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The coordination chemistry of carbon dioxide and its relevance for catalysis: a critical survey

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Contents

Abstract

The ability of carbon dioxide to act as a ligand in transition metal complexes is now well documented and several coordination modes of CO_2 have been described. Spectroscopic

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methodologies allowing the characterization of CO_2 complexes even if crystallographic data are not available have now been developed. The binding of CO_2 to a metal centre generally leads to "activation" of the CO_2 molecule, and various reactions of coordinated CO_2 are known. However, activation by coordination is not a necessary prerequisite for catalytic conversion of carbon dioxide to useful chemicals. Recent theoretical and experimental work suggests that only weak interactions between CO_2 and the active metal centre are sufficient to bring about catalytic reactions involving the formal insertion of CO_2 in an M—X bond as a key step.

Keywords: Carbon dioxide; Catalysis; Transition metal complexes; Ligands; Mechanisms

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Abbreviations

bipy	2,2'-bipyridine
cp	η^5-C_5H_5
cp*	η^5-C_5Me_5
cod	*cis,cis*-1,5-cyclooctadiene
Cy	cyclohexyl
cyclam	1,4,8,11-tetraazacyclotetradecane
diars	1,2-bis(diphenylarsino)ethane
dcpb	1,4-bis(dicyclohexylphosphino)butane
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dcpp	1,3-bis(dicyclohexylphosphino)propane
depe	1,2-bis(diethylphosphino)ethane
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulphoxide
hfacac	hexafluoroacetylacetonate
P_2	chelating bidentate phosphine
THF	tetrahydrofuran
tppts	sodium salt of tris-*m*-(sulphonatotriphenyl)phosphine

1. Aims of the present review

In this review we survey the coordination modes known today for carbon dioxide as a ligand in transition metal complexes and discuss their relevance for catalytic reactions of CO_2. A number of reviews [1–18,155,176–179] of both the coordination chemistry of CO_2 and catalytic CO_2 activation have been published, some of which give a detailed and excellent introduction to the field. However, considerable progress has been made in both areas over the last few years and therefore it seems appropriate to provide a short update. This appears to be even more desirable as it is only now that experimental and theoretical studies allow a critical discussion of the pertinence of CO_2 coordination to a transition metal centre for catalysis. I try to achieve this goal by highlighting prominent examples and recent developments rather than giving a fully comprehensive summary.

Coordination compounds of the platinum group metals have been applied successfully as reagents or catalysts in many useful conversions of carbon dioxide and stable CO_2 complexes are known for all metals of the iron, cobalt and nickel triad. The following discussion will therefore focus on this part of the periodic system, although some other examples are included if they are of special interest in a certain context. The review was written in Spring 1995 and updated at proof stage in April 1996.

2. Carbon dioxide as a ligand in transition metal complexes

2.1. *Principles of the interaction of CO_2 and transition metal centres*

The CO_2 molecule is the prototype of a linear triatomic molecule. The central carbon atom possesses sp hybridization and the C—O distance of 1.16 Å is shorter than a C—O double bond involving an sp^2 carbon centre. The different electronegativities of oxygen and carbon lead to a negative polarization on the oxygen atom and a positive partial charge on the central carbon atom. Thus, the CO_2 molecule exhibits several distinct positions that require specific electronic properties for a potential coordination centre as shown in Fig. 1.

The first reports on the possibility of coordinating CO_2 to transition metal centres came from Vol'pin et al. in 1969 [19] and Jolly et al. in 1971 [20], but information on the binding mode of the CO_2 ligand was scarce at that time. It is clear from Fig. 1 that coordination of CO_2 results in a net transfer of electron density from the metal to the LUMO of the ligand if the complexation takes place via the double bond or the central carbon atom. The LUMO of CO_2 is an antibonding orbital and therefore electron transfer should result in a weakened C–O interaction. Furthermore, according to Walsh's rules [21], a bending of the linear CO_2 molecule similar to the bent structure of the radical anion $CO_2^{\bullet -}$ [22] is expected. Both predictions

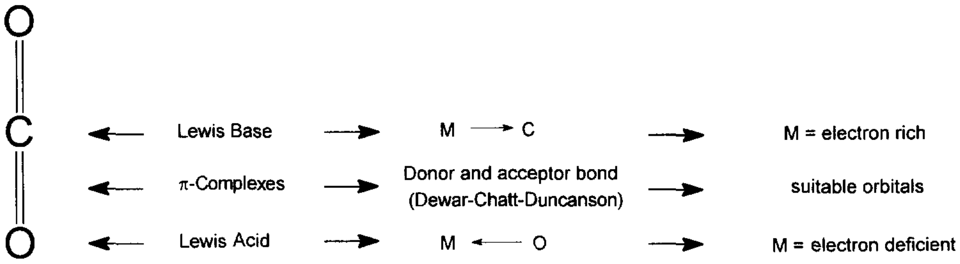
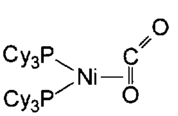


Fig. 1. Reactive positions of the CO_2 molecule and the electronic properties of a transition metal centre required for complexation.

were confirmed in the very first examples of the two binding modes that were structurally characterized, i.e. [Ni(PCy$_3$)$_2$(η^2-CO$_2$] (**1**) [23–25] and [Rh(diars)$_2$(Cl)(η^1-CO$_2$)] (**2**) [26]. The coordination of CO$_2$ via the lone pair at oxygen leaves the LUMO empty and therefore the CO$_2$ molecule should retain its linear arrangement. However, no X-ray diffraction data of CO$_2$ adducts of transition metal complexes containing a linear M–OCO unit are available.



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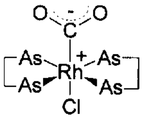

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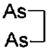


= Ph$_2$As-(CH$_2$)$_2$-AsPh$_2$
= diars

Detailed theoretical studies of CO$_2$ bonding in transition metal complexes have been carried out namely by the groups led by Sakaki and Dedieu and are summarized in the literature [3,27–29]. More recently, Ni(0) and Ni(I) complexes of CO$_2$ have been treated at a high theoretical level [30–32]. The 14e species (H$_3$P)$_2$Ni clearly prefers coordination of CO$_2$ via the C=O double bond [31], whereas the penta-coordinate neutral Ni(NH$_3$)$_4$F shows a remarkably strong charge transfer interaction to CO$_2$, leading to complexation through the central carbon only [32]. Density functional calculations have been used to investigate the interaction of Cu$^+$ and its 2,2′-bipyridine (bipy) complex with CO$_2$ [33]. The bipy ligand reduces the electrostatic interaction between Cu$^+$ and the negatively polarized oxygen atoms of CO$_2$ and at the same time enables a better π back-donation from the metal to the LUMO of CO$_2$. Thus, the side-on η^2 coordination is considerably stabilized relative to the end-on η^1 bonding in the bipy complex compared with the free Cu$^+$ ion. Similarly, Fe$^+$ forms a linear end-on complex with CO$_2$ in the gas phase, as shown by Schwarz and Schwarz [34], while the phosphane complex [Fe(depe)$_2$(η^2-CO$_2$] of the same metal in the zero oxidation state prefers the side-on coordination via a C–O double bond as shown by X-ray diffraction [35]. A side-on complexation has also been postulated for [Fe(CO)$_3$(CO$_2$)]$^-$ generated via the gas phase reaction of [Fe(CO)$_3$]$^-$ and CO$_2$ [36]. Most recently, different coordination modes have been calculated for [WCl$_4$(η^2-CO$_2$)] (side on) and [W(CO)$_5$(OCO)] (end on) on a UP2 level and have been rationalized by different covalent contributions to the metal–ligand interface [180].

In addition to the complexation of a single metal centre, CO$_2$ may also act as a bridging ligand, and the number of structurally characterized complexes of this type has steadily increased in the last few years (see Section 2.3.4). In principle, there are many possibilities for the realization of a bridging CO$_2$ ligand [1]. However, all complexes crystallographically characterized up to now follow the same general pattern, involving complexation of one metal centre through carbon and further bonding to one or two other metal atoms through oxygen. This binding mode of CO$_2$ was observed for the first time in an X-ray crystal diffraction examination of the osmium cluster [(H)(CO)$_{10}$Os$_3$(μ_3-η^3-CO$_2$)Os$_6$(CO)$_{17}$][(Ph$_3$P)$_2$N] by Lewis and coworkers in 1976 [37].

