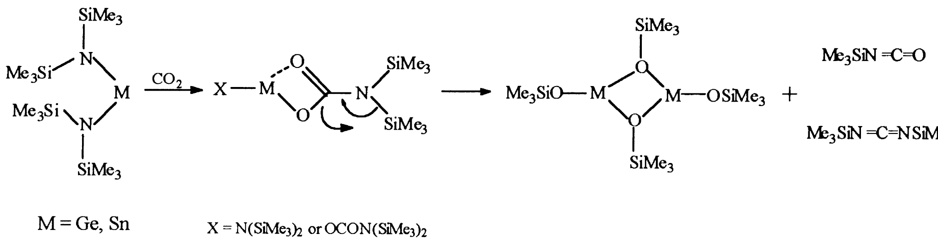
The complex [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$] reacts with CO_2 at 60°C in THF to give the formate complex [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\eta^2\text{-}OC(O)H\}$] in 95% yield [100]. The reaction of the η^2-(O,O′) formate complex with different π-acids or heterocumulene molecules results in opening of the bidendate formate ligand, giving rise to the monodentate formate-containing complexes [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\eta^1\text{-}OC(O)H\}L$] ($L = CS_2$, CO or 2,6-$Me_2C_6H_3NC$) as a consequence of the coordination of the incoming ligand (Scheme 20).

The complex [$(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$] has been reported to undergo insertion of two equivalents of CO_2 in petroleum ether at r.t. to afford the bis(formato) complex [$(\eta^5\text{-}C_5Me_5)Ta(\eta^1\text{-}OC(O)H)(\eta^2\text{-}(O,O')OC(O)H)(\eta^2\text{-}CHPMe_2)$], as shown in Scheme 21 [101].

The insertion of CO_2 into the Mn–H bond of the complexes [$Mn(NO)_2(L)_2H$] ($L = PMe_3$, PEt_3) in toluene at room temperature gives the η^1-formate complexes [$Mn(NO)_2(L)_2\{OC(O)H\}$] ($L = PMe_3$, PEt_3) in high yields (94–98%) [102]. The complexes [$Mn(CO)_3(L)_2H$] ($L = PMe_3$, PEt_3) do not react with CO_2 even under more vigorous reaction conditions. This is attributed to the nucleophilicity of the



Scheme 27.



Scheme 28.

$$R_2NH + CO_2 \rightleftharpoons R_2NCOOH \xrightarrow[-\ HNR_2]{[L_nM\text{-}NR_2]} [L_nM\text{-}O_2CNR_2]$$

Scheme 29.

nitrosyl-substituted complexes for the reaction with CO_2, while the carbonyl derivatives have not attained sufficient nucleophilicity for the same reaction [102].

The reactions of the complexes $[ReH(CO)_{5-n}(PMe_3)_n]$ ($n = 2, 3, 4$) with CO_2 have also been reported. The complex with $n = 2$ does not react with CO_2 even at elevated temperatures. The complexes with $n = 3$ and 4 react with CO_2 (1 bar) in toluene at r.t., yielding the η^1-formate complexes $[Re\{OC(O)H\}(CO)(L)_n(PMe_3)_3]$ ($L = CO, PMe_3$) in high yield (98%). This is proposed to be due to the increased nucleophilicity of the complexes with $n = 3$ and 4 compared with the complex with $n = 2$ [103].

The η^1-formate complex *fac*-$[Re(bipy)(CO)_3\{OC(O)H\}]$ has been prepared by irradiation of the complex *fac*-$[Re(bipy)(CO)_3(PPh_3)]^+$ in the presence of triethanolamine and CO_2. The formate complex *fac*-$[Re(bipy)(CO)_3\{OC(O)H\}]$ was thought to be the 'real' photocatalyst for the reduction of CO_2 to CO [104]. However, in a subsequent paper, the same research group reported that the reduction of CO_2 to CO is more efficiently photocatalyzed by *fac*-$[Re(bipy)(CO)_3(PR_3)]^+$ [$PR_3 = P(OEt)_3$ and $P(O^iPr)_3$] than by the formate complex [105].

The reaction of *cis*-$[Ru(dmpe)_2H_2]$ with CO_2 has been investigated [106]. Addition of CO_2 at 20°C results in the formation of two formate complexes: the major product is the *trans* formate hydride, *trans*-$[Ru(dmpe)_2H\{OC(O)H\}]$, while the minor species is the bis(formate) complex *cis*-$[Ru(dmpe)_2\{OC(O)H\}_2]$. When the addition of CO_2 is performed at -78°C, both the bis(formate) and the *cis*-formate hydride, *cis*-$[Ru(dmpe)_2H\{OC(O)H\}]$, are observed (see Scheme 22). The crystal structure of the complex *trans*-$[Ru(dmpe)_2H\{OC(O)H\}]$ has been determined [106].

$$[1,2\text{-}M_2(NMe_2)_4(PR_2)_2] + CO_2 \longrightarrow [M_2(O_2CNMe_2)_2(O_2CPR_2)_2(NMe_2)_2]$$

M = Mo, W; R = ^tBu

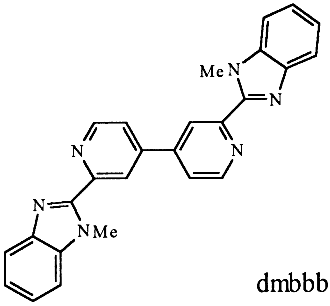
Scheme 30.

