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CO_2 Activation

Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge?

Mirza Cokoja, Christian Bruckmeier, Bernhard Rieger, Wolfgang A. Herrmann, and Fritz E. Kühn**

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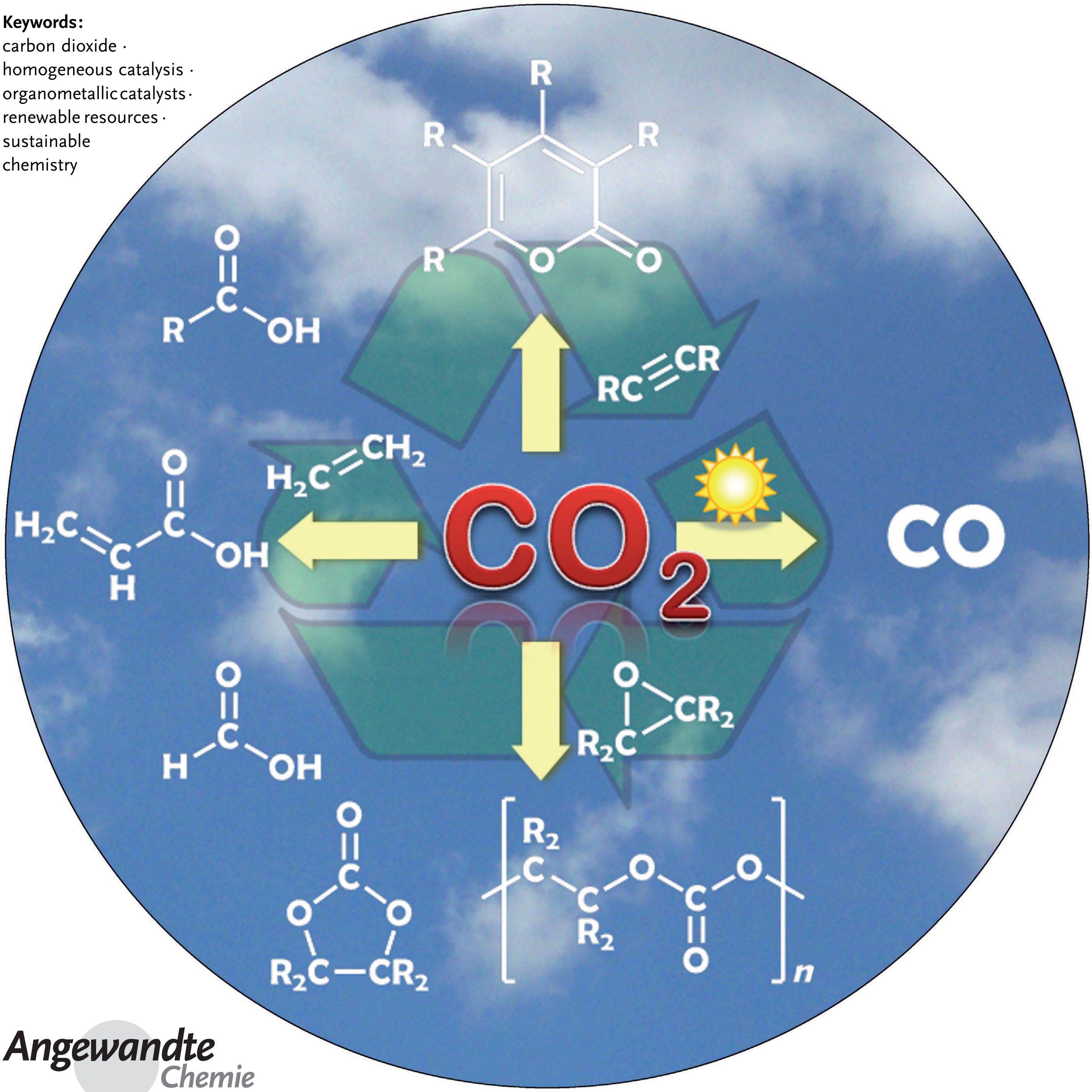

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***A** plethora of methods have been developed over the years so that carbon dioxide can be used as a reactant in organic synthesis. Given the abundance of this compound, its utilization in synthetic chemistry, particularly on an industrial scale, is still at a rather low level. In the last 35 years, considerable research has been performed to find catalytic routes to transform* CO_2 *into carboxylic acids, esters, lactones, and polymers in an economic way. This Review presents an overview of the available homogeneous catalytic routes that use carbon dioxide as a* C_1 *carbon source for the synthesis of industrial products as well as fine chemicals.*

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1. Introduction

Carbon dioxide and its steadily increasing concentration in the atmosphere over the most recent part of human history is a permanent subject in the media, politics, and in science.[1,2] The effects of climate changes—caused by greenhouse gases—on nature are threatening the development of the climate and have led to recurring discussions on how this man-made, unwanted interference could be brought to an end. However, despite all the efforts to reduce CO_2 emissions, the increasing hunger for energy by an ever-growing human population is unceasing and there is no doubt that CO_2 emissions will not stagnate, but will rise even further. Scientific effort focuses on the question as to whether the abundant CO_2 can at least be utilized to produce materials of commercial interest.[2] Carbon dioxide, besides being a natural gas and biomass, will be one of the most abundant carbon sources in the future, since fossil sources (coal, petroleum) are limited. The use of CO_2 as a chemical feedstock will almost certainly not reduce its atmospheric concentration significantly; however, it may provide access to high-value products from a nontoxic, renewable, and low-cost resource. The transformation of alternative, yet unreactive, carbon sources originating from the carbon cycle is an important goal of catalysis.

Only 1 ‰ of the total abundance of CO_2 on Earth is currently being used for chemical synthesis, which is mainly ascribed to its chemical inertness, but also because CO_2 capture and storage is expensive.[1] Currently, CO_2 is used in the chemical industry for the production of bulk chemicals, such as urea, salicylic acid, cyclic carbonates, and polypropylene carbonate.[2] The reduction to CO, methane, or methanol has been far less investigated, as these reactions are very unfavorable from a thermodynamic point of view, and the energy barriers can only be overcome with catalysts. One of the ultimate goals of research today is to exploit ubiquitous and "green" energy sources, such as sunlight, for the catalytic transformation of CO_2. This Review aims to draw attention to the transformation of CO_2 in solution through the assistence of homogeneous catalysts. This is an attractive alternative to the known industrially driven procedures, since it exploits the abundance of carbon dioxide and offers an alternative access to raw chemicals. An overview of the so far available organometallic concepts for the catalytic activation of CO_2 is presented. A specific focus is the question, which of these routes is the most promising for the future in terms of end product (fuels, polymers, basis chemicals, etc.), scale-up, and the energy required to perform the conversion.

2. Coordination of CO_2 to Transition-Metal Complexes

Since the first description of the reaction of metal complexes with carbon dioxide several decades ago, a plethora of transition-metal complexes with CO_2 as a ligand have been synthesized and structurally characterized, and the coordination chemistry of CO_2 has been summarized in several reviews.[3–7] CO_2 is a weak electrophile and requires a Lewis basic metal center for coordination. Of all the possible coordination modes of CO_2 to a transition-metal center, the most common—and most convenient in terms of catalysis—are the σ bonding of the metal to the carbon atom (**1**, Figure 1) and the π coordination of one C═O bond to the metal center (**2**). σ-O coordinated CO_2 (**3**), such as in the complex $[\{(^{Ad}ArO)_3tacn\}U^{III}(CO_2)]$ (($^{Ad}ArOH)_3tacn$ = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane) is also known,[8] but is more difficult to obtain,

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[*] Dr. M. Cokoja, Prof. Dr. W. A. Herrmann, Prof. Dr. F. E. Kühn
Chair of Inorganic Chemistry, Molecular Catalysis Catalysis Research Center, Technische Universität München
Ernst-Otto-Fischer Strasse 1, 85747 Garching (Germany)
E-mail: fritz.kuehn@ch.tum.de

Dipl.-Chem. C. Bruckmeier, Prof. Dr. B. Rieger
WACKER-Chair of Macromolecular Chemistry, Catalysis Research Center, Technische Universität München
Ernst-Otto-Fischer Strasse 1, 85747 Garching (Germany)
E-mail: rieger@tum.de

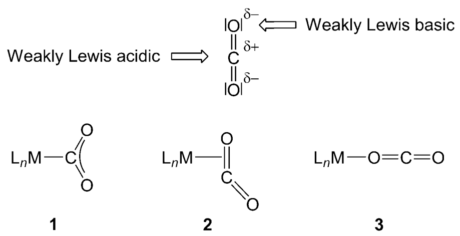


Figure 1. Properties of CO_2 as a ligand (top) and possible coordination modes of CO_2 to a transition-metal complex (bottom).