The above considerations demonstrate the large variety of possible structures of

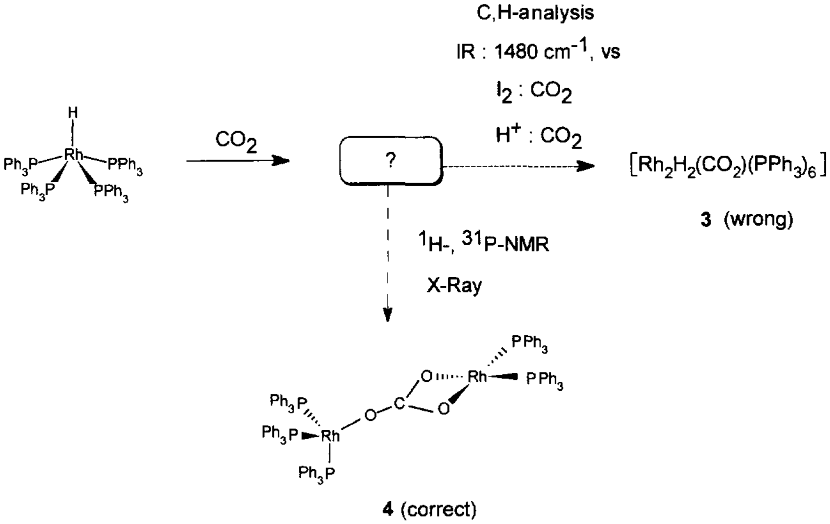
CO_2 complexes and the subtle balance between them. Therefore, it seems appropriate to address briefly the analytical methods available for the characterization of CO_2 complexes before discussing some recent developments in the chemistry of these compounds.

2.2. *Characterization of CO_2 complexes*

The characterization of CO_2 complexes in solution or in the solid state is based mainly on investigations using the following techniques.

(i) elemental composition or molecular mass determination;
(ii) chemical properties, particularly generation of CO_2 by acidolysis, oxidation with I_2 or ligand replacement;
(iii) IR spectroscopy;
(iv) NMR spectroscopy;
(v) X-ray diffraction studies.

Older reports on CO_2 complexes are often based on composition, reactivity and IR data only, and should be viewed with some caution as CO_2 adducts are difficult to distinguish from carbonate and hydrogen carbonate species on these grounds. Thus, the postulated CO_2 complex $[Rh(OH)(CO_2)(CO)(PR_3)]$ was found to be a bicarbonato complex [38], and what appeared to be $[Rh_2(H)_2(CO_2)(PPh_3)_6]$ (**3**) had to be reformulated as the benzene solvate of the CO_3^{2-}-bridged dimer **4** on the basis of NMR and X-ray data [39] (Scheme 1). Some side-on CO_2 complexes of rhodium have been claimed from IR data [40], but could not be obtained by two other independent investigations [41]. However, in the last few years, Mascetti and coworkers have shown in a series of publications that careful analysis of IR spectra combined with the use of ^{13}C- and ^{18}O-labelled CO_2 may provide detailed information on structure and bonding in CO_2 complexes [42–44].



Scheme 1. Interpretation of reactivity and IR data only can be misleading.

The use of ^{13}C-NMR spectroscopy in the investigation of CO_2 complexes has become increasingly important during the last 15 years. The ^{13}C resonance of CO_2 is shifted from a value of $\delta \approx 124$ for free dissolved CO_2 to a lower field upon coordination to a transition metal. Values in a range of 150 to 250 ppm have been reported, and the chemical shifts may differ widely even for complexes with the same coordination mode as found in $[Ni(PCy_3)_2(\eta^2\text{-}CO_2)]$ (**1**) (158.6 ppm) [45] and $[Mo(PMe_3)_3(CN^tBu)(\eta^2\text{-}CO_2)_2]$ (210.4 ppm) [46]. The coupling constant between ^{13}C and the metal nucleus or other ligands is often more useful for the investigation of CO_2 complexes, and allows, for example, discrimination between CO_2 adducts and CO_3^{2-} compounds. The complexes [Ni(dcpe)][CO_3] and $[Ni(dcpp)(\eta^2\text{-}CO_2)]$ exhibit nearly identical chemical shifts for the central carbon (166.2 ppm and 164.2 ppm respectively), but the carbonate resonance appears as a singlet while a coupling of $^2J_{CP(trans)} = 45$ Hz is observed for the CO_2 complex [47].

In conclusion, NMR and IR data are useful for demonstrating the existence of a CO_2 adduct and may give specific information on the coordination mode. A combination of IR and ^{13}C-NMR spectroscopy can lead to a full determination of the structure of a CO_2 complex, particularly when isotopically labelled CO_2 is employed, and structural assignments in CO_2-bridged complexes are often based solely on these methodologies (see Section 2.3.4 for details).

Nevertheless, our knowledge about binding of CO_2 to transition metal centres is mainly based on X-ray diffraction studies. Unfortunately, CO_2 compounds tend to be unstable in solution and crystal growing may be a tedious task in many cases. Furthermore, the discussion of solution properties like reactivity or catalytic activity on the basis of solid state structures is not always straightforward. Solid state CP-MAS NMR spectroscopy may serve as a link between solid state and solution, and can be used even for non-crystalline solids. This approach has been applied successfully to a study of the structural dynamics of $[(PCy_3)_2Ni(CO_2)]$ (**1**) (see Section 2.3.1) [44,45].

2.3. Stable complexes of CO_2

2.3.1. Coordination via a C=O double bond

It is now more than 20 years since the first X-ray crystal structure of a CO_2 complex was reported by Aresta et al. [23]. Complex **1** contains the ligand in a side-on η^2 coordination mode, i.e. CO_2 is bound to the metal via its C=O double bond [23–25]. A number of other complexes of this type have been structurally characterized, and comprehensive reviews are available [1–3,8–12,15,179].

Recently, a detailed study of the structural dynamics of complex **1** in solution has been reported [45]. The structures in the solid state and in solution at temperatures below 200 K are identical, as indicated by CP-MAS and variable-temperature NMR experiments. Two separate signals appear for the PCy_3 ligands, indicating that CO_2 is fixed in a rigid η^2 coordination at the Ni centre. At temperatures above 240 K, the two ^{31}P signals of solutions of **1** show coalescence to one singlet, demonstrating that the two PCy_3 ligands become chemically equivalent through apparent rotation of the CO_2 ligand. A mechanism that involves a slightly bent end-on Ni–OCO intermediate is assumed for the observed equilibration (Scheme 2) on the basis of additional IR spectroscopic investigations, reactivity arguments and theoretical calculations [30,44].

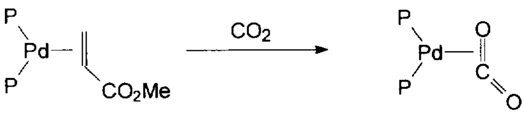
Apparent CO_2 rotation has been also observed in *trans*-$[Mo(PMe_3)_4(\eta^2\text{-}CO_2)_2]$ and related complexes [46,48]. A concerted rotational mechanism not involving any η^1 bound intermediates has been elucidated experimentally [46] and is again supported by ab-initio calculations [49].

Some analogues of **1** bearing chelating phosphane ligands $Cy_2P(CH_2)_nPCy_2$ have also been investigated [25,47]. The ligand dcpe with $n=2$ leads to disproportionation of CO_2 [47] or formation of binuclear species [25], while stable monomeric adducts are obtained with depp ($n=3$) and depb ($n=4$) [47]. Interestingly, these complexes show no dynamic behaviour even at room temperature, as indicated by the fact that the ^{13}C signals appear as doublets owing to coupling with the trans ^{31}P atom only. The smaller *cis* coupling that was found to be $^2J_{CP(cis)} = 10$ Hz in the low temperature spectrum of **1** [45] was not observed in $[\{Cy_2P(CH_2)_nPCy_2\}Ni(\eta^2\text{-}CO_2)]$.

A distinct effect of the auxiliary ligands on the stability of CO_2 complexes is not surprising in view of the general considerations outlined in Section 2.1 and is also described for palladium complexes. The 14e fragment $[Pd(PCy_3)_2]$ was shown to be unreactive towards CO_2 even in liquid CO_2 [50], while a moderately stable complex $[Pd(PMePh_2)_2(\eta^2\text{-}CO_2)]$ (**5**) has been obtained and characterized spectroscopically under mild conditions (Scheme 3) [51].