Reaction of [Cp*Ru(PCy$_3$)Cl] with 1–2 atm of CO$_2$ in the presence of NaBH$_4$ initially forms the formate complex [Cp*Ru(PCy$_3$)(η^2-O$_2$CH)] which is gradually converted into formic acid and [Cp*Ru(PCy$_3$)(CO)H)] [107]. The reaction of [Ru{MeSi(CH$_2$PMe$_2$)$_3$}(PMe$_3$)H(Ar)] with CO$_2$ does not yield a formate complex, but yields the carbonate complex [Ru{MeSi(CH$_2$PMe$_2$)$_3$}(PMe$_3$)(CO$_3$)] instead [108].

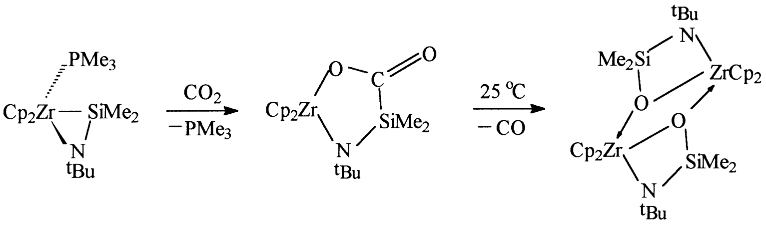
It is worth highlighting the recent developments in the hydrogenation of CO$_2$ [18,20,21] by Ru [109–116] and Rh [117–126] catalysts. The ruthenium complexes [RuH$_2$(PMe$_3$)$_4$] and [RuCl$_2$(PMe$_3$)$_4$] have been found to be very reactive catalysts for the hydrogenation of CO$_2$ in a supercritical mixture of CO$_2$ and H$_2$, for the formation of formic acid, formate esters and DMF, in the presence of NEt$_3$, alcohols or HNMe$_2$ [18,109–112]. A total yield of 420000 mol DMF per mol catalyst (TOF = 6000 h^{-1}) has been reported by Jessop et al. [111,112] for the reaction of H$_2$, CO$_2$ and HNMe$_2$ catalyzed by [RuCl$_2$(PMe$_3$)$_4$]. More recently, Baiker and coworkers reported the solvent-free synthesis of DMF and of methyl formate by using highly reactive ruthenium complexes with bidentate phosphine ligands [113]. The synthesis of DMF proceeds very rapidly at 100°C with up to 99% yield and always with 100% selectivity to DMF. An extremely high turnover frequency (TOF) of 360000 h^{-1} in DMF synthesis is obtained using the [RuCl$_2$(dppe)$_2$] catalyst [113].

Baiker and coworkers [114] have also prepared a hybrid immobilized ruthenium complex catalyst using the sol–gel process. The catalyst shows high activity in the synthesis of DMF from H$_2$, CO$_2$ and HNMe$_2$ under supercritical conditions. The turnover numbers obtained with the Ru catalyst markedly exceed previously reported values for heterogeneous catalysts, but are lower than those of the homogeneous catalyst [RuCl$_2$(PMe$_3$)$_4$] [111,112].

Electrochemical reduction of CO$_2$ to CO by *trans*-(Cl) and *cis*-(Cl)-[Ru(bipy)(CO)$_2$Cl$_2$], *cis*-(CO)-[Ru(bipy)(CO)$_2$(CO$_2$Me)Cl] and their derivatives has been reported [115]. Tanaka and coworkers have reported that electrochemical reduction of CO$_2$ catalyzed by mono- and dinuclear complexes [Ru(bipy)$_2$(dmbbbpy)][(PF$_6$)$_2$] and [Ru(bipy)$_2$(dmbbbpy)Ru(bipy)$_2$][(PF$_6$)$_4$] selectively produces formic acid and C$_2$O$_4^{2-}$, depending on the presence and the absence of water, respectively, in acetonitrile [116].



dmbbbpy



Scheme 31.

The authors suggested that two-electron reduction of the mono- and dinuclear complexes causes dechelation of dmbbbpy, the resultant five-coordinate Ru and monodentate dmbbbpy$^-$ may provide two binding sites for an attack of CO_2, which would facilitate a coupling reaction of CO_2 affording oxalate [116]. This work has demonstrated the effect of water in determining the product selectivity. In order to obtain oxalate, an anhydrous condition is essential. Catalytic production of oxalate selectively by the reduction of CO_2 using $[(CpM)_3(\mu_3\text{-}S)_2]^{2+}$ (M = Co, Rh and Ir) has been reported before [117].