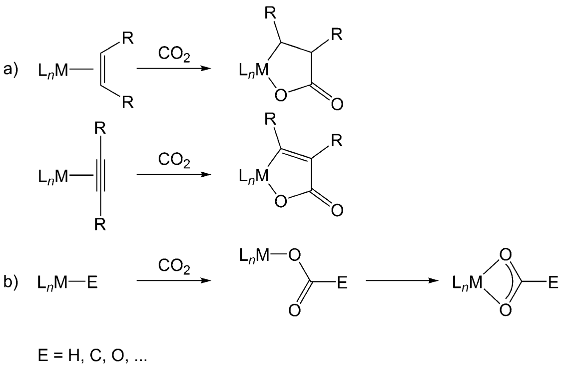
since CO_2 has to be forced to coordinate end-on at the metal center by the shape of the ligands. The major problem is the cleavage of the transformed CO_2 moiety from the metal center, which renders any catalytic application difficult. The task of researchers is, therefore, to find a synthetic protocol, by which CO_2 can be activated and transformed with catalytic amounts of transition-metal complexes. Despite reports of many different methods, which have been developed over the last 40 years to utilize CO_2 either as a direct ligand to transition-metal centers or as a reactant with ligands at the metal centers, there are only a few concepts concerned with how to catalytically convert CO_2.[9]

Mirza Cokoja studied chemistry at the Ruhr-University Bochum. He received his PhD under the guidance of R. A. Fischer in 2007. In 2008, he carried out postdoctoral research with B. Chaudret at the CNRS Laboratoire de Chimie de Coordination in Toulouse, France. Since 2009, he has been a research group leader at the Chair of Inorganic Chemistry of the Technische Universität München (TUM). His research interests are the activation of small molecules with organometallic catalysts, oxidation catalysis, and the synthesis of metal–organic building blocks for the design of porous coordination polymers.

Wolfgang A. Herrmann studied chemistry at the TUM and obtained the diploma in the group of E. O. Fischer. He received his PhD in 1973 at the University of Regensburg under the direction of H. Brunner. After postdoctoral research with P. S. Skell (Pennsylvania State University), he completed his Habilitation in Regensburg, where he was appointed Associate Professor in 1979. He received a full professorship in Frankfurt/Main in 1982 and moved to the TUM in 1985 as successor to E. O. Fischer. Since 1995, he has served as President of the TU München. He has published more than 760 papers to date.

Fritz E. Kühn studied chemistry at the TUM, where he received his PhD with W. A. Herrmann in 1994. After postdoctoral research with F. A. Cotton (Texas A&M University, 1995/96), he completed his Habilitation in Munich to become "Privatdozent" in 2000. From June 2005 to March 2006 he was Deputy Chair of Inorganic Chemistry at TUM. In April 2006 he was appointed Principal Researcher at the Instituto Técnológico e Nuclear (ITN) in Sacavém, Portugal. In December 2006 he returned to the TUM as Professor of Molecular Catalysis and since October 2007 he has also been acting Chair of Inorganic Chemistry. He is author of ca. 250 scientific publications.

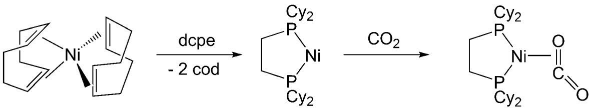
It is symptomatic that even the most recent reports still go back to the initial research from the 1970s and 1980s, published by the research groups of Inoue, Musco, Hoberg, Walther, and Behr, who performed seminal research in the field of catalytic CO_2 activation. In essence, there are only two general routes (Scheme 1): reaction of CO_2 with a) olefins or alkynes, and b) the insertion of CO_2 into metal–element bonds, which, dependent on the co-reactants, lead to different transformation products, such as carboxylates, esters, or carbonates. In nearly all cases, late transition metals were used (d^8–d^{10}: Fe^0, Rh^I, Ni^0, Pd^0, Pd^{II}), since they are very basic and capable of binding a weak ligand such as CO_2 through backbonding.



Scheme 1. Basic principles for the utilization of CO_2 as a C_1 feedstock with organometallic reagents.

3. Reactions of CO_2 with Unsaturated Hydrocarbons at Metal Centers

The oxidative coupling of carbon dioxide with olefins and alkynes is well studied. Ever since the first report by Aresta et al. on the isolation of a complex displaying a side-on CO_2 ligand bound to [Ni(dcpe)] (dcpe = 1,2-bis(dicyclohexylphosphino)ethane), which was formed in situ by a ligand displacement reaction of $[Ni(cod)_2]$ (cod = *cis,cis*-1,5-cyclooctadiene) and dcpe (Scheme 2),[10] research has focused on the exploration of the activation of coordinated CO_2 ligands. This $\{Ni(CO_2)\}$ complex proved to be very active towards olefins and alkynes, as shown in the pioneering studies by the research groups of Inoue, Hoberg, and Walther.

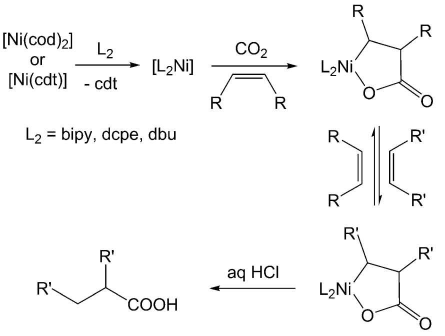


Scheme 2. Synthesis of $[(\eta^2\text{-}CO_2)Ni(dcpe)]$ by Aresta et al. Cy = cyclohexyl.

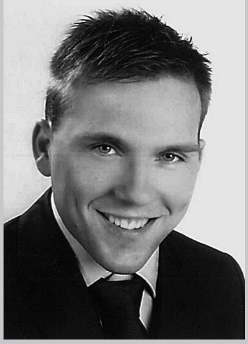
3.1. Coupling of CO_2 and Olefins

3.1.1. Stoichiometric Reactions—Synthesis of Metallalactones

Around 30 years ago, the research groups of Hoberg and Walther started examining the oxidative coupling of carbon dioxide (1 bar) and olefins at nickel centers. The reaction results in the formation of stable nickelalactones at room temperature in THF solution (Scheme 3).[11–14] Typically, nickel(0) olefin compounds, such as $[Ni(\eta^4\text{-cod})_2]$[15] or $[Ni(\eta^6\text{-cdt})]$[16] were used as starting materials to react with bulky σ-donor ligands such as phosphines or bidentate ligands (dcpe, bipy, etc.). The in situ formed 14 valence electron species $[NiL_2]$, being carbenoid ($d^{10}ML_2$) and thus extremely strong nucleophiles, can bind an olefin. In the second step, CO_2 can be "inserted" into the M-η^2–olefin bond, thereby forming a metallacycle. The reaction is reversible. Treatment of a solution of a nickelalactone with a different olefin results in olefin substitution and the formation of a new nickelalactone (Scheme 3).[17] DFT calculations performed by Pápai et al. indicate that the cycloolefin ligands at the nickel(0) center are replaced by the bidentate ligand in the first step, followed by coordination of an olefin substrate.[18] It was argued that the formation of the metallalactone does not necessarily require the coordination of CO_2 to the metal center prior to the coupling reaction, but rather appears to be a concerted reaction.



Scheme 3. Synthesis of nickelalactones and protonation to carboxylic acids. bipy = 2,2′-bipyridine, cdt = *trans,trans*-1,5,9-cyclododecatriene, dbu = diazabicyclo[5.4.0]undec-7-ene.



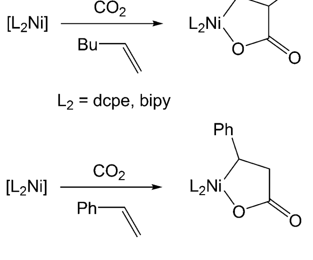
Christian Bruckmeier studied chemistry supported by a scholarship of the Studienstiftung des deutschen Volkes at the TUM. He obtained his Diploma in 2009 in the group of B. Rieger focusing on the liberation of methyl acrylates from nickelalactones. For his PhD he received a scholarship from the Fonds der Chemischen Industrie and he is an associated member of the DFG Graduiertenkolleg Chemical Photocatalysis. His PhD is concerned with the photocatalytic reduction of carbon dioxide.