The first unambiguously characterized stable complex of Rh(I) containing side-on bound CO_2 as a ligand has been prepared recently using the sterically congested T-shaped fragment $[Rh\{HC(CH_2CH_2P^tBu_2)_2\}]$ [216]. The use of the chelating ligand depe allowed the isolation and X-ray crystallographic characterization of the Fe(0) complex **6** containing η^2-bound CO_2 [35]. This binding mode was postulated for $[Fe(PMe_3)_4(CO_2)]$ in 1977 [52], but recent IR studies suggested the participation of η^1 coordination through the central carbon atom [42]. The solid state structure of **6** shows an ideal η^2 arrangement, but again it has been argued that coordination via carbon may play some role in solution as the CO_2 oxygen in **6** is readily attacked by electrophilic reagents [35]. One should keep in mind, however, that complex **1** also reacts readily with H^+ and other electrophiles [53], but η^1 carbon coordination

Scheme 2. Mechanism for the apparent CO_2 rotation in complex **1** in solution above 240 K.

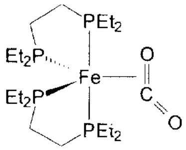


P = PMePh2

5, 90 % yield

Scheme 3. Synthesis of the first stable CO_2 complex of palladium.

of CO_2 can be ruled out for this complex on the basis of experimental and theoretical results [30,31,45].



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Side-on complexes of CO_2 with early transition metals are also well known [1–3,8–12,15,179]. The complex $[Nb(\eta^5\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$ was the first example to be structurally characterized [54], and the chemistry of this and related compounds has been thoroughly investigated in the last few years mainly by the group led by Nicholas [55–58,181]. A derivative with the $SiMe_3$ group replaced by Ph was obtained by aerobic oxidation of the corresponding CO complex and structurally characterized [57]. The latter reaction presents an example where a η^2 CO_2 ligand is generated by conversion of another ligand rather than by direct reaction with CO_2. Preliminary X-ray diffraction data of $[W(CO)(CO_2)(dppe)_2]$ suggest that a η^2-bound CO_2 moiety is also present in this first CO_2 complex of tungsten to be structurally characterized [59]. This is in reasonable contrast to experimental and theoretical findings for the pentacarboxyl derivative [65,180].

2.3.2. Coordination via carbon only

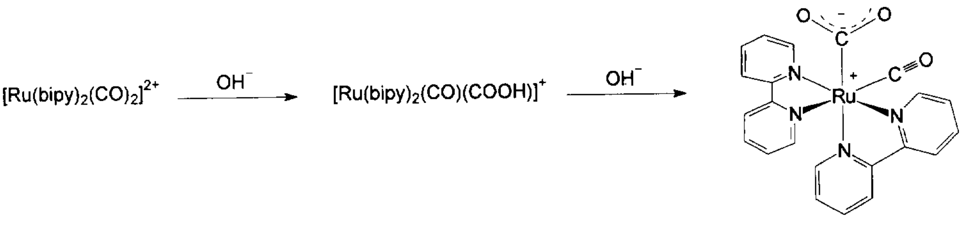
The coordination of CO_2 to a transition metal via only the central carbon atom leads to a high partial negative charge at the outer oxygen atoms, as indicated schematically in formula **2**. Consequently, the highly nucleophilic oxygen atoms readily bind to additional electron-deficient centres leading to polynuclear bridged systems, as discussed in Section 2.3.4, or to secondary reactions like coupling of two CO_2 molecules as in $[Ir(Cl)(PMe_3)_3(C_2O_4)]$ [60].

The stabilization of η^1 carbon bound CO_2 by intramolecular hydrogen bonds has been reported for the complexes $[Co^I(cyclam)(L)(CO_2)]^+$ ($L = CH_3CN$, THF) on the basis of IR and NMR spectroscopical investigations [61]. A three-dimensional network of intermolecular hydrogen bonds between the η^1-CO_2 moiety and water molecules has been observed for the complex $[Ru(bipy)_2(CO)(\eta^1\text{-}CO_2)]$ (**7**) which exists as a hydrate $\mathbf{7}\cdot 3H_2O$ in the solid state [62,63,178]. The ruthenium complex **7** was not obtained by direct reaction with CO_2, but by nucleophilic attack of OH^- to a carbonyl ligand of $[Ru(bipy)_2(CO)_2][PF_6]$ according to Scheme 4. As in complex **2**, the two C–O distances in the CO_2 ligand of complex **7** are not exactly identical (1.245 and 1.283 Å).

2.3.3. Coordination via oxygen only

No structural information on transition metal complexes bearing the end-on CO_2 ligand is currently available from X-ray crystal structure analyses and there are only a limited number of reports that claim the characterization of stable adducts of this type by IR spectroscopy [2,64].

The complex $[(W(CO)_5(OCO)]$ was generated in the gas phase and was shown



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Scheme 4. Synthesis of $[Ru(bipy)_2(CO)(\eta^1\text{-}CO_2)]\cdot 3H_2O$ and schematic representation of the molecular structure of the ruthenium complex 7.

by matrix isolation techniques to contain a linear oxygen-bound CO_2 ligand [65]. Furthermore, end-on complexes of "naked" metal cations and CO_2 have been reported for Mg^+ [66] and Fe^+ [34] in the gas phase. The bonding energy of the mainly electrostatic interaction between the metal centre and the lone pair has been estimated to 14.7 kcal mol^{-1} for Mg^+ [66] and to 8 kcal mol^{-1} for Fe^+ [34] and the tungsten complex $[(W(CO)_5(OCO)]$ [67]. Theoretical calculations are in good agreement with these values [180].

2.3.4. CO_2 as a bridging ligand

As pointed out earlier, bridging of two metal centres via CO_2 occurs mainly when further metals coordinate to the negatively polarized oxygen atoms of a η^1 carbon bound CO_2 ligand. Bridged CO_2 complexes of this type can be classified according to five different binding modes, as shown in Fig. 2. Examples of all types are now known, and many of them have recently been characterized for the first time by X-ray crystallography (Table 1). The carbon-bound metal M is a transition metal in all cases, while M′ and M″ can be any type of metal including elements of group 14, particularly tin. The coordinated oxygen atoms in structures **I–III** are available for further secondary interactions with other metal centres in the solid state [74,79]. Additional direct M–M′ interactions are possible in complexes of type **I** [68,182].

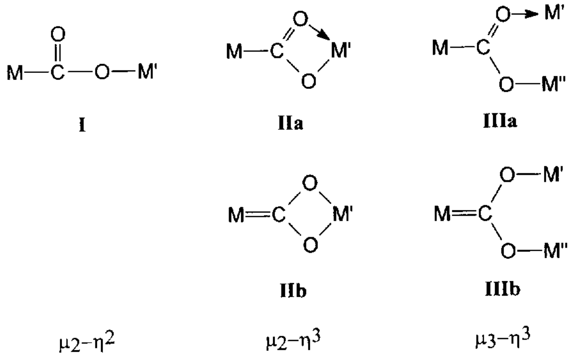


Fig. 2. Classification of binding modes in CO_2-bridged polynuclear metal complexes.