The effects of ligands on the catalytic hydrogenation of CO_2 to formic acid using in situ catalysts formed from $[Rh(COD)(\mu\text{-}Cl)]_2$ and monodentate and bidentate phosphorus ligands have been studied [118,119]. The mechanism of the Rh-catalyzed hydrogenation of CO_2 to formic acid has recently been investigated by kinetic and theoretical studies [120–122]. The synthesis of formic acid using water-soluble rhodium catalysts with sulfonated phosphanes has been reported by Gassner and Leitner [123]. The reaction conditions (water–amine mixtures) are similar to those used for separation of CO_2 from flue gases.

A series of complexes of the type $[RhP_2(hfacac)]$ (P_2 = bidentate chelating phosphane, hfacac = hexafluoroacetylacetonate) has been investigated for CO_2 hydrogenation to formic acid. It is found that ^{103}Rh NMR shifts of these complexes in solution are mainly determined by the P–Rh–P angles as obtained from solid-state structures, and are correlated to the catalytic activity of these complexes [124,125]. The accessible molecular surface (AMS) model has been introduced as a new approach for the description of steric ligand effects in homogeneous catalysis, particularly for the rhodium-catalyzed hydrogenation of CO_2 [125].

A cationic rhodium complex $[Rh(\eta^2\text{-}(O,P)Cy_2PCH_2CH_2OCH_3)_2][BPh_4]$ is an efficient catalyst for the hydrogenation of CO_2 to produce formic acid. The addition of triethylamine and water, respectively, is crucial for the synthesis of formic acid in high yields [126].

4.2. Insertion of CO_2 into the M–O bond

A variety of transition metal complexes with M–OR groups undergo insertion reactions with CO_2. If R is an organic moiety, alkyl or aryl carbonate complexes are formed; if R is hydrogen, hydrogen carbonate species are obtained [22,27–31] (see Scheme 23).

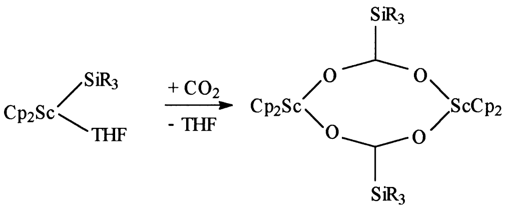
The reaction of the methoxide tungsten complex **[VI]** (see Scheme 24) with an atmosphere of CO_2 in CH_2Cl_2 at 40°C for ca. 72 h results in the formation of the η^1-carbonate complex **[VII]**, isolated as an air-stable yellow solid in 24% yield. Regeneration of **[VI]** when either a THF solution or a solid sample of **[VII]** is placed under vacuum demonstrates the reversible nature of this CO_2 insertion [127].

Although the insertion of CO_2 into the W–O bond of $[Et_4N][W(CO)_5OPh]$ proceeds quickly at ambient temperature and atmospheric pressure to afford the corresponding phenyl carbonate complex $[Et_4N][W(CO)_5\{O_2COPh\}]$ [128], the complex $[Et_4N][W(CO)_4(PPh_2Me)OPh]$ reacts slowly with CO_2, compared with $[Et_4N][W(CO)_5OPh]$ [129]. The aryloxide complex $[Et_4N][W(CO)_5\{O\text{-}2,6\text{-}Ph_2\text{–}C_6H_3\}]$ is not reactive to CO_2 even under more vigorous conditions [129]. This lack of CO_2 reactivity is proposed to be due to the steric interference of the bulky ligand. The heterobinuclear complex $[Et_4N][W(CO)_5OPh\{Cr(CO)_3\}]$ is also not reactive to CO_2 [130].

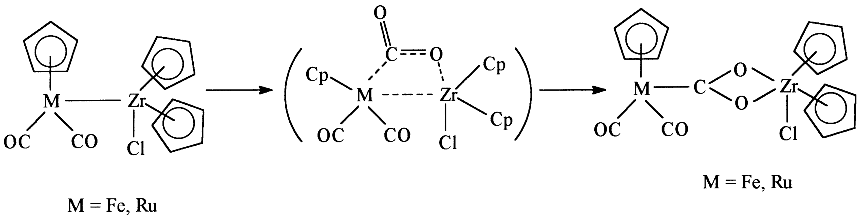
The Mn(I) and Re(I) alkoxide complexes *fac*-$[M(CO)_3(P\text{–}P)(OR)]$ (M = Mn or Re; P–P = dppe or dppp; R = CH_3, C_2H_5 or CF_3CH_2) react readily at r.t. with CO_2 by insertion of CO_2 into the M–O bond, giving rise to the corresponding carbonate complexes *fac*-$[M(CO)_3(P\text{–}P)\{O_2COR\}]$ [131]. Benzene solutions of the alkoxide complexes can even absorb CO_2 from the atmosphere. It is also found that the insertion and deinsertion of CO_2 from these complexes are reversible under mild conditions. The crystal structure of the carbonate complex *fac*-$[M(CO)_3(dppe)\{O_2COCH_3\}]$ has been determined [131].

The fixation of CO_2 by hydroxo metal complexes to afford the metal bicarbonate or carbonate species is relevant to the fixation of CO_2 by some metalloenzymes. The enzyme, whose function is apparently related directly to the fixation of CO_2 by hydroxo metal complexes, is carbonic anhydrase [132]. The proposed mechanism for CO_2 hydration by the carbonic anhydrase is shown in Scheme 25 [132].