Bernhard Rieger studied chemistry at the Ludwig-Maximilians-Universität München (LMU) and received his PhD in 1988. After research at the University of Massachussetts at Amherst and in the plastics laboratory of BASF SE he received his Habilitation in 1995 at the University of Tübingen. In 1996 he became Professor at the Department Materials and Catalysis at the University of Ulm. Since 2006 he has been Professor at the TUM at the WACKER-Chair of Macromolecular Chemistry and director of the Institute of Silicon Chemistry. He has received a teaching award from the Federal State of Baden-Württemberg and the Philip-Morris Award.

However, Bernskoetter and Tyler showed by NMR experiments that treatment of molybdenum(0) ethylene complexes with CO_2 results in both the CO_2 and ethylene being π bound to the molybdenum center prior to conversion into acrylate ligands (see Section 3.1.2).[19]

Acid hydrolysis of nickelalactones leads to ligand protonation, that is, to free carboxylic acid and decomposition of the nickel complex. To date, however, all reports on the oxidative coupling of CO_2 and olefins at nickel centers involve either hydrolysis to obtain the respective carboxylic acid or methanolysis to obtain the methyl carboxylate esters. Since the discovery that CO_2 and unsaturated hydrocarbons undergo this type of reaction, extensive studies were performed to elucidate the mechanism of the reaction and gain control over the reaction products in terms of regioselectivity for unsymmetric alkenes.

Hoberg et al. found that in the case of substituted olefins, the moiety R is located preferably at the α position next to the carbonyl group (Scheme 4). However, when styrene is used, the phenyl group is located at the β position, particularly at higher reaction temperatures.[17] Later, it was found that nickelacyclopropionates, obtained by the oxidative coupling of ethylene and CO_2, allow the insertion of another ethylene molecule into the Ni–C bond, thereby yielding a C_5-membered nickelalactone.[20] In analogy to the reaction of CO_2 with olefins, the oxidative coupling with heteroolefins $E{=}CR_2$ ($E = O$, NR) also leads to metallacycles. Walther and coworkers reported on the oxidative coupling of CO_2 with aldehydes at [Ni(bipy)] that resulted in nickelacarbonates.[21,22] Interestingly, the aldehyde O atom is located at the α position next to the C=O group. Hoberg et al. treated imines with CO_2, which afforded a nickel-2-oxazolidinone, where the N atom selectively adopts the α position to the

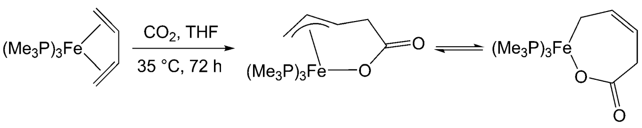


Scheme 4. Regioselectivity of the oxidative coupling depending on the olefin substituents.

carbonyl group.[17] Very recently, Baum and co-workers revisited this reaction and treated several imines with CO_2. However, the reaction resulted in the dimerization of the imines or the formation of 1,2-diamines.[23]

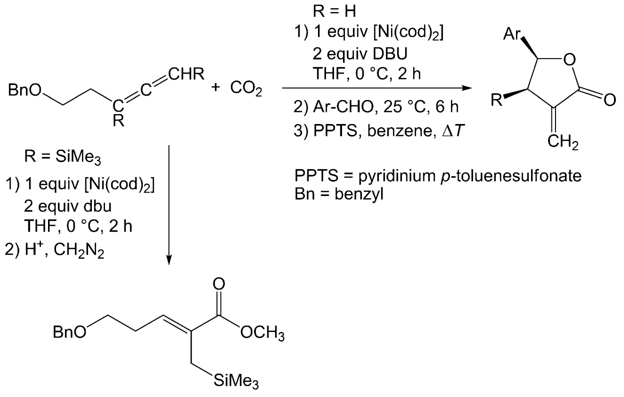
Reactions with allenes and conjugated 1,3-dienes were also studied. Hoberg and Schaefer prepared sorbic acid from [Ni(cod)$_2$], dcpe or bipy as ligands, 1,3-pentadiene, and 1 bar CO_2 in THF at room temperature.[24] It was found that the coupling of 1,3-dienes with CO_2 at nickel(0) does not proceed via a nickelalactone, but rather gives allyl carboxylates (see Section 3.2.2), which also have to be protonated to release the CO_2-containing product.[25] When tmeda is used as the ligand, another CO_2 molecule reacts with the allyl carboxylate to yield a α,ω-dicarboxylate ligand at the nickel(0) center.[26] Allenes such as $R_2C{=}C{=}CH_2$ ($R = H$, CH_3) undergo the coupling reaction to give a 1:1 mixture of 1- and 2-butenoic acids upon hydrolysis, thus indicating that the coupling of the allene is not regioselective.[27]

Apart from nickel(0) complexes, some iron(0) complexes also mediate the coupling reaction of CO_2 and olefins to form metallalactones. Hoberg et al. investigated the reaction of [Fe(η^4-butadiene)(PMe$_3$)$_3$] with 3 bar CO_2 in THF, and were able to isolate an iron(II) allylcarboxylate complex at $-80\,°C$.[28,29] Hydrolysis at room temperature in THF solution gave two products, and it was found that the isolated complex is in equilibrium with the ferracyclobutenoate (Scheme 5). When the diethylene complex was used instead of butadiene, it was demonstrated that, depending on the phosphine (dcpe versus PMe$_3$), the obtained ferracyclopropionate undergoes β-H elimination. However, the carboxylate ligand rearranges to an oxaferracyclobutanone rather than leaving the iron center. Both the ferracyclopropionate (with dcpe) and the oxaferracyclobutanone (with PMe$_3$) can react further with CO_2 to afford dicarboxylates.[30]



Scheme 5. Reaction of [Fe(η^4-butadiene)(PMe$_3$)$_3$] with CO_2.

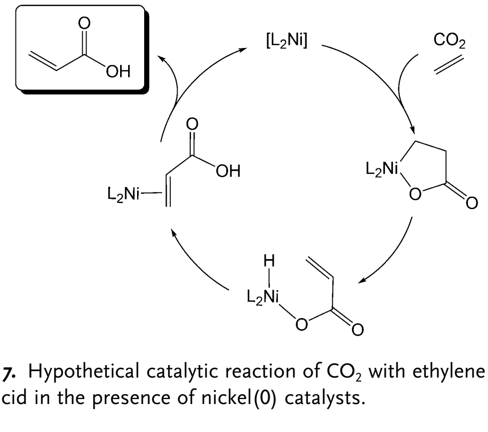
Although the complex-mediated oxidative coupling of CO_2 and olefins always involves aqueous product workup, which destroys the metal complex and is thus inconvenient in terms of recovering the complex and its reusability, this concept is still considered as useful in the literature. Several recent reports rely on this method for the regioselective synthesis of carboxylic acids. Mori and co-workers reported on the oxidative coupling of CO_2 (1 bar), various aryl aldehydes, and allenes to form five-membered lactones in yields of 56–66% (Scheme 6).[31] The reaction of CO_2 with trimethylsilylallene and [Ni(dbu)$_2$] formed in situ produces allyl silane esters in yields of 45–78%.[32]



Scheme 6. Oxidative coupling of allenes, CO_2, and aryl aldehydes with nickel(0) complexes.