Table 1
Structurally characterized complexes containing a bridging CO_2 moiety

Complex	IR ν_{OCO} (cm^{-1})	δ $M\text{-}^{13}CO_2$ (ppm)	d M–C (Å)	Type[a]	Reference
$[(L)(CO)_4Re(\mu_2\text{-}\eta^2\text{-}CO_2)Re(CO)_3(L)_2]$[b]	—	—	2.184(9)	**I**	[70]
$[(dppp)(CO)_3Re(\mu_2\text{-}\eta^3\text{-}CO_2)Re(CO)_3(dppp)]$	—	191.7[c]	2.191(13)	**IIa** s	[72]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)W(cp)_2][BF_4]$	—	247.4	2.04(4)	**IIb** s	[75]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)Ti(tmtaa)][BF_4]$[d]	—	226.2	2.081(9)	**IIb** ns	[77]
$[(cp^*)(PPh_3)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)SnPh_3]$	1395, 1188	207.6	2.058(9)	**IIb** ns	[76]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)SnPh_3]$	1429, 1174	206.9	2.100(9)	**IIb** ns	[185]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^2\text{-}CO_2)SnMe_3]$	1510, 1179	196.1	2.103(5)	**I**	[187]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)Re(CO)_3(PPh_3)]$	1437, 1282	206.4	2.089(6)	**IIb** s	[185]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)Zr(cp)_2(Cl)]$	1348, 1288	217.9	2.097(5)	**IIb** s	[188]
$[(cp^*)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)Mo(CO)_2(cp)]$	1319, 1285	217.8	2.08(1)	**IIb** s	[189]
$[(CO)_5Re(\mu_3\text{-}\eta^3\text{-}CO_2)Re(CO)_4]_2$	1380, 1295, 1260	—	—	**IIIa**	[78]
$[(cp)(CO)(PPh_3)Fe(\mu_2\text{-}\eta^2\text{-}CO_2)Re(CO)_4(PPh_3)]$	1505, 1135	211.9	1.994(3)	**I**	[69]
$[(cp)(CO)(PPh_3)Fe(\mu_2\text{-}\eta^3\text{-}CO_2)Re(CO)_3\{P(OEt)_3\}]$	1435, 1252	245.9	1.932(7)	**IIb** s	[186]
$[(cp)(CO)(PPh_3)Fe(\mu_2\text{-}\eta^3\text{-}CO_2)SnPh_3]$	1432, 1174	228.2	1.931(5)	**IIa** ns	[69, 73]
$[(cp)(CO)(PPh_3)Fe(\mu_2\text{-}\eta^3\text{-}CO_2)SnBu_3]$	1433, 1113	220.3	1.936(4)	**IIa** ns	[187]
$[(cp)(CO)(PPh_3)Fe(\mu_2\text{-}\eta^3\text{-}CO_2)SnMe_3]$	1438, 1134	220.4	1.934(6)	**IIa** ns	[187]
$[(cp^*)(CO)_2Fe(\mu_2\text{-}\eta^3\text{-}CO_2)SnPh_3]$	1450, 1152	218.4	1.956(3)	**IIa** ns	[187]
$[(\eta^5\text{-indenyl})(CO)(PPh_3)Fe(\mu_2\text{-}\eta^3\text{-}CO_2)SnPh_3]$	—	—	1.933(3)	**IIa** ns	[190]
$[(cp^*)(CO)_2Ru(\mu_2\text{-}\eta^3\text{-}CO_2)Zr(cp)_2(Cl)]$	1339, 1287	220.4	2.050(4)	**IIb** s	[188]
$[(CO)_2Ru\{(\mu\text{-}(iPrOP)_2PN(Et)P(OiPr)_2\}_2\text{-}(\mu_2\text{-}\eta^2\text{-}CO_2)Ru(CO)_2]$	1710, 1505	—	2.05(2)	**I**	[68]
$[(PMe_2Ph)_3Os(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-}CO_2)Rh_2(cod)_2]$	1365, 1260	193	2.062(19)	**IIIa**	[79]
$[(H)(CO)_{10}Os_3(\mu_3\text{-}\eta^3\text{-}CO_2)Os_6(CO)_{17}][(Ph_3P)_2N]$	1270	—	1.96(5)	**IIIb**	[37]
$[Co(pr\text{-}salen)(THF)(\mu_2\text{-}\eta^3\text{-}CO_2)K]$[e]	1650, 1280, 1215	—	1.99	**IIa** ns	[74]
$\{[Co(en)_2(\mu_2\text{-}\eta^2\text{-}CO_2)](ClO_4)\times H_2O)\}_n$[f]	1645	—	1.924(20)	**I**	[183]
$[(cp^*)Ir(\mu\text{-}tBuN)(\mu_2\text{-}\eta^2\text{-}CO_2)Zr(cp)_2]$	1588	164.0	2.098(10)	**I**	[71]
$[(dppp)(CH_3)Pt(\mu_2\text{-}\eta^2\text{-}CO_2)Pt(CH_3)(dppp)]$	—	—	—	**I**	[184]
$[(Et_3P)_2Pt(\mu_2\text{-}\eta^2\text{-}CO_2)Ge\{N(TMS)_2\}]$[g]	1622, 1091	171.4	2.086(9)	**I**	[182]

[a] See Fig. 2. s and ns refer to symmetrical and non-symmetrical CO_2 units, respectively. [b] $L=H_2NCH_2CH{=}CH_2$. [c] Assignment differs from original paper. [d] tmtaa = dianion of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine. [e] pr-salen = dianion of n-propyl substituted

The metallocarboxylate structures **IIa** and **IIIa** in Fig. 2 differ from the dioxocarbene structures **IIb** and **IIIb** mainly in the nature of the central carbon atom of the CO_2 ligand. It resembles a carboxylic carbon in structures of type **a**, whereas it can be described as a carbene-like carbon in type **b**. The contribution of carbene-like bonding is indicated by strong low field shifts in the ^{13}C resonance of the central carbon of CO_2 and by short M—C bonds. In some cases, hindered rotation around the M—C bond is observed by variable-temperature NMR spectroscopy [77]. Further evidence may come from IR data and from the C—O bond lengths, but these two criteria fail to distinguish between a dioxocarbene and a symmetrical delocalized carboxylate. It is noteworthy that symmetrical and unsymmetrical CO_2 bridging units are both possible for type **a** and **b** bonding (Table 1).

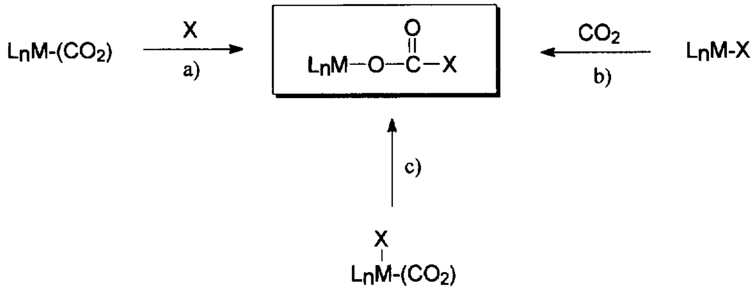
The largest body of crystallographic data is available for bimetallic complexes of type **I** and **II** and has emerged mainly from systematic work during the last two years by the team of Gibson [69,185–190]. It was long believed that the difference between the two characteristic IR frequencies ν_{asym} and ν_{sym} of the CO_2 unit provides a diagnostic tool for the discrimination between symmetrical and unsymmetrical binding modes [179]. However, very recent work by Gibson revealed that only ν_{sym} reflects the symmetry of the CO_2 unit, whereas ν_{asym} is strongly influenced by the coordination geometry of the second metal M′ [189]. Generally, ν_{sym} is found at higher frequencies for symmetrical units (ca. 1250–1280 cm^{-1}) than for unsymmetrical bridges (ca. 1130–1170 cm^{-1}). The borderline between the situation **IIa** and **IIb** is less clear cut and even the energy barrier between structures **I/II** appears to be very low [187]. Although the spectroscopic and structural criteria used for the classification in Table 1 are helpful for the description of CO_2 bridged complexes, a theoretical treatment of the bonding situation seems thus highly desirable.

In addition to the complexes presented in Table 1, a large number of bridged CO_2 complexes has been unambigously characterized by spectroscopic techniques by the groups of Cutler, Cooper and others [80,81,189 and references cited therein]. The most versatile synthetic approach to CO_2-bridged complexes is the cation exchange of alkali metallocarboxylates, which are readily accessible from the corresponding alkali metallates and CO_2 [69,76,81 and references cited therein]. The latter reaction involves nucleophilic attack of the electron-rich metal centre at the Lewis acidic carbon of CO_2 rather than CO_2 insertion into a metal—metal bond. Direct insertion of CO_2 into a bond between two transition metals has only been observed most recently by the groups of Cutler [80] and Bergman [71]. Other pathways to CO_2 bridged complexes include the reaction of metal carbonyls with OH^- [78] or with metaloxo complexes [75,77]. Formation of a CO_2 bridging unit via thermolysis of a carboxyethylene-bridged bimetallic complex has also been observed [191].

3. The participation of CO_2 complexes in stoichiometric and catalytic conversions of carbon dioxide

3.1. Introduction

The different coordination modes of CO_2 to transition metal centres were described in the previous section. It is clear that CO_2 is in an “activated state” when the



Scheme 5. Pathways for C—X bond formation from CO_2: (a) attack of an external reagent at coordinated CO_2 in a stable CO_2 complex; (b) reaction of free CO_2 with a metal complex containing the group to be transferred; (c) simultaneous coordination of CO_2 and the second substrate at the metal centre where the M–CO_2 interaction may or may not be identical with that found in stable CO_2 complexes.

bonding involves the central carbon of CO_2. The activation is evident from structural data like the bent OCO moiety and increased C–O distances, and from spectroscopical data like low field shifts in ^{13}C-NMR and low frequency OCO vibration modes in IR spectroscopy. One can expect that this "activation" is also reflected in the reactivity of coordinated CO_2.