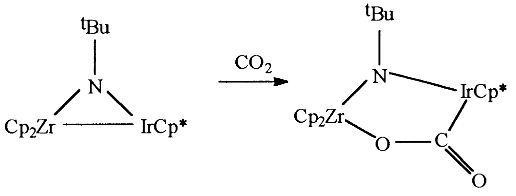
A variety of zinc-containing carbonic anhydrase model systems have been described [133]. A series of hydroxo complexes of the first-row divalent metal ions (Mn, Fe, Co, Ni, Cu, Zn), containing the ligand $HB(3,5\text{-}{}^iPr_2pz)_3$ [hydrotris(3,5-diisopropyl-1-pyrazolyl)-borate] as shown in Scheme 26, are found to react with CO_2 to afford μ-carbonato-dinuclear complexes, of which the molecular structures have been determined [133]. The zinc complex $[Tp^{tBu,Me}Zn\text{–}OH]$ ($[Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate] reacts with CO_2, forming the unstable bicarbonate complex $[Tp^{tBu,Me}ZnOC(O)OH]$ in solution from which the dinuclear



Scheme 32.



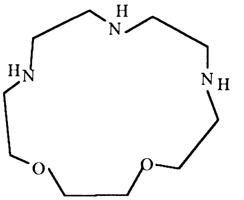
Scheme 33.



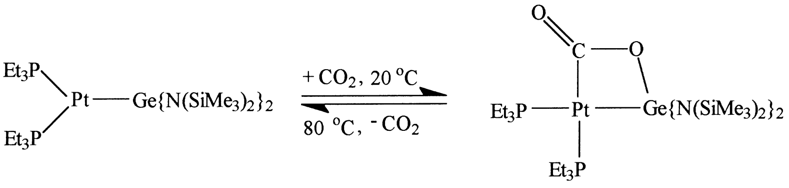
Scheme 34.

carbonate complex [$Tp^{tBu,Me}ZnOC(O)OZnTp^{tBu,Me}$] crystallizes [134]. The zinc hydroxide complexes [$Tp^{Cum,Me}Zn{-}OH$] [$Tp^{Cum,Me}$ = hydrotris(3-cumenyl-5-methylpyrazolyl)borate] and [$Tp^{tBu,Me}Zn{-}OH$] can be converted to the alkyl carbonate complexes [$Tp^{*}Zn{-}OCO_2R$] by reaction with alcohol and CO_2 or dialkyl dicarbonates. The zinc complexes catalyze the formation of diethyl carbonate from ethanol and CO_2 [135].

Solutions containing the Cu(II) and Zn(II) complexes with the macrocyclic ligand L (L = [15]aneN_3O_2) rapidly absorb atmospheric CO_2 to give the carbonate bridged trinuclear [$\{ZnL\}_3(\mu_3\text{-}CO_3)][(ClO_4)_4]$ and [$\{CuL\}_3(\mu_3\text{-}CO_3)][(ClO_4)_4]$ complexes [136]. The crystal structures of both complexes have been reported. The process of CO_2 fixation is believed to be due to the presence of the hydroxo species $[M(II)L(OH)]^+$ (M = Zn, Cu) [136].



[15]aneN_3O_2



Scheme 35.

4.3. Insertion of CO_2 into the M–N bond

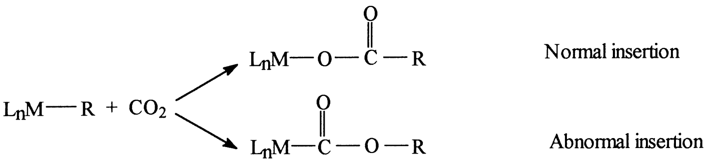
The insertion of CO_2 into the M–N bond has been investigated not only for transition metals [22,27–31], but also for the Group 14 elements Ge and Sn [137].

The complexes $[Cp^*Ti(NR_2)_3]$ (R = Me or Et) react rapidly with CO_2 in toluene to give the corresponding insertion products $[Cp^*Ti(\eta^2\text{-}O_2CNR_2)_3]$ (R = Me or Et) [138]. Hydrolysis takes place if the solutions of these complexes are exposed to wet air, which leads to the formation of the complexes $[\{Cp^*Ti(\eta^2\text{-}O_2CNR_2)\}_2(\mu\text{-}O)_2]$ (R = Me or Et). The structure of the complex where R = ethyl has been determined [138].