3.1.2. Synthesis of Acrylic Acid—A Challenge for Homogeneous Catalysis

Acrylic acid is an important basic chemical for the synthesis of polyacrylates, which find use as special plastics and superabsorbers. At present, acrylic acid is synthesized on a scale of more than 3×10^6 tons per year through the industrial SOHIO process by the oxidation of acrolein over heterogeneous molybdenum/vanadium oxide catalysts at 300 °C. Acrolein itself is available from the oxidation of propene over bismuth/molybdenum oxides.[33] It is, therefore, of great interest to develop a cost-efficient route to acrylic acid under mild conditions. The formation of nickelalactones from olefins and CO_2 (see Section 3.1.1) implies that it could be possible to eliminate the carboxylate ligand from the nickel center by β-H elimination to form a nickel acrylate complex. This should result in the cleavage of the acrylic acid and the recovery of the nickel(0) complex, thereby resulting in a full catalytic cycle (Scheme 7). In this context, the synthesis of acrylic acid from the cheap starting materials ethylene and CO_2 is particularly attractive. However, β-H elimination is not favored for steric reasons: the rigid five-membered ring does not allow the β-H atoms to come close to the nickel center. Hence, the nickelalactones are in most cases quite stable molecules, and cleavage of the Ni–C or the Ni–O bond would not occur without decomposing the nickel

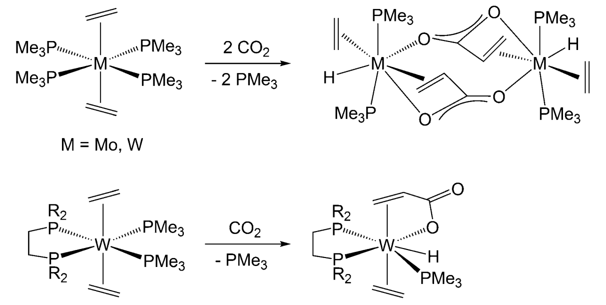


Scheme 7. Hypothetical catalytic reaction of CO_2 with ethylene to give acrylic acid in the presence of nickel(0) catalysts.

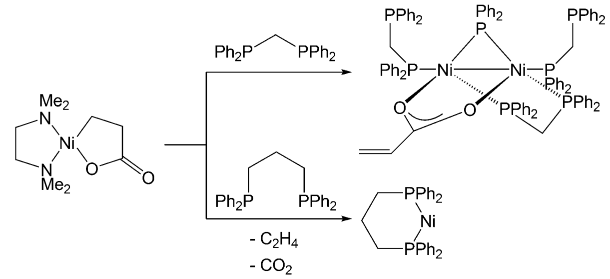
complex. Thus, most studies describe the transformation of CO_2 to carboxylic acids by acid hydrolysis of the nickelalactones, which requires stoichiometric amounts of nickel, thus preventing a catalytic application.

Hoberg et al. observed that when styrene was used as a coreactant in the oxidative coupling with CO_2 in the presence of $[Ni(dbu)_2]$, treatment with aqueous hydrochloric acid resulted in the formation of cinnamic acid as a side product.[34] This led to the conclusion that β-H elimination must have occurred in a side reaction to form a (RCOO)nickel(II) hydride complex.[35] However, this finding could not be used to steer the reaction into a catalyzed process, since the hydride was transferred to the dbu ligand. In other cases where different ligands were present at the nickel center, β-hydride elimination was not observed at all. The appearance of nickel hydrides as a product of the β-H elimination from a nickelalactone led to an extensive investigation of the nickel-catalyzed synthesis of acrylic acid (Scheme 8). Carmona et al. have shown that complexes of the type $[M^0(\eta^2\text{-}C_2H_4)_2)(PR_3)_4]$ (M = Mo, W; R = CH_3) readily react with CO_2 (1 bar at 25 °C) to yield monomeric and dimeric complexes, which contain an acrylate ligand and a hydride (Scheme 8).[36,37] Very recently, Bernskoetter and Tyler showed that the complex $[\{(Ph_2PCH_2CH_2)PPh\}Mo(N_2)_2(C_2H_4)]$ reacts with CO_2 to form an analogous complex.[19] DFT calculations by Schubert and Pápai revealed that a phosphine ligand dissociates from the nickel center in the first step. Subsequently, a CO_2 molecule occupies the vacant coordination site, and then oxidative coupling to a metallalactone occurs. This metallalctone has to adopt a nonplanar conformation to facilitate an agostic interaction between the metal center and a β-hydrogen atom to form an acrylate.[38] However, all experimental work performed to date indicates two key problems: First, it is difficult to control both the formation of the acrylate from metallalactones and the reductive elimination, that is, cleavage of the acrylate ligand, and, second, recovery of the metal complex and formation of a new metallalactone is difficult. Unfortunately, the catalytic cycle presented in Scheme 7 has not yet been realized.

Yamamoto et al. studied the coordination of acrylic acid to nickel(0) complexes and observed a rapid rearrangement to a nickelalactone, thus indicating that the β-H elimination to yield an acrylate is not favored.[39] Walther and co-workers showed that the nature of the chelating bisphosphine ligand at the nickel center has a pronounced effect on the reactivity of the oxidative coupling of CO_2 and ethylene (Scheme 9).[40] The exchange of the tmeda ligand in the (tmeda)nickelalactone by 1,3-bis(diphenylphosphino)propane (dppp) leads to a reversion of the coupling reaction, whereas the substitution by bis(diphenylphosphino)methane (dppm) gives a dinuclear nickel compound with acrylate moieties. In this reaction, one PPh_2 moiety is cleaved from the dppm, and this scavenges the nickel hydride to give Ph_2PCH_3, similar to the role of the dbu ligand in the study by Hoberg et al. (see Section 3.1.1). Thus, the acrylic acid could not be liberated.

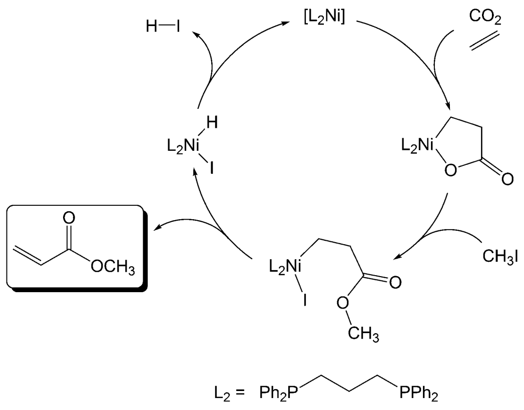


Scheme 8. Carmona's synthesis of acrylate-ligated molybdenum and tungsten complexes by oxidative coupling of CO_2 with ethylene and subsequent β-H elimination.



Scheme 9. Formation of acrylate ligands from nickelalactones.

Based on these findings, several studies on the influence of the nature of the ligand at the nickel center (steric and electronic effects) on the ability for β-H elimination to occur were performed by treating different bidentate ligands with a model nickelacyclopropionate complex with ligands such as tmeda[41] or pyridine;[42] however, the results were unsatisfying.[43] In 2007, Buntine and co-workers presented DFT calculations which showed that the formation of nickel hydrides through β-H elimination of nickelalactones is energetically unfavorable because of the ring strain and the accessibility of the β-hydrogen atom to the nickel center.[44] An elongation of the Ni–O bond leading to an agostic interaction between the β-H atom and the nickel center was, however, proposed on the basis of their calculations. Hence, the β-H elimination should be more favorable if the ring opened up, for example, by cleavage of the Ni–C or Ni–O bond. Pápai and co-workers also performed DFT calculations on β-H elimination from palladaesters, and found that esterification of metallalactones should enable the β-H elimination to occur.[45] Rieger and co-workers recently confirmed the theoretical findings experimentally, and showed that β-H transfer to the nickel center can be induced by a splitting of the Ni–O bond.[46] The oxidative addition of methyl iodide to the (dppp)nickel lactone affords a nickel(II) iodide species with a C-bound methyl propionate ligand, which is then cleaved through β-H elimination (Scheme 10) to yield methyl acrylate. The resulting [(dppp)Ni(H)(I)] complex undergoes reductive elimination, thus generating [(dppp)Ni] and closing the catalytic cycle. This is the first report on the liberation of an acrylate from a metallalactone. However, the reaction is not catalytic, and acrylic acid is obtained in a yield of 33 % when CH_3I is used as the solvent in the reaction. Furthermore, the authors encountered a significant degree of decomposition of the complex to elemental nickel.



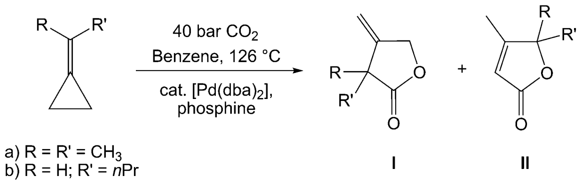
Scheme 10. Synthesis of methyl acrylate from CO_2, ethylene, and methyl iodide, mediated by [(dppp)Ni].

More recently, it was shown that the bidentate ligand has a large effect on the conversion of nickelalactones into acrylates upon treatment with CH_3I: when the ligand is too bulky, the ring-opened product, shown in Scheme 10, cannot undergo β-H elimination. The best yields of methyl acrylate so far (56 %) were obtained with the tmeda ligand.[47] All the studies on transition-metal-catalyzed reactions of CO_2 with ethylene performed over the last decades have shown that, from a thermodynamics viewpoint, it is very difficult to liberate acrylic acid from nickelalactones, unless the ring is opened and thus access of the β-hydrogen atom to the nickel center sterically facilitated.