There are now a considerable number of reports on the reactivity of metal-bound CO_2 and some reviews on earlier work are available [1–3,8–12,15,177–179]. In recent years, detailed experimental studies have been carried out with stable η^2-CO_2 complexes of the early transition metals [55–57,82,181] and examples involving metals of groups 8–10 have also been addressed [35,45,47,51,53]. The cleavage of a C—O bond is frequently observed and yields metal oxides which may react further with CO_2 leading to a net conversion of two molecules of CO_2 to CO and CO_3^{2-}. The same conversion may occur via intermediate coupling of two CO_2 molecules at a metal centre [60,83,84].

Another common reaction of η^2-CO_2 complexes is the electrophilic attack at oxygen leading to metallacarboxylic acids (often referred to as hydroxycarbonyl complexes) and their derivatives [35,51,53]. Naturally, electrophilic attack at oxygen is also the prevalent reactivity of stable η^1-CO_2 complexes [62,63] and CO_2-bridged complexes where M′ and M″ are alkali cations [69,76,81]. These complexes are also intermediates in photochemical and electrochemical reactions of CO_2 to CO [18,178]. Far less is known about the reactivity of CO_2 ligands bridging two transition metal centres. The Cutler group [85], in an elegant labelling study, was able to demonstrate that the apparent CO_2 reduction in $[(cp)(CO)_2Ru(\mu_2\text{-}\eta^3\text{-}CO_2)Zr(Cl)(cp)_2]$ actually proceeds via hydride transfer to CO and subsequent rearrangement.

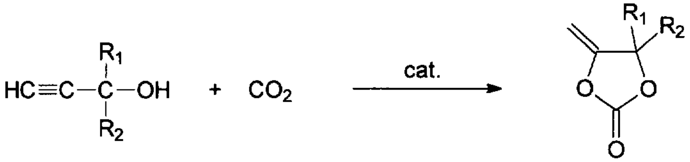
From the point of view of synthesis, the most interesting reactions of CO_2 result in the formation of new bonds between the carbon atom and a second group X. Many reactions of this type are known to proceed in the presence of stoichiometric or catalytic amounts of transition metal complexes. In principle, these conversions can occur following any of the three pathways outlined in Scheme 5. In the following sections we highlight recent developments of synthetically useful processes where new C—X bonds are formed and summarize our present understanding of their mechanisms.

3.2. Formation of new C—O and C—N bonds

One example of a conversion that results in a new C—O bond and occurs at coordinated CO_2 is the reaction of **1** and its derivatives with O_2 to form peroxocarbonates with the formula $[(R_2P)_2Ni(CO_4)]$ [23,47]. However, it was observed in 1970 for platinum [86], and also more recently for rhodium [87], that the reaction of dioxygen complexes with CO_2 can lead to the same products. The simultaneous interaction of CO_2 and O_2 at metal centres is of special interest in view of recent reports on the influence of CO_2 on rhodium-catalysed aerobic oxidation reactions [88–90].

Another reaction leading to the formation of a new C–O bond is the formal insertion of CO_2 into M–OH or M–OR groups. These reactions have been thoroughly investigated because of their relation to the function of carbonic anhydrase, a zinc-containing enzyme that catalyses the formation of HCO_3^- and CO_3^{2-} from aqueous CO_2 [91]. It is now generally accepted that the enzymatic reaction involves nucleophilic attack of a Zn^{2+}-bound hydroxy group at CO_2. The CO_2 is not coordinated to the metal but is held in place by hydrogen bonds within the pocket of the protein shell of the enzyme. A variety of zinc-containing carbonic anhydrase model systems have been described, namely by the groups led by Kimura and Vahrenkamp [10,92–94]. The pathway involving free CO_2 also seems to be valid for CO_2 insertion into M–OR groups of other transition metal complexes, as demonstrated by Darensbourg, Bergman and others [95–97]. Recent studies show that low valent hydroxy-bridged complexes of platinum group metals are also capable of CO_2 insertion into μ-M–OH groups [98,99]. Although intermediate CO_2 coordination cannot be excluded a priori, it seems unlikely in view of the above results and the related reaction of low valent platinum amide complexes discussed below.

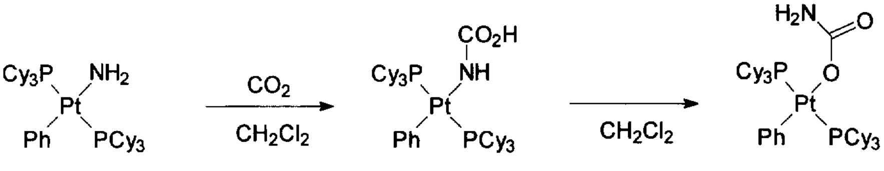
The synthesis of cyclic carbonates from oxiranes and CO_2 is well known and is carried out on the industrial scale using Lewis acid catalysts [1,2,12]. Polymeric epoxides give polymeric cyclic carbonates upon reaction with CO_2 in the presence of alkali halides [192]. Comparably few examples of transition metal catalysed reactions of CO_2 with oxiranes to yield cyclic carbonates are known [100,101,193–195]. Many of them may operate merely as Lewis acids, but there is evidence for CO_2 insertion into oxometallacyclobutanes as the C—O bond forming step in some cases [100]. More recently, Darensbourg et al. [196–198] have investigated the known Zn^{2+} catalysed copolymerisation of epoxides and CO_2. They were able to perform the reaction in supercritical CO_2 as both solvent and reactant [198] and suggested that the C—O bond formation occurs most likely as discussed above for zinc-alkoxides [196]. Propargylic alcohols were coupled with CO_2 to give exocyclic unsaturated cyclic carbonates according to Scheme 6 using ruthenium [102] and palladium catalysts [103]. The mechanism of C—O bond formation involves nucleophilic attack of the alcoholate on CO_2 and transition metal complexes of CO_2 are not required for this step as is clearly shown by the fact that the reaction is also



Scheme 6. Exocyclic unsaturated cyclic carbonates from propargylic alcohols and CO_2.

catalysed by tertiary phosphines alone [104]. The palladium-catalysed synthesis of non-cyclic benzyl allyl carbonate from benzyl alcohol, allyl chloride and CO_2 has been described and was found to proceed via a similar pathway [105]. The transition metal centre catalyses the nucleophilic replacement of chloride by benzyl carbonate, while the C—O bond formation between CO_2 and benzyl alcohol only requires general base catalysis.

Nucleophilic attack of nitrogen is a key step in formal insertion reactions of CO_2 into M–N bonds [1,2,8–12]. Traces of free amine have been shown to promote the reaction with CO_2 in most cases, but the attack of metal-bonded nitrogen similarly to oxygen in carbonic anhydrase is also possible. Formation of the nitrogen-bonded carbamate **9** from the reaction of the platinum amide complex **8** with CO_2 has been observed as a first example for the latter pathway [106]. Complex **9** readily rearranges to the more stable oxygen-bonded carbamate **10** (Scheme 7). The formation of the nitrogen-bonded intermediate **9** strongly suggests that neither coordinated CO_2 nor free amine is involved in this reaction as such pathways would lead directly to **10**. In view of these results, nucleophilic attack of either free or coordinated nitrogen to the central carbon of CO_2 may be expected to be operating in the metal-complex-mediated syntheses of *N*,*N*′-dialkyureas $OC(NHR)_2$ [105,107] and urethanes $OC(NR_2')OR'$ [108,109,199,200] from amines and CO_2. Again, some of these reactions can be carried out in the absence of transition metals [110].



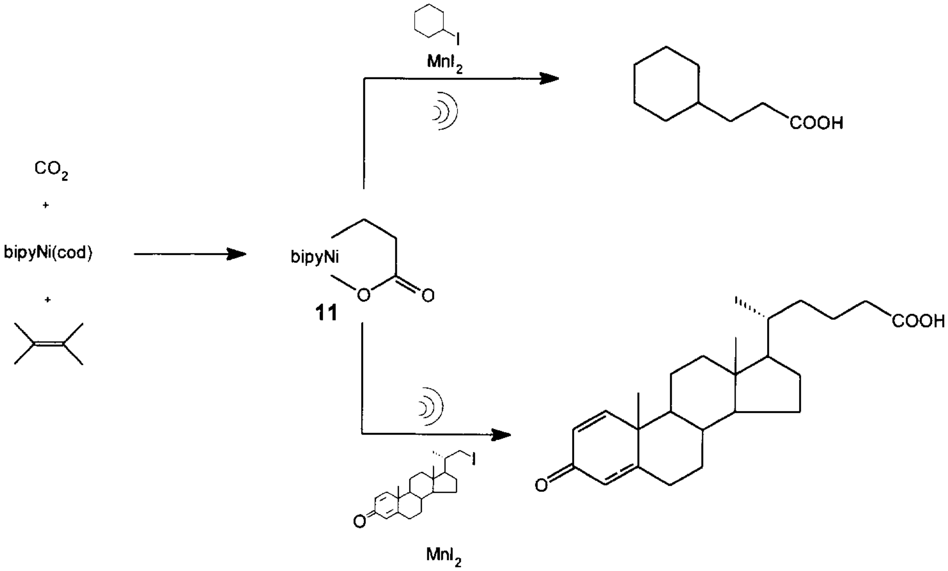
Scheme 7. Nucleophilic attack of metal-bound nitrogen at CO_2 to yield new C—N bonds.