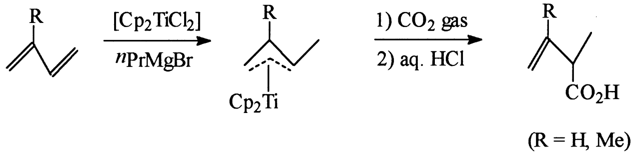
A comparative study for the insertion of CO_2 into W–C, W–N, and W–O bonds has been carried out for three related complexes $[Cp^*W(NO)(NHCMe_3)(CH_2CMe_3)]$, $[Cp^*W(NO)(NHCMe_3)(OCMe_3)]$ and $[Cp^*W(NO)(OCMe_3)(CH_2CMe_3)]$ [139]. The only compound that reacts with CO_2 to give the CO_2-inserted product $[Cp^*W(NO)(\eta^2\text{-}O_2CNHCMe_3)(CH_2CMe_3)]$ is the W–N bond-containing complex $[Cp^*W(NO)(NHCMe_3)(CH_2CMe_3)]$. This study shows that the more nucleophilic amidonitrogen is the preferential site of CO_2 insertion.

The reaction of the complexes $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NR)Cl_2]$ (R = ^{t}Bu or CHMePh) with CO_2 leads to their conversion into the oxo derivative $[Ti(\mu\text{-}\eta^5\text{-}C_5H_4SiMe_2O)Cl_2]_2$ with elimination of the alkyl isocyanates O=C=NR (R = ^{t}Bu or CHMePh) as organic products (see Scheme 27). This is believed to be due to a metathesis process between CO_2 and the M–N bond (which is of partial double-bond character) [140].

Other examples of the metathesis between CO_2 and the M–N bond are the reactions of $[M\{N(SiMe_3)_2\}_2]$ (M = Ge and Sn) with CO_2 to give $[M\{OSiMe_3)_2\}_2]$, $Me_3SiN{=}C{=}O$ and $Me_3SiN{=}C{=}NSiMe_3$ [137]. The mechanism by which the metathesis process occurs is proposed as the insertion of CO_2 into the corresponding M–NR_2 bonds, as shown in Scheme 28. Metathetical exchange between CO_2 and the tin(II) dimer, $[Sn\{N(SiMe_3)_2\}(\mu\text{-}O^tBu)]_2$ produces two new heteroleptic tin(II) dimers, $[Sn\{N(SiMe_3)_2\}(\mu\text{-}O^tBu)_2Sn(OSiMe_3)]$ and $[Sn(OSiMe_3)(\mu\text{-}O^tBu)]_2$ [141]. The inser-



Scheme 36.



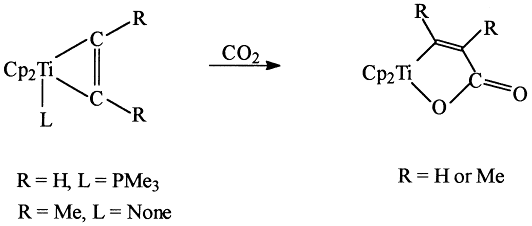
Scheme 37.

tion of CO_2 into the Pd–N bond of *trans*-$[PdPh(PMe_3)_2(NHPh)]$ gives *trans*-$[PdPh(PMe_3)_2(O_2CNHPh)]$ [142].

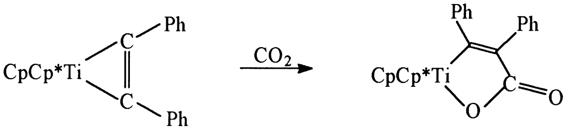
The dialkyl carbamato complexes $[M(O_2CNR_2)_n]$ ($M = Nb$ or Ta, $R = Et$, $n = 5$; $M = Nb$, $R = Et$ or ^iPr, $n = 4$) have been prepared from the corresponding metal chlorides with CO_2 and HNR_2 in toluene [143]. The reaction of $[Pd(\eta^3\text{-allyl})Me(PPh_3)]$ with diethylamine under an atmosphere of CO_2 has been reported to give a dinuclear complex $[\{Pd(PPh_3)\}_2(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu\text{-}O_2CNEt_2)]$ in 63% yield [144,145]. The dimethyl complexes $[PdMe_2L_2]$ (L = tertiary phosphine) react with CO_2 and dialkylamines HNRR′ (R, R′ = H, alkyl and phenyl) to give the corresponding carbamate complexes $[PdMe(O_2CNRR')L_2]$ [146]. These reactions may be better regarded as ligand substitutions rather than CO_2 insertions because the formation of the carbamate complexes may go via the routes shown in Scheme 29 [28].

4.4. Insertion of CO_2 into the M–P bond

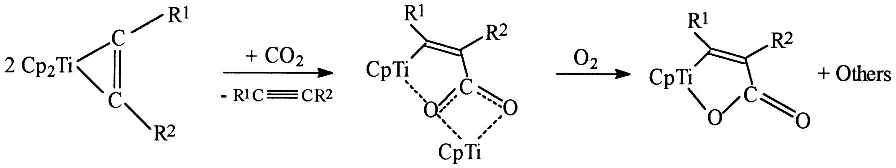
Only two examples for the insertion of CO_2 into an M–P bond are available [147,148]. The insertion of CO_2 into both the M–N and the M–P bonds of the complexes $[1,2\text{-}M_2(NMe_2)_4(P^tBu_2)_2]$ (M = Mo and W) initially yields $[1,2\text{-}M_2(O_2CNMe_2)_2(O_2CP^tBu_2)_2(NMe_2)_2]$ (M = Mo and W) [147,148]. The molybdenum compound is labile to ligand exchange reactions in solution to yield



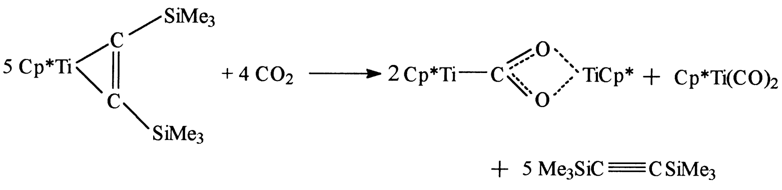
Scheme 38.