3.2. Catalytic Conversion of Olefins and CO_2

3.2.1. Palladium-Catalyzed Synthesis of Lactones from CO_2 and Olefins

In 1979, Inoue et al. published a report on the synthesis of five-membered lactones by the reaction of CO_2 and methylenecyclopropanes by using palladium phosphine complexes as catalysts.[48] Treatment of isopropylidenecyclopropane with 40 bar CO_2, 2.35 mol % [Pd(dba)$_2$] (dba = dibenzylideneacetone), and 10 mol % PPh_3 or dppe in benzene at 126 °C for 20 h gives a mixture of two lactones in nearly quantitative yield (Scheme 11). When PPh_3 is used, the main product is compound **I**, whereas the use of the chelating dppe ligand leads preferencially to compound **II**. The authors, however, gave information on neither the activity nor the reusability of the catalyst. From a mechanistic viewpoint, the cyclopropane most probably undergoes ring opening at the catalytically active [Pd(PR$_3$)$_n$] species as the first step to generate a palladacyclobutane. In the next step, CO_2 can insert into the Pd–C bond of the palladacycle to give a palladalactone from which product **II** is formed. Binger and Weintz reported that the palladium-catalyzed reaction of methylenecyclopropanes with 60 bar CO_2, shown in Scheme 11, leads to lactones, which, however, undergo a further palladium(0)-catalyzed reaction with the starting material.[49] The C–H bonds in the 2- and 4-positions of the butenolide **II** can easily be activated by palladium to afford C–C coupling products of the butenolide and the ring-opened cyclopropane moiety. The reaction continues until all the protons in the 2- and 4-positions have been cleaved. Binger and Weintz suppressed this undesired side reaction by changing the reaction conditions, that is, the metal precursor (0.33 mol %) and ligand (3.3 mol %) concentration as well as the solvent (DMF), which led to an increase in the product yield to 51 %.

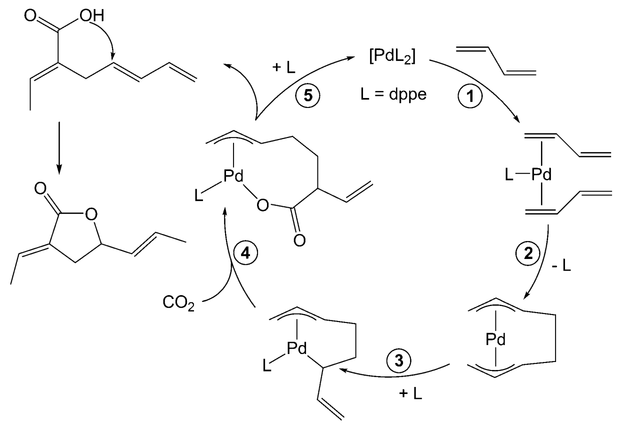


Scheme 11. Palladium-catalyzed synthesis of lactones by coupling of CO_2 and methylenecyclopropanes.

3.2.2. Palladium- and Nickel-Catalyzed Telomerization of Dienes and CO_2

Whereas the oxidative coupling of monoolefins with CO_2 at transition metals is in all the reported cases based on a stoichiometric reaction of C_2H_4, CO_2, and the metal to form a metallalactone, which can only give carboxylic acids by complex decomposition, the reactions of CO_2 and dienes follow an entirely different reaction pattern.[50,51] Usually, the reactions are metal-catalyzed and yield more than one product, since dienes tend to telomerize at late transition metals. This is a reaction type which has long been known to be catalyzed by metallic nickel; for example, the synthesis of cdt was originally carried out from 1,3-butadiene and nickel metal.[52] The research groups of Inoue and Musco were the first to report the reaction of carbon dioxide and dienes catalyzed by palladium(0) complexes.[53,54] Treatment of 1,3-butadiene with 50 bar CO_2 and 0.15 mol % [Pd(dcpe)$_2$] or [Pd(PPh$_3$)$_4$] at 120 °C for 20 h (in DMF, DMSO, *t*BuOH, or benzene) gave mixtures of butadiene oligomers, such as 1,3,6-, 1,3,7-, and 2,4,6-octatriene. However, traces of the lactone 2-ethylidene-hept-5-en-4-olide and unsaturated carboxylic acids were also found, most probably formed according to Scheme 12. The insertion of CO_2 into the palladium–allyl bond (Scheme 12, step 4) was confirmed by Jolly et al., who isolated nickel and palladium carboxylates from the reaction of [Ni(η^3-(2-methylallyl)$_2$] and [Pd(η^3-allyl)$_2$] complexes, respectively, with a stream of CO_2 in the presence of phosphines.[55,56] It was found that bidentate phosphine ligands increase the yield of lactones.[57] Soon after, several research groups reported the synthesis of acids and lactones by using homogeneous catalysts. Hoberg et al. attempted to extend this concept to nickel, but it was found that unlike palladium, nickel does not undergo reductive elimination of the allyl carboxylate ligand (Scheme 12, step 5), but remains stable as a nickel(II) complex, and hydrolysis is necessary to release the carboxylic acid (see Section 3.1.1).

Later, Hoberg et al. found a route to the catalytic conversion of 1,3-butadiene and CO_2 with nickel(0) catalysts.[58] Treatment of a THF/DMF solution of 1,3-butadiene



Scheme 12. Palladium-catalyzed reaction of CO_2 with 1,3-butadiene by the research groups of Inoue and Musco.

with 20 bar CO_2 in the presence of $[Ni(cod)_2]$ and 3 equivalents $P(O\textit{i}Pr)_3$ (catalyst concentration: 0.12 mol %) for 30 h at 60 °C leads to a olefin-functionalized cyclopentane carboxylic acid in a conversion of 95 % and a turnover number (TON) of 30 (Scheme 13). However, despite this finding, no further report on the catalytic telomerization of butadiene and the incorporation of CO_2 by using nickel catalysts have appeared.

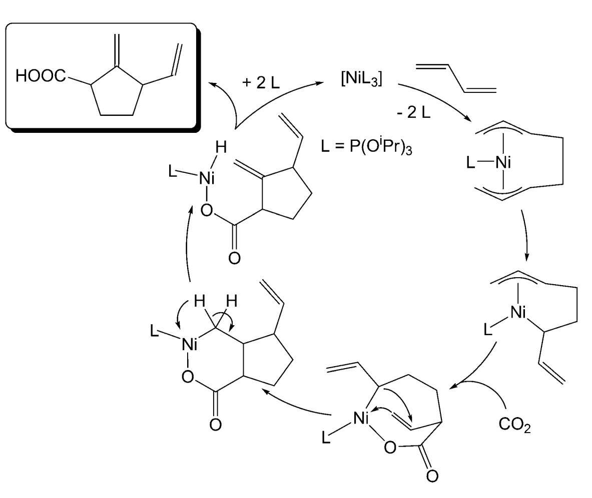
Walther et al. found that the reaction of 2,3-dimethyl-1,3-butadiene and CO_2 in the presence of $[(tmeda)Ni^0]$ does not lead to cleavage of the corresponding carboxylic acid or lactone; instead, thermal treatment of the metallalactone releases the product and the complex decomposes.[59] Similarly, Behr and Kanne treated 1,3,7-octatriene and CO_2 with stoichiometric amounts of [(bipy)Ni(cod)] to obtain mono- and diesters after methanolysis.[60]

More recently, Walther and co-workers have shown that nickel(0) complexes with N-heterocyclic carbenes as ligands lead to a variety of stable nickel(II) lactones.[61] Thus, it appears that nickel-mediated conversions of dienes and CO_2 are not catalytic and the only way to obtain the transformation products is by the hydrolysis described in Section 3.1.1.[62,63] Thus, this route has never found broad application.