3.3. Formation of new C–C bonds

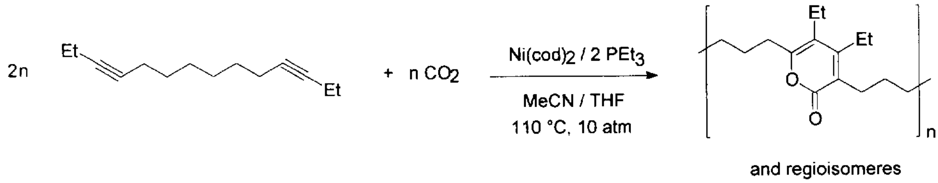
Naturally, reactions leading to the formation of new C–C bonds are the most interesting processes from a synthetic point of view and have been reviewed extensively [1,11–14,177]. The coupling of alkenes and CO_2 at Ni(0) leads to five-membered cyclic complexes like **11** [111,112]. They were shown to be versatile stoichiometric reagents for further transformations by the groups led by Hoberg, Dinjus and Walther [1,11,16,113 and references cited therein]. Recent examples [114–117] include the synthesis of steroid derivatives and the use of ultrasonic activation to increase the yields of organic products obtained from **11** and alkyl halides (Scheme 8). Little information on the mechanism of the coupling step itself is available from experimental work, but ab-initio calculations carried out by Dedieu and Ingold [30] for the 14e fragment $(NH_3)_2Ni$ as a model strongly suggest the participation of η^2-CO_2 complexes similar to **1**.

The catalytic formation of 2-pyrones is possible using Ni(0) and other transition metal catalysts if alkynes are coupled with CO_2 [1,7,11–16]. A recent example describes the use of Fe and Rh clusters as catalysts [118]. The nickel-catalysed reaction was first observed by Inoue et al. [119] and developed to a synthetically useful methodology by Walther and coworkers [120,121]. Tsuda and coworkers [122–124] were able to use this system for some interesting syntheses of highly functionalized cyclic compounds. Furthermore, they synthesized novel polymeric materials based on CO_2 as a C1 building block using long chain α,ω-alkynes as coupling partners (Scheme 9) [124–126]. Polymeric 4-pyrones were obtained from alkynes bearing NH_2-endgroups even in the absence of a metal catalyst [201]. Reetz et al. [127] have found that nickel-catalysed pyrone formation is possible from 3-hexyne and CO_2 under supercritical conditions without the need for additional solvents.

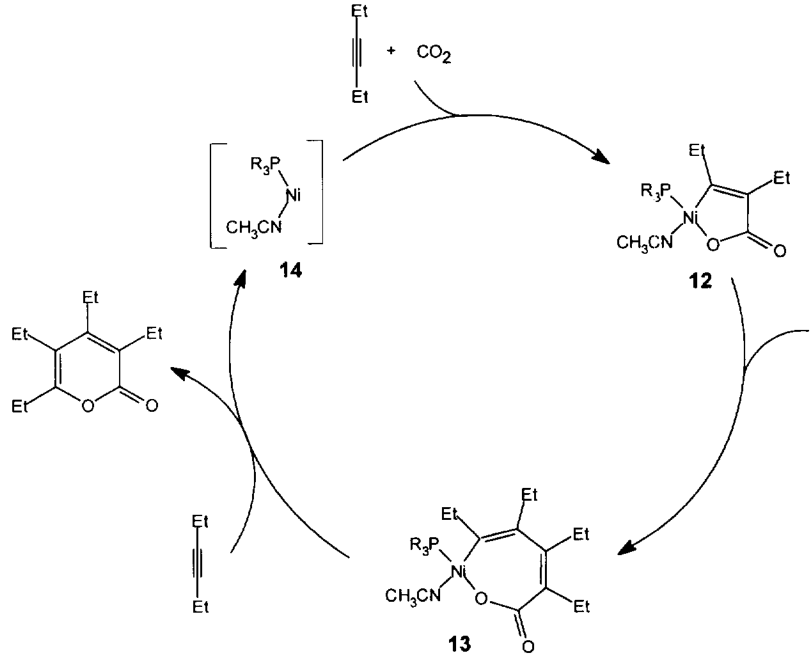
The mechanism of pyrone formation at Ni(0) complexes summarized in Scheme 10 is based on related stoichiometric reactions [113,128] and is consistent with experimental details [120,121,129]. The initial coupling product **12** is similar to the cyclic



Scheme 8. C–C coupling of CO_2 and ethylene at Ni(0) complexes and further transformations of the resulting cyclic complex **11** under ultrasonic activation.



Scheme 9. Novel polymeric materials via nickel-catalysed copolymerization of diynes and CO_2.



Scheme 10. The mechanism for the Ni(0)-catalysed formation of pyrones from 3-hexyne and CO_2.

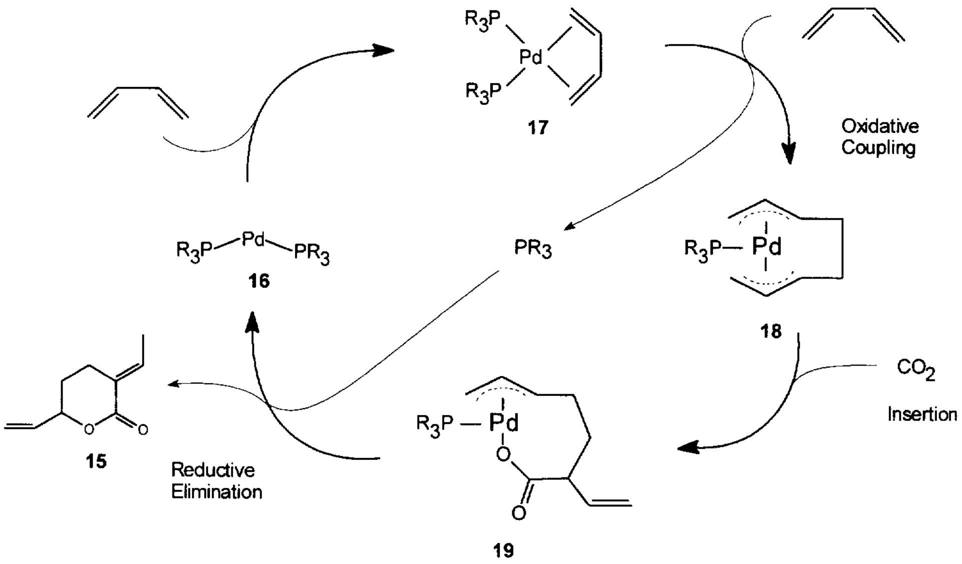
complex **11**, but the sp^2 centre next to nickel seems to be more reactive and allows the insertion of further alkyne to achieve the catalytic formation of pyrones. It is proposed that the same initial coupling product **12** is formed from alkynes and CO_2 at electrochemically generated Ni(0) centres using the methodology developed by the team of Duñach [130,131], whereby complex **12** reacts to give unsaturated carboxylates instead of pyrones in the presence of Mg^{2+} ions emitted from the sacrificial anode under these conditions.

It is tempting to assume attack of the alkyne at coordinated CO_2 as the pathway of formation of **12**, similarly as for **11**. However, a detailed ab-initio MO study by Sakaki et al. [132] suggests that alkyne coordination is favoured at Ni(0) over CO_2 coordination. Although a complex $[(H_3P)Ni(C_2H_2)(\eta^2\text{-}CO_2)]$ was analysed as possible intermediate, only a weak Ni–O interaction is predicted between Ni and CO_2 during the course of C–C bond formation. The regioselectivity of the coupling involving unsymmetrically substituted alkynes is predicted correctly on the basis of these calculations [202]. One should also mention in this context the formation of cyclic compounds analogous to **12** from the reaction of alkyne complexes of Ti(II) and Zr(II) with CO_2 as studied in recent years mainly by the group of Rosenthal [133,134,203].