Scheme 39



Scheme 40.



Scheme 41.

$[Mo_2(O_2CP^tBu_2)_4]\cdot 2C_6H_6$ a compound having a Mo–Mo quadruple bond supported by a paddle-wheel arrangement of four phosphinocarboxylate ligands which support the Mo–Mo bond [147,148] (see Scheme 30).

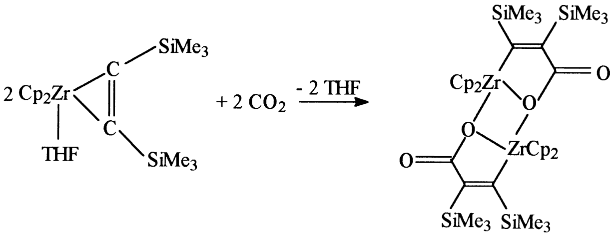
4.5. Insertion of CO_2 into the M–Si bond

The insertion of CO_2 into the Zr–Si bond of $[Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)]$ has been observed at low temperature (using $^{13}CO_2$) leading to the formation of cyclo-$[Cp_2ZrOC({=}O)SiMe_2N^tBu]$, which decomposes at 25°C to give CO and the dimerization product as shown in Scheme 31 [149].

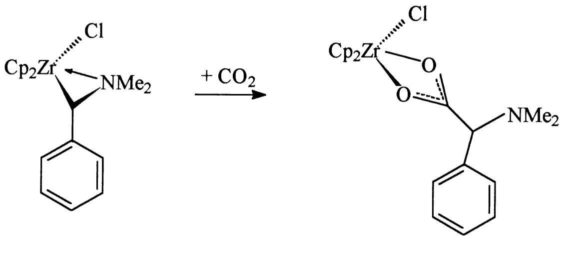
The insertion of CO_2 into the Sc–Si bond of $[Cp_2Sc(SiR_3)(THF)]$ $[R = (SiMe_3)_3$ and $^tBuPh_2]$ occurs readily to form the dimeric silanecarboxylate complexes $[Cp_2Sc(\mu\text{-}O_2CSiR_3)]_2$. The crystal structure of the complex where $R = SiMe_3$ has been reported [150] (see Scheme 32).

4.6. Insertion of CO_2 into the metal–metal (M–M') bond

Activation of CO_2 by simultaneous interaction with electron-rich and electron-



Scheme 42.



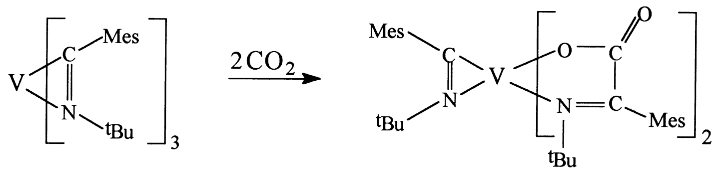
VIII **IX**

Scheme 43.

deficient metal centres has been of continuous interest since the concept of bifunctional CO_2 activation was first introduced by Floriani and coworkers in 1974 [46–48]. Recently, Cutler and coworkers [151] have shown the first examples of direct insertion of CO_2 into the early–late transition metal bond. The insertion of CO_2 into the M–Zr bond (M = Fe, Ru) of $[Cp(CO)_2M-Zr(Cl)Cp_2]$, forming the μ-η^1(C):η^2(O,O′) compounds $[Cp(CO)_2M-CO_2-Zr(Cl)Cp_2]$, may involve a bifunctional CO_2 activation step, as shown in Scheme 33 [151].

A series of CO_2-bridged heterobimetallic complexes of the type $[LM-CO_2-L'M']$ are known, although most of them have been prepared by other routes [28,32,152]. Recently, Bergman and coworkers [99] have reported another direct insertion of CO_2 into an M–M′ bond, namely the Ir–Zr bond of the complex $[Cp_2Zr(\mu\text{-}N^tBu)IrCp^*]$, to give the unique heterobimetallic complex $[Cp_2Zr(\mu\text{-}N^tBu)\{\mu\text{-}OC(O)\}IrCp^*]$, as shown in Scheme 34. The crystal structure of the complex $[Cp_2Zr(\mu\text{-}N^tBu)\{\mu\text{-}OC(O)\}IrCp^*]$ has been determined [99].