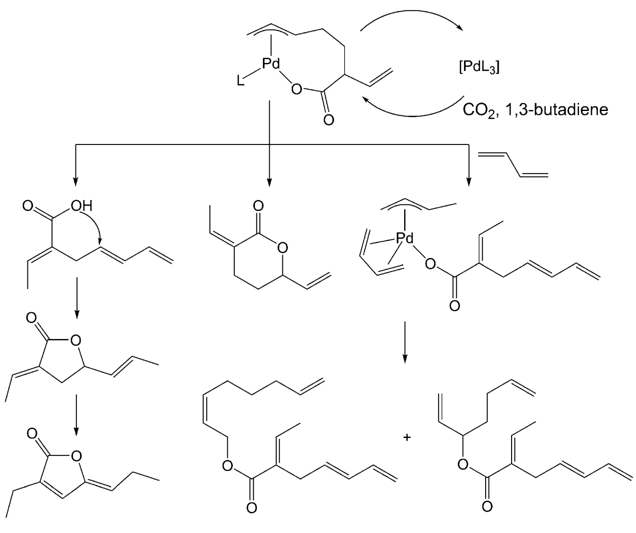
Soon after, it was found that palladium(0) complexes catalyze the synthesis of carboxylic acids from dienes and CO_2. Studies also focused on the utilization of nickel(II) and palladium(II) compounds as catalysts for this type of reaction. Döhring and Jolly probed the co-oligomerization of allenes and CO_2 with catalytic amounts of $[Pd(\eta^3\text{-allyl})_2]$ and mono- or bisphosphines in toluene, and obtained a mixture of six-membered lactones and esters.[64] Behr and co-workers improved the original synthetic procedures of Inoue and Musco by using palladium(II) acetate or acetylacetonate complexes and phosphines in acetonitrile as the solvent, which led to a significant increase in the yield of the lactones.[65] They found that the basicity and the cone angle of the phosphines have a large influence on the product distribution: sterically demanding phosphines favor lactones, whereas smaller ones usually lead to open esters.[66] In general, it was found that six major products (Scheme 14) may be obtained with palladium catalysts having acetate ligands[67,68] or $[Pd(NCMe)_4][BF_4]_2$.[69]

Ruthenium hydride catalysts were also tested, but they were found to be quite inactive. In an analogous manner, Behr and He also used the complex $[Rh^I(\eta^2\text{-}C_2H_4)_2(acac)]$ as the catalyst for the trimerization of the lactone 2-ethyl-2,4,9-undecatrien-4-olide from 1,3-butadiene and CO_2.[70] Dinjus and Leitner investigated the reaction of isoprene and CO_2 with a set of palladium catalysts and phosphines, but obtained very low yields (ca. 1 %).[71]

All the studies highlighted in this section show that molecular palladium complexes can catalyze the transformation of dienes and CO_2 to give carboxylate-containing compounds. Nevertheless, the major drawback is the difficulty in controlling the product distribution. Although some progress has been made,[72] the reaction conditions are rather harsh.



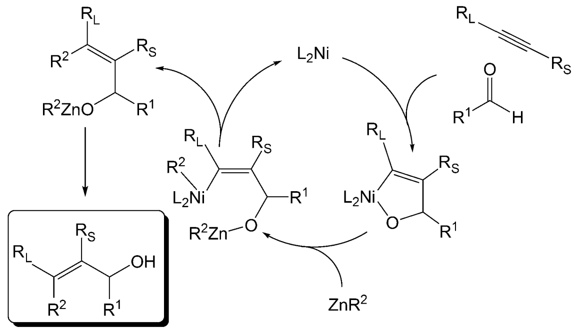
Scheme 13. Nickel(0)-catalyzed conversion of 1,3-butadiene and CO_2 into carboxylic acids according to Hoberg et al.



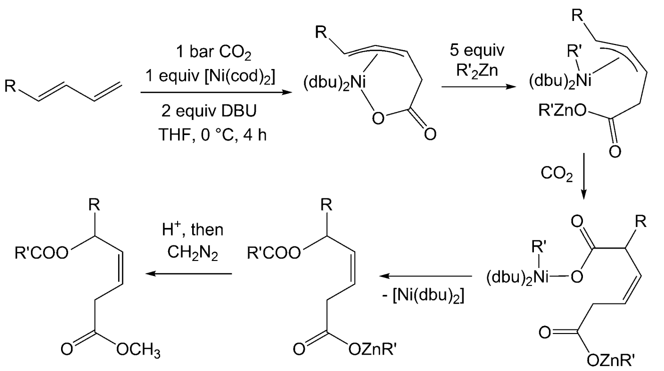
Scheme 14. Product distribution in the palladium(II)-catalyzed reaction of 1,3-butadiene and CO_2.

3.2.3. Catalyzed Synthesis of Carboxylic Acids from Olefins and CO_2—Carboxylate Cleavage by Transmetalation

As seen in the Sections 3.1 and 3.2.1, there are numerous examples of the transformation of CO_2 at transition-metal centers. However, the cleavage of the converted species is often a problem, since these either contain stable ligands (esters, carboxylates etc.) or require ligand rearrangements—which would lead to cleavage from the metal (e.g. β-H elimination)—that are not favored for thermodynamic or steric reasons. Hence, the reactions which give acids, esters, or lactones are usually stoichiometric, thus requiring a large amount of metal complexes. The metal complexes, however, are rather difficult to synthesize and are very air sensitive, so these methods are not recommended, particularly on a large scale or for industrial applications. In the last few years, several research groups have focused on the chemical dissociation of carboxylate ligands by oxophilic reagents. In 1997, Oblinger and Montgomery reported the synthesis of allylic alcohols from alkynes and aldehydes by using nickel(0) catalysts (5 mol%; Scheme 15).[73] After formation of an oxanickelacycle, similar to the oxidative coupling of CO_2 and olefins, the Ni–O bond is activated by ZnR_2 compounds, which transfer one R moiety to nickel center, while the RZn group binds to the oxygen atom (Scheme 15). Reductive elimination releases the product and the nickel catalyst is regenerated. Subsequent hydrolysis produces the respective allyl alcohols in good yields. Catalyst workup procedures as well as turnover frequencies and numbers were unfortunately not mentioned.



Scheme 15. Illustration of the cleavage of a Ni–O bond with organozinc compounds, first reported by Montgomery and Oblinger. R_L = large moiety, R_S = small moiety.

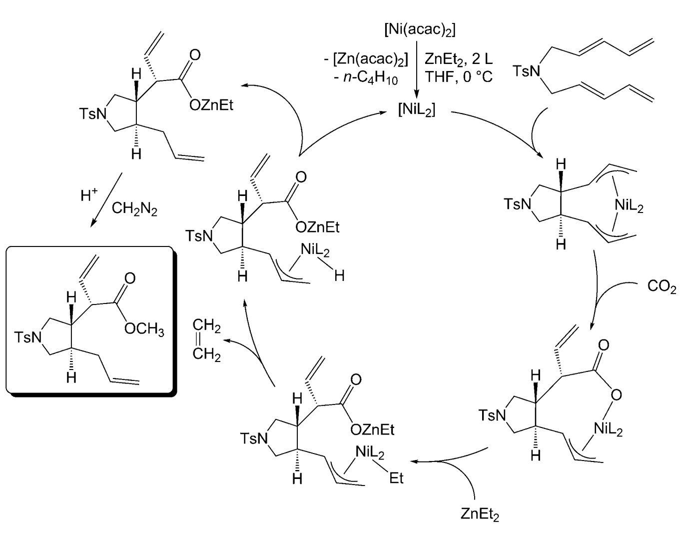


Scheme 16. Stoichiometric reaction of 1,3-dienes, CO_2, Ni^0, and ZnR'_2 (R' = Ar, Me) to unsaturated diesters.

Soon after, Mori and co-workers systematically developed this concept[74] and combined it with the earlier work of Hoberg and Walther. They used diorganozinc reagents to cleave products from the reactions of olefins and alkynes (see Section 3.3) with CO_2 from the transition metals.[75] The first report describes the coupling of 1,3-dienes and CO_2 (1 bar) mediated by nickel(0) complexes, and the subsequent transmetalation using dimethyl- or diarylzinc (Scheme 16).[76] The transmetalation affords a [Ni^{II}R'] species, which readily undergoes reductive elimination, thereby releasing the R'OOCR product and reforming the nickel(0) catalyst. However, the workup process of the product (removal of zinc) destroys the nickel complex and it was thus not applied as a catalyst. However, the reaction had the potential to be carried out with catalytic amounts of nickel(0), since it could be recovered without decomposition.