It has recently been reported that terminal alkynes and CO_2 can be catalytically coupled with bromoalkanes to give alkyl esters of 2-alkynoic acid using Cu(I) or Ag(I) catalysts [135]. The key step in this reaction seems to be the well-known insertion of CO_2 into Cu acetylides that does not require intermediate formation of a CO_2 complex [136,137].

The transition-metal-catalysed coupling of 1,3-dienes with CO_2 leading to either lactones or long-chain esters as main products is a process of potential synthetic interest [1,12–17]. The reaction was first observed by the group of Inoue [138], and some efficient catalytic systems based on palladium have been developed by Behr and coworkers [139,140] and by Braunstein et al. [141] for the synthesis of δ-lactone (**15**) from 1,3-butadiene and CO_2. More recently, there have been attempts to use Pd(II) and Pd(0) complexes that were fixed to heterogeneous supports as catalysts for the telomerization of 1,3-butadiene and CO_2, but all systems studied so far suffer from metal leaching [142,143].

The generally accepted mechanism involving low-valent Pd(0) complexes **16** as key intermediates in the catalytic cycle of the telomerization of 1,3-butadiene and CO_2 is depicted in Scheme 11. Dinjus and Leitner [144] were able to rationalize the remarkable ligand effects observed in this reaction under the assumption that the P–Pd–P angle in **16** plays an important role in the activity of the catalyst. Only



Scheme 11. The mechanism of palladium-catalysed telomerization of 1,3-butadiene and CO_2 to form δ-lactone **15**.

ligands that are predicted by MMX calculations to give bent complexes of type **16** yield highly active catalysts; a linear arrangement leads to poor activity. In agreement with this finding, the chelating ligand $Cy_2P(CH_2)_4PCy_2$ forms a very active Pd catalyst for the formation of δ-lactone from CO_2 and 1,3-butadiene. Furthermore, this ligand allows the co-oligomerization of CO_2 with isoprene for the first time, even though the reaction still proceeds with very low yields [144].

The C—C bond formation between CO_2 and the diene occurs at the bis-π-allyl complex **18** as indicated in Scheme 11 and demonstrated by stoichiometric model reactions [145,146]. The insertion into the Pd—C bond occurs via a σ,η^1-allyl intermediate, and it is possible in principle to accommodate a η^2-CO_2 ligand during this process. On the other hand, Amatore et al. [147] have demonstrated that palladium-catalysed electrochemical formation of aryl carboxylic acids from aryl halides and CO_2 most likely involves nucleophilic attack of Ar^- at free CO_2 as the C—C bond-forming step. Again, 14e fragments $(R_3P)_2Pd$ are believed to be the catalytically active species in this reaction. Therefore we can conclude that CO_2 coordination is not crucial for the catalytic C–C bond formation with CO_2 at palladium phosphane complexes, although stable adducts of CO_2 with the fragment $(R_3P)_2Pd$ are known [51].

3.4. Formation of new C–H bonds

One of the most promising approaches to the use of CO_2 as a raw material on a large scale is its reduction to formate which can be achieved by electron transfer in electrochemical or photochemical systems or by direct reaction of CO_2 with H_2 [18]. In many cases, the electron transfer in photo- or electrochemical activation of CO_2 mediated by transition metal compounds involves formation of a C-bonded CO_2 complex [3,18,148–150,178]. A corresponding catalytic cycle has been proposed by Tanaka and coworkers [151] for the electrocatalytical reduction of CO_2 to HCO_2^- using complexes $[(bipy)_2Ru(CO)(L)]^{2+}$ ($L=CO$, Cl^-) as catalysts. The crystallographic characterization of the CO_2 complex **7** [62,63] and its protonated form [206] supports this proposal. Closely related complexes are also involved in the reduction of CO_2 beyond the formate level [207,208]. Meyer and his colleagues have shown that a different pathway involving formation of ruthenium hydride species and subsequent CO_2 insertion into the Ru–H bond is also possible for specific formation of the formate group [152]. The two alternatives have been compared in detail in the photosensitized reduction of CO_2 using cobalt macrocyclic complexes [153,154], whereby only the insertion process can lead to HCO_2^-.

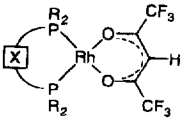
Reduction of CO_2 beyond the formate level by molecular hydrogen using homogeneous transition metal catalysts is still scarce [209]. In contrast, the transition metal complex catalysed formation of formic acid and its derivatives from H_2 and CO_2 was demonstrated for the first time in the early 1970s, but again it was not until recently that very efficient catalytic systems were developed [18,155]. We and the group of Nicholas have recently investigated independently rhodium phosphane complexes as catalysts for this process [156–159], whereby formic acid concentrations up to 3.5 mol l^{-1} could be achieved under the conditions developed in our team. The key to high formic acid yields in organic solvents is the choice of suitable reaction conditions and the optimized parameters shown in Scheme 12 were derived from straightforward thermodynamic considerations [158]. The use of dipolar nonprotic solvents and amine bases leads to stabilization of the hydrogenated product and provides ideal conditions for high catalytic activities.

Complexes of type [$(P_2)Rh(hfacac)$] (**20**) [159] have been shown to be the most active catalyst precursors under these conditions allowing turnover rates up to 1335 h^{-1} and total turnover numbers greater than 3000. Rational fine tuning of these catalysts seems possible, as correlations between solid state structures, ^{103}Rh-NMR shifts and the catalytic activities have been observed with various groups R and X (*intrinsic ligand effects*). The changes in activities observed with catalysts generated in situ from [$\{(cod)Rh(\mu\text{-}Cl)\}_2$] and monodentate or bidentate ligands with phosphorus as donor atom must be partly attributed also to ligand effects during the formation of the catalytically active species [210].

Highly efficient hydrogenation of CO_2 to formic acid is also possible in water/amine mixtures similar to those used for CO_2 sequestring from flue gases, if water soluble rhodium catalysts containing the phosphine ligand tppts are used [160]. Up to 3440 catalytic cycles within 12 h are possible using the complex [$(tppts)_3RhCl$] as a catalyst under mild conditions similar to those described in Scheme 12. More recently, ruthenium complexes bearing nitrogen ligands have been applied successfully in $EtOH/NEt_3$ [211].

The Noyori group has shown that ruthenium complexes serve as very active catalysts for the formation of formic acid [161], DMF [162] or formate esters [212] from supercritical mixtures of CO_2 and H_2 in the presence of NEt_3, $HNMe_2$ or alcohols, respectively. Temperatures up to 100 °C and total pressures greater than 200 atm are employed in these processes, and additives like traces of water or DMSO greatly enhance the catalytic activity [213]. A total yield of 370 000 moles of DMF per mole of catalyst could be achieved owing to the special solubility properties of products and reactants in the supercritical phase. It is noteworthy that formic acid does not react to DMF under the much milder conditions summarized in Scheme 12 if NEt_3 is replaced with $HNMe_2$ [158]. A recent account on the potential of supercritical carbon dioxide as a medium for homogeneous catalysis is found in Ref. [214].