Reversible reaction of CO_2 with the three-coordinate complex $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ has been reported by Litz et al. [153], as shown in Scheme 35. The structure of CO_2 complex showed a side-bound CO_2 molecule to the Pt–Ge moiety, forming a highly distorted four-membered metallacycle. The presence of the germylene ligand and the formation of a Ge–O bond is believed to be crucial for the reaction of $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ with CO_2. Despite the apparent analogy to metal–carbene chemistry shown in the formation of the metallacycle, alkenes such as ethylene and norbornene do not react with $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ to form a metallacyclobutane [153].



X

Scheme 44.

'Grignard-analogous' rhodium phosphane complexes $[\mathrm{Rh}\{(\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}\}_2]$ [MgCl] ($n = 2, 3$) have recently been reported to react with CO_2 to form $MgCO_3$ and CO [154]. The authors believe that the highly nucleophilic rhodium centre provides the two electrons required for this process.

4.7. Insertion of CO_2 into the M–C bond

This insertion reaction is of paramount importance in the utilization of CO_2 as a source of carbon [7,16,17,27–31]. There are two possible modes of CO_2 insertion into the M–C bond of a complex: normal insertion leads to the formation of a carboxylate complex, and inverse insertion (or abnormal insertion) to the formation of a 1-metalated formate ester (or alkoxycarbonyl complex), as shown in Scheme 36. Recent reviews of the results on CO_2 insertion into the M–C bond have covered the work up to 1993 [27–31]. Therefore, only the most recent results will be presented.

The reaction of CO_2 with $[\mathrm{Cp_2Ti}(\eta^3\text{-allyl})]$ complexes (isolated or prepared in situ) takes place in a highly regioselective manner to give the β,γ-unsaturated carboxylic acid as the sole regioisomer [155] (see Scheme 37).

Cyclopentadiene can also be used to prepare 2-cyclopentene-1-carboxylic acid via the same process. Replacement of the achiral Cp ligands of $[\mathrm{Cp_2TiCl_2}]$ with chiral ligands neomenthyl-η^5-cyclopentadienyl (NMCp) results in asymmetric CO_2 fixation to produce chiral β,γ-unsaturated carboxylic acids [155].

The insertion of CO_2 into the Ti–C bond of the acetylene complexes $[\mathrm{Cp_2Ti(PMe_3)(C_2H_2)}]$ and $[\mathrm{Cp_2Ti(C_2Me_2)}]$ gives the five-membered metallacycles, as shown in Scheme 38 [156,157].

In the interaction of the tolane complex $[\mathrm{CpCp^*Ti(PhC_2Ph)}]$ with CO_2, the insertion of a CO_2 molecule into the Ti–C bond of the titanacyclopropene ring takes place with the formation of the titanafuranone metallacycle, as shown in Scheme 39 [158].

The reaction of CO_2 with tolane, bis(trimethylsilyl)acetylene and phenyl(trimethylsilyl)acetylene complexes of titanocene $[\mathrm{Cp_2Ti(R^1C_2R^2)}]$ ($R^1 = R^2 = \mathrm{Ph}$; $R^1 = R^2 = \mathrm{SiMe_3}$; $R^1 = \mathrm{Ph}$, $R^2 = \mathrm{SiMe_3}$) results in the displacement of ca. 0.5 mol of free acetylene with the formation of the unusual binuclear alkenylcarboxylate complexes of trivalent titanium $[\mathrm{Cp_2TiC(R^1){=}C(R^2){-}C(O)OTiCp_2}]$, as shown in Scheme 40 [159,160]. More recently, the same research group has reported the reaction of the binuclear complex with oxygen to form the titanafuranone metallacycles as shown in Scheme 40 [161].

In the interaction of CO_2 with the bis(trimethylsilyl)acetylene complex $[\mathrm{Cp^*_2Ti(Me_3SiC_2SiMe_3)}]$, full displacement of bis(trimethylsilyl)acetylene from the titanium coordination sphere takes place and CO_2 undergoes disproportionation to form $[\mathrm{Cp^*_2Ti(CO)_2}]$ and the binuclear carbonate complex $[\{\mathrm{Cp^*_2Ti}\}_2\mathrm{CO_3}]$ [160–162] (see Scheme 41). The structure of $[\{\mathrm{Cp^*_2Ti}\}_2\mathrm{CO_3}]$ has been established by an X-ray diffraction study [160]. These studies of the reactivity of the titanium complexes with CO_2 have demonstrated [156–162] that the ligands play a significant role in directing the reaction pathways of these complexes.

The zirconium bis(trimethylsilyl)acetylene complex [$Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$] readily reacts with CO_2 at r.t. to form the dimeric zirconafuranone metallacycle [163] (see Scheme 42).

The insertion of CO_2 into the Zr–C bond of the complex [**VIII**] gives the product [**IX**] in low yield [164] (see Scheme 43).

Treatment of the zirconium porphyrin dimethyl complex [$Zr(OEP)Me_2$] (OEP = dianion of octaethylporphyrin) with CO_2 generates the acetate complex [$Zr(OEP)(OAc)_2$] [165]. The reaction proceeds rapidly in the dark. Controlled experiments with radical traps indicate that no radicals are involved in this reaction. Recently, the insertion of CO_2 into the Zr–C bond of the heterobimetallic complex [$Cp(PMe_3)_2RuCH{=}CHZr(Cl)Cp_2$] has been reported [166] to produce the carboxylate complex [$Cp(PMe_3)_2RuCH{=}CHCO_2Zr(Cl)Cp_2$].