Soon after, Mori and co-workers showed that treatment of bis-1,3-dienes and CO_2 with 10 mol% [Ni(acac)$_2$] or [Ni(cod)$_2$], phosphines, and an excess of diethylzinc led to a ring-closing carboxylation of the dienes in very good yields and stereoselectivities.[77,78] A remarkable feature of this reaction is the role of $ZnEt_2$ not only as a transmetalation agent, but also as a reduction medium, thus allowing the use of [Ni(acac)$_2$] as a precatalyst, which is not air sensitive and commercially available, and is reduced by the zinc compound to give the catalytically active nickel(0) phosphine complex. As already described in Section 3.2.1 (Scheme 13), dienes react with nickel(0) to afford bisallyl species. The addition of CO_2 (1 bar) leads to its insertion into one of the nickel–allyl bonds (Scheme 17).

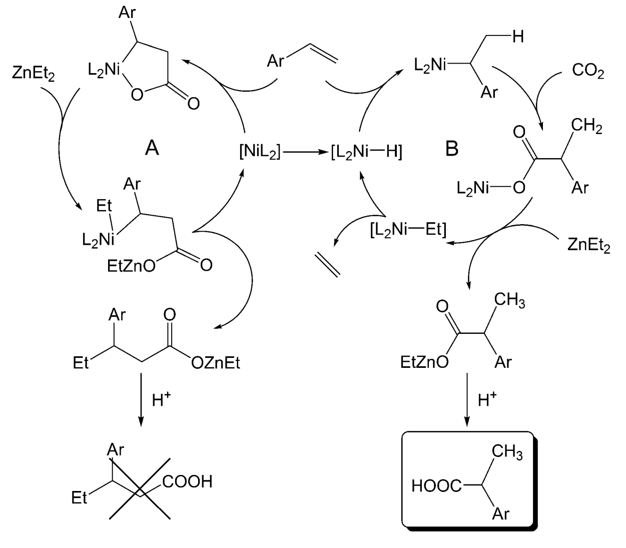
$ZnEt_2$ transfers one ethyl group to the nickel center and the ZnEt moiety cleaves the Ni–O bond. The ethyl ligand at the nickel center is transformed through β-H elimination to



Scheme 17. Nickel(0)-catalyzed stereoselective ring-closing carboxylation of bis-1,3-dienes. Ts = toluene-4-sulfonyl.

ethylene and a nickel hydride species, which is unstable and transfers its hydrogen atom to the allyl group, thus cleaving the carboxylation product. The final product is formed after workup with hydrochloric acid and diazomethane. The reaction is not only catalytic, it also leads to a high stereoselectivity at the α-carboxylate atom. The stereoselectivity can be directed by addition of chiral mono- or diphosphine ligands. The highest enantiomeric excess was obtained with 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl (MeO-MOP). However, the authors did not quantify the catalytic activity in terms of turnover frequencies or numbers. Thus, it is unclear whether the cleaved zinc carboxylate species can be separated from the recycled catalyst, so that it can be used as a "real" catalyst, or if the "catalyst" must be destroyed to make isolation of the transformation product possible, irrespective of whether the reaction itself is stoichiometric or not. In analogy to the described reactions of CO_2 and olefins catalyzed by nickel(0) complexes, Mori and co-workers also treated trimethylsilylalkynes with CO_2 (1 bar) in the presence of the in situ formed $[Ni^0(dbu)_2]$ catalyst (20 mol%) in THF at 0°C.[79] The corresponding oxanickelacycle was formed, with the $SiMe_3$ group located at the α position to the Ni center. The subsequent treatment with dialkylzinc compounds led to the transfer of one alkyl group from the zinc to the nickel center. The ZnR moiety causes ring opening and binding of the carboxylate moiety. Workup with HCl and CH_2N_2 afforded α,β-unsaturated methyl carboxylates in yields of 49 to 76%. Mori and co-workers also developed synthesis protocols to some natural products where the reaction of a alkyne precursor and CO_2 is a key step, for example, in the synthesis of erythrocarine[80] and tamoxifen.[81]

Very recently, Rovis and co-workers adopted the transmetalation concept as a key step in the catalytic oxidative coupling of olefins and CO_2 with nickel catalysts.[82] The reaction of styrene or styrene derivatives with *para* substituents and 1 bar CO_2 in THF at room temperature (Scheme 18) in the presence of a $[L_2Ni^0]$ complex (10 mol%; L = pyridine, dbu, or $CsCO_3$) and an excess of $ZnEt_2$ (15-fold excess relative to Ni) surprisingly does not yield a product which would form as a result of the reaction of the olefin and CO_2 to give a metallalactone (Scheme 18, path A) and 3- or 4-phenylvaleric acid, according to Hoberg's findings (Scheme 4). Instead, 2-phenylpropionic acid (and derivatives) forms in yields between 56 and 92%, depending on the substituent on the phenyl ring. Rovis and co-workers postulated the reaction of a nickel hydride with styrene (Scheme 18, path B) prior to insertion of CO_2 into the Ni−C bond (see Section 4). Although the product clearly indicates that path B operates, the source of the nickel hydride is unclear. Most probably, hydrides are formed as by-products in the reduction of $[Ni(acac)_2]$ with $ZnEt_2$ and the subsequent β-H elimination. The long-term catalytic potential of this system was not demonstrated by the authors; the reaction mixture was worked up with HCl.

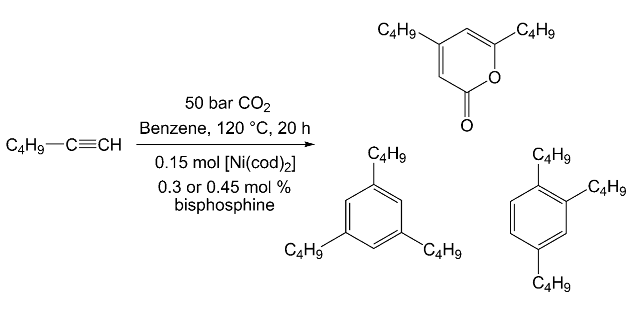


Scheme 18. Mechanism proposed by Rovis et al. for the nickel-catalyzed carboxylation of styrene with CO_2.

The examples presented in this section show that transmetalation with diorganylzinc compounds is a promising step towards the utilization of CO_2 and olefins as synthons for a truly catalytic synthesis of elaborate enantioselective molecules, which can be synthesized at very moderate CO_2 pressures, at ambient temperature or even below, and which can be applied in the synthesis of fine chemicals. Nevertheless, it has not yet been reported whether the catalysts can be used in more than one cycle, most probably because a convenient route to separate the product from the catalyst has not yet been found.

3.3. Coupling of CO_2 and Alkynes

Soon after Aresta's publication concerning the synthesis of $[(Cy_3P)_2Ni(\eta^2\text{-}CO_2)]$, Inoue et al. published the first report on the catalytic properties of nickel(0) compounds for the conversion of CO_2 into organic molecules. Treatment of 1-hexyne with 50 bar CO_2, 1.5 mol% $[Ni(cod)_2]$, and various bisphosphines (dppm, dppe, dppp, or bis(diphenylphosphino)butane (dppb)) in benzene at 120°C for 20 h gave a mixture of cyclotrimerization products (Scheme 19).[83] Notably, the alkyne also undergoes cyclotrimerization at the nickel(0) center without incorporation of CO_2, even at a pressure of 50 bar. The desired product 4,6-dibutyl-2-pyrone is only formed in a maximum 10% yield, whereas the other two main products, 1,3,5- and 1,2,4-tributylbenzene, are



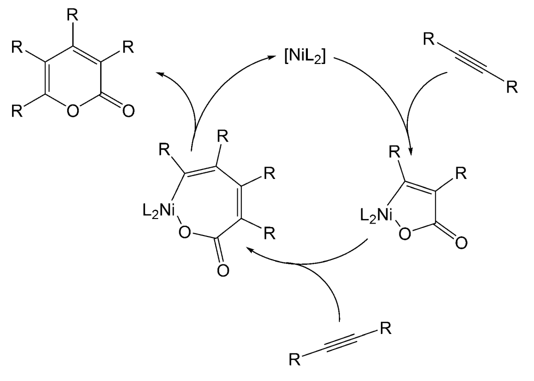
Scheme 19. Nickel(0)-catalyzed oxidative coupling of CO_2 and alkynes.

formed in maximum yields of 16.4 % and 3.3 %, respectively. Analogously, Albano and Aresta used the complex [(dppe)Rh][BPh$_4$] as a catalyst (0.75 mol %) for the oligomerization of methylacetylene (CH$_2$Cl$_2$, 60 °C, 12 h), which gave a mixture of dimeric, trimeric, and aromatic products.[84] When the reaction was carried out in the presence of CO$_2$ (60 bar, CH$_3$CN, 120 °C), 4,6-dimethyl-2-pyrone was detected as one of the products, but only in 3 % yield. Inoue et al. found that the maximum conversion of 1-hexyne and the maximum yield of pyrone is obtained when dppb is used in a fourfold excess as the ligand to the nickel. Later, it was found that the same reaction gives much better yields of pyrone when 3-hexyne is used (4.5 mol % [Ni(cod)$_2$] and 9 mol % dppb; maximum yield: 54 % at a conversion of 99 %), along with several by-products.[85]

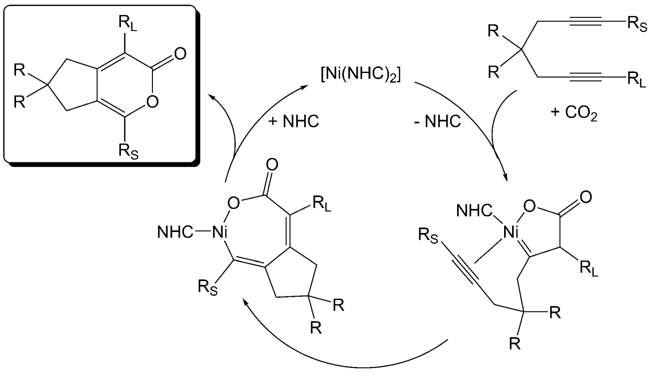
Inoue et al. proposed a mechanism involving the formation of nickelacyclopentadiene from the nickel catalyst and two equivalents of alkyne, followed by subsequent insertion of CO$_2$ to afford the pyrone. Hence, the insertion of another alkyne molecule into the metallacycle leads to the formation of side products, thus competing with the incorporation of CO$_2$.[86] Tsuda et al. treated diynes and CO$_2$ (50 bar) with equimolar[87] or catalytic (10 mol %)[88,89] amounts of [Ni(cod)$_2$] and several bisphosphines in benzene or THF at elevated temperatures for 20 h to obtain bicyclic pyrones in good to moderate yields. It was found that electron-donating substituents at the terminal alkyne carbon atom promote cycloaddition. Walther et al. studied the influence of the nature of the phosphine ligands and the solvent on the product distribution. In general, the use of phosphine ligands with rather small cone angles leads to an increase in the pyrone yield; the reaction of 3-hexyne with 10 bar CO$_2$ in a 1:1 mixture of THF and acetonitrile in the presence of 1.7 mol % [Ni(cod)$_2$] and 3.4 mol % PEt$_3$ leads to a 100 % conversion and to a yield of 96 % of tetraethyl-2-pyrone.[90] Walther et al. proposed that a oxanickelacycle is formed in the first step of the reaction, analogous to the reaction of olefins and CO$_2$, and this is followed by insertion of another alkyne into the Ni−C bond of the oxanickelacycle (Scheme 20).[91] This is in contrast to Inoue's proposal, but was confirmed by other research groups, who isolated an oxanickelacycle from the reaction of [NiL$_2$] with CO$_2$ and an excess of alkyne.[92] On the basis of DFT calculations, Buntine and co-workers suggested that, in analogy to the reaction of CO$_2$ and olefins at nickel(0) complexes, the reaction with alkynes leads to a thermodynamically very stable product from the oxidative coupling of one alkyne and CO$_2$.[93]

More recently, several research groups revisited the catalyzed oxidative coupling of alkynes and CO$_2$. Louie et al. focused on the synthesis bicyclic pyrones from diynes and CO$_2$ in the presence of nickel(0) complexes with N-heterocyclic carbene (NHC) ligands.[94] The reaction of various diynes at 1 bar CO$_2$ and 5 mol % [Ni(cod)$_2$] in toluene, benzene, or THF at 60 °C only gave good yields when NHCs were used as the ligands. This can be attributed to the fact that the applied NHCs are sterically very bulky ligands and side reactions such as cycloadditions of alkynes without incorporation of CO$_2$ or the formation of 14 valence-electron intermediate [Ni(alkyne)$_2$] species cannot occur. A proposed mechanism for the formation of bicyclic pyrones is presented in Scheme 21. The authors showed that diynes having asymmetric substituents at the terminal alkyne carbon atoms tend to form oxynickelacycles with CO$_2$. The alkyne bears the larger substituent R$_L$, since the second alkyne unit bearing the smaller substituent R$_S$ comes closer to the sterically demanding NHC ligand, thus controlling the regioselectivity of the reaction.[95]

Duñach et al. selected another approach to access nickel(0) catalysts for the conversion of CO$_2$ and several alkynes and diynes.[96–98] Instead of using [Ni(cod)$_2$] or other nickel(0) precursors, which are very difficult to synthesize and to handle, the authors reduced [Ni^{II}(bipy)$_3$][BF$_4$]$_2$ electrochemically to [Ni^0(bipy)$_2$] and MgBF$_4$ by using Mg as the anode. For example, the one-pot reaction of 1-octyne, 1 bar CO$_2$, and 10 mol % [Ni^{II}(bipy)$_3$][BF$_4$]$_2$ in DMF and 3 % methanol at 20 °C gave a conversion of 70 % and 95 % yield of 2-methyleneoctanoic acid. However, at the end of the reaction, the mixture was worked up with hydrochloric acid, so that the reusability of the [Ni^{II}(bipy)$_3$] precatalyst species is, at best, questionable. The authors propose the formation of a oxanickelacycle from the in situ formed nickel(0), the alkyne, and CO$_2$, followed by carboxylate transfer to Mg^{2+} to give [Mg(OOCR)$_2$], which has to be treated with H$^+$ to give the final product.



Scheme 20. Proposed mechanism for the catalytic transformation of CO$_2$ and alkynes to pyrones (L$_2$ = (PR$_3$)$_2$, bipy, tmeda).



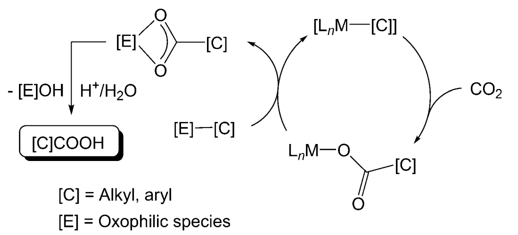
Scheme 21. Proposed mechanism for the cycloaddition of diynes and CO$_2$ in the presence of [Ni(NHC)$_2$] catalysts.

Furthermore, simple copper(I) and silver(I) halide salts were used as catalysts for the reaction of CO_2 and alkynes, and are possible alternatives to the use of nickel(0) compounds, which are difficult to handle. Inoue and co-workers reported the synthesis of alkyl alkynoates from alkynes, CO_2 (1 bar), and alkyl halides catalyzed by CuBr (2 mol%) in polar aprotic solvents at 100 °C for 4 h.[99] The authors postulated that CuBr reacts initially with the alkyne to afford copper acetylenide, which is followed by insertion of CO_2 into the Cu–C bond. The subsequent reaction with alkyl halides leads to the formation of an ester and recovery of the catalyst. Similarly, Anastas and co-workers treated phenylacetylene, (3-bromoprop-1-yn-1-yl)benzene, and CO_2 with AgI (5–10 mol%) to obtain arylnaphthalene lactones in moderate yields.[100] Yoo and Li used copper(I) halides as catalysts (30 mol%) for the synthesis of cyclic carbamates in good yields through a coupling reaction of aldehydes, amines, alkynes, and CO_2.[101]

Similar to the reactions of olefins and CO_2, the nickelacycles obtained from alkynes and CO_2 were also transformed by treatment with aqueous acids. Hoberg et al. performed studies on the oxidative coupling of alkynes and CO_2 at nickel(0) centers. However, as in the case of olefins and CO_2, all the studies involved stoichiometric amounts of the nickel complex, and the products were usually treated either with aqueous acids to give carboxylic acids, or with carbon monoxide to give anhydrides of succinic acid and $[Ni(CO)_4]$.[77,102,103] Nevertheless, some other research groups reported the synthesis of carboxylic acids by hydrolysis of metallalactone products formed from CO_2 and alkynes.[104–109]

4. Insertion of CO_2 into M–C σ Bonds