The mechanism of CO_2 hydrogenation using rhodium catalysts in organic solvents has been investigated experimentally in detail and insertion of CO_2 into an Rh–H bond of cationic [156] or neutral [158,163] hydride complexes has been shown to be a key step of the catalytic cycle depending on the reaction conditions and the



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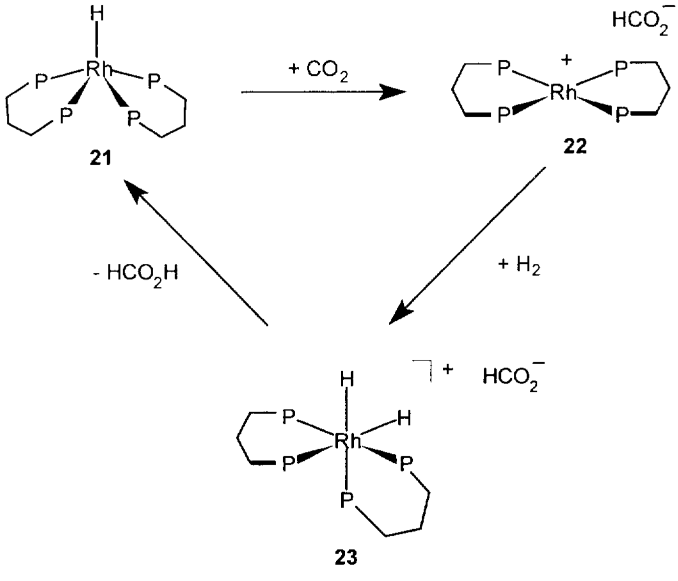
Scheme 12. Rhodium-catalysed hydrogenation of CO_2 to formic acid in dipolar aprotic organic solvents.

catalyst precursor. All steps of a possible catalytic cycle were observed for the first time by NMR spectroscopy using the moderately active catalyst [$(dppp)_2RhH$] (**21**) in DMSO (Scheme 13) [163]. The insertion step has been shown to be fully reversible by NMR spectroscopic investigation of the $^{13}CO_2/^{12}CO_2$-exchange in formate complexes of type **22**. The exchange rate shows a first-order dependence on the CO_2 concentration as seen from the typical kinetics depicted in Fig. 3. Most interestingly, the half-life time of the exchange in complexes [$\{Ph_2P(CH_2)_nPPh_2\}_2Rh(HCO_2)$] ($n=2$, 3) qualitatively reflects the catalytic activities of the corresponding hydrides in CO_2 hydrogenation [163], although the insertion process appears to be too fast to account for the rate limiting step of the catalytic cycle.

Complexes **20** and related catalyst precursors having a P_2/Rh ratio of 1:1 lead to 14e species [P_2RhH] as the active intermediates [158,215], which can follow an identical sequence of events according to experimental and theoretical investigations [164,165]. Ab-initio calculations suggest σ-metathesis as a low energy alternative to oxidative addition in the H_2 activation process [164,165], but we will focus on the CO_2 insertion step in the present context.

Sakaki and Musashi [166] have studied the CO_2 insertion into the Rh–H bond by ab-initio calculations using the neutral rhodium hydride [$(H_3P)_3RhH$] as a model for complex **21**. No evidence for a stable CO_2 complex was found on the reaction pathway and only a weak Rh–O interaction occurs in the transition state (Fig. 4). The transition state for CO_2 insertion into the Rh–H bond of the highly unsaturated 14e species [$(H_3P)_2RhH$] is very similar to the one shown in Fig. 4, allowing for a somewhat stronger metal–oxygen interaction [164,165]. An η^2 association complex



Scheme 13. Catalytic cycle of the rhodium-catalysed hydrogenation of CO_2 to formic acid using catalyst **21**.

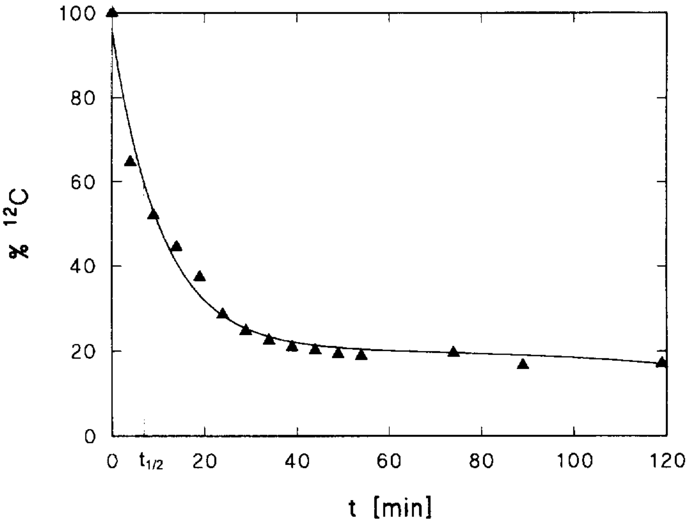


Fig. 3. $^{13}CO_2/^{12}CO_2$ exchange in the rhodium formate complex **22** in DMSO-d_6 at 1 atm and room temperature.

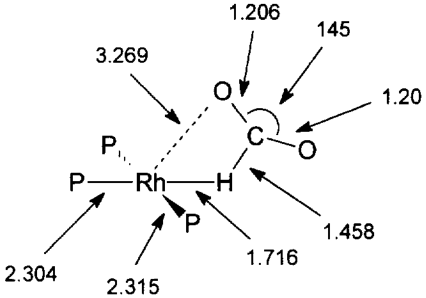


Fig. 4. Transition state for the insertion of CO_2 into the Rh—H bond of $[(H_3P)_3Rh(H)]$ as obtained from ab-initio MO calculations.

between $[(H_3P)_2RhH]$ and CO_2 is formed *prior* to the transition state, but converts to the formate species with an extremely small — if any — energy barrier [165]. As in related systems [156], there is strong kinetic evidence that the liberation of formic acid rather than CO_2 insertion is rate limiting in the catalytic cycle [165]. Transition states with only weak M–O interaction have also been computed for the insertion of CO_2 into the metal hydride bonds of $[(H_3P)_2CuH]$ [167], $[Cr(CO)_5H]^-$ [168] and main group metals [169]. Detailed kinetic investigations of CO_2 insertion reactions are in full agreement with the absence of a stable pre-association complex for related systems [170–173].

Taken together, there is convincing evidence that complexes containing CO_2 coordinated as in stable CO_2 complexes are not a necessary prerequisite for efficient catalysis in the hydrogenation of CO_2 to formic acid. It is worth mentioning in this context that the η^2-CO_2 complex **1** has been shown to react with dihydrogen to yield the hydrido formate $[(Cy_3P)_2Ni(H)(O_2CH)]$ [45]. However, labelling studies carried out by Darensbourg and coworkers [171,172] strongly suggest that the mechanism of this conversion involves dissociation of CO_2, formation of a nickel hydride and subsequent insertion of CO_2. The latter pathway is also assumed to account for the formation of small amounts of formic acid from H_2 and CO_2 in the presence of the palladium CO_2 complex **5** [51]. It has also been demonstrated recently by the Milstein group that formation of $[(H)(HCO_2)Rh\{HC(CH_2CH_2PtBu_2)_2\}]$ from the corresponding η^2-CO_2 complex and H_2 occurs via insertion of dissociated CO_2 at a non-classical η^2-dihydrogen complex of Rh(I) [216]. Hydride transfer to η^2 coordinated CO_2 was observed in the formation of formato complexes of Nb and Ta by aerobic oxidation of the corresponding hydrido carbonyl complexes, but again CO_2 dissociation and subsequent insertion cannot be excluded [174]. Similar arguments apply to the ruthenium-mediated formation of formate from CO_2 and $NaBH_4$ [175].

4. Conclusions

Our understanding of CO_2 binding and activation by transition metal complexes has considerably increased since the first stable CO_2 complexes were reported 25 years ago. Different binding modes of CO_2 in homonuclear and polynuclear metal complexes have been structurally characterized and spectroscopic methods are available to distinguish between them. Any type of binding known to date to result in stable isolable coordination compounds containing CO_2 as a ligand leads to a net electron transfer to the LUMO of CO_2 and thus to its “activation”. Accordingly, coordinated CO_2 undergoes reactions that are impossible for free CO_2, and complexes containing CO_2 ligated as in stable complexes are most likely involved in C–O cleavage reactions and in electrochemical or photochemical CO_2 activation processes.

Many stoichiometric and most catalytic reactions involving “CO_2 activation” proceed via formal insertion of CO_2 into highly reactive M—X bonds under the formation of new C—X bonds. These reactions do not necessarily require coordination of CO_2 as in stable complexes, but are generally initiated by nucleophilic attack of X at the Lewis acidic carbon atom of CO_2. Weak interactions between the metal centre and the lone pairs of one oxygen of CO_2, similar to those found for gas phase complexes of “naked” metal ions and CO_2, are often sufficient to support the insertion process by pre-organization of the CO_2 molecule. Most of the synthetically useful transition-metal-mediated transformations of CO_2 known to date seem to follow this general pathway.

It may be necessary to point out that the understanding of how CO_2 is activated in a certain reaction is not of mere academic interest (if something like that actually exists). The optimization of existing processes and the search for new reactions involving CO_2 as a environmentally friendly and economically feasible source of carbon can only be successful if we understand the underlying principles of CO_2

activation. Although it seems as if we have moved a little closer towards this ambitious objective in the last quarter of the century, the effective "activation" of CO_2 by transition metal compounds is still a goal that is hard to reach and remains an exciting research area in organometallic chemistry.

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