The insertion of CO_2 into the V–C bonds of [$V(Mes)_3(THF)$] (Mes = 2,4,6-$Me_3C_6H_2$) gives the tris(carboxylate) derivative [$V(O_2CMes)_3$]$_n$ [167]. The reaction of the tris(iminoacyl) complex [$V\{\eta^2\text{-}C(Mes){=}N^tBu\}_3$] with CO_2 leads to the double insertion of CO_2 into the V–C bonds with the formation of the complex [**X**] [168]. The complex [**X**] has been characterized by X-ray crystallography (see Scheme 44).

A series of interesting compounds containing coordinated alkyl groups and CO_2 [$Cp'_2Nb(\eta^2\text{-}CO_2)R$] (R = CH_3, CH_2Ph, CH_2CMe_3, CH_2SiMe_3) have been reported [169]. These complexes may serve as model complexes for the intermediates of the CO_2 insertion into M–C bonds. The complexes [$Cp'_2Nb(\eta^2\text{-}CO_2)R$] can be prepared by sodium amalgam reduction of the corresponding alkyl chloride derivatives [$Cp'_2Nb(Cl_2)R$] in the presence of CO_2 [169]. Alternatively, these complexes can be made by aerobic oxidation of the corresponding metal carbonyl complexes [170]. The η^2-CO_2 coordination mode in the complex [$Cp'Nb(\eta^2\text{-}CO_2)(CH_2Ph)$] has been confirmed by X-ray crystallography [169].

The thermal and photochemical decarbonylation rather than insertion was observed for the complex [$Cp'_2Nb(\eta^2\text{-}CO_2)CH_3$] [169,171,172]. Recent studies of the reactivity of the complexes [$Cp'_2Nb(\eta^2\text{-}CO_2)R$] (R = CH_3, CH_2Ph, CH_2CMe_3, CH_2SiMe_3) reveal that the reaction courses significantly depend on the nature of the alkyl group [169]. Although there is no report of the successful insertion of the ligand CO_2 into the Nb–R bond so far, a model complex [$Cp'_2Nb(\eta^2\text{-}(O,O')O_2CMe$] (for the formal insertion of CO_2 into the Nb–R bond) has been reported [100].

The insertion of CO_2 into the M–C bond (M = Cr, Mo, W) of some neutral and anionic compounds has been summarized in earlier reviews [27–31]. Recent studies have shown that the 16-valence electron diaryl complex [$Cp^*W(NO)Ph_2$] undergoes CO_2 insertion to give the η^2-carboxylate complex [$Cp^*W(NO)(\eta^2\text{-}O_2CPh)Ph$] [173].

A coordinatively unsaturated acetylide complex [$Cp^*Ru(PPh_3)(C{\equiv}CPh)$], generated in situ from the reaction of the vinylidene complex [$Cp^*Ru(Cl)(PPh_3)$-$({=}C{=}CH_2Ph)$] with NEt_3, has been reported to react with CO_2 to produce the carboxylate complex [$Cp^*Ru(PPh_3)(\eta^2\text{-}O_2CC{\equiv}CPh)$]. The formation of the carboxylate complex can be explained by migratory insertion of the nucleophilic acetylide ligand to a weakly coordinated carbonyl carbon of CO_2 [174].

The carboxylation of the phenyl ligand of [$NiBrPh(bipy)$] with CO_2 in DMF gives a mixture of benzoic acid and biphenyl after acid hydrolysis. This reaction is proposed to involve the insertion of CO_2 into the Ni–aryl bond [175].

5. Conclusion

The knowledge of CO_2 binding and activation has considerably increased since the first stable CO_2 complex $[Ni(CO_2)(PCy_3)_2]$ was structurally characterized more than two decades ago. Different binding modes of CO_2 in mononuclear and polynuclear metal complexes have been characterized and spectroscopic methods are available to distinguish between them. Binding of CO_2 to a metal centre leads to a net electron transfer from the metal to the LUMO of CO_2 and thus leads to its activation. Accordingly, coordinated CO_2 undergoes reactions that are impossible for free CO_2.

Many stoichiometric and most catalytic reactions involving CO_2 activation proceed via formal insertion of CO_2 into highly reactive M–E bonds with the formation of new C–E bonds. These reactions might not necessarily require strong coordination of CO_2 as in stable complexes, but are generally initiated by nucleophilic attack of E at the Lewis acidic carbon atom of CO_2. Weak interaction between the metal and the lone pairs of one oxygen atom of CO_2 may play a role in supporting the insertion process.

It may be necessary to emphasise that only if we understand the underlying principles of CO_2 activation can the goal of using CO_2 as an environmentally friendly and economically feasible source of carbon be achieved. Although we are more knowledgeable about CO_2 activation, the effective activation of CO_2 by transition metal complexes is still a goal that is hard to reach and remains an exciting research area in organometallic chemistry.

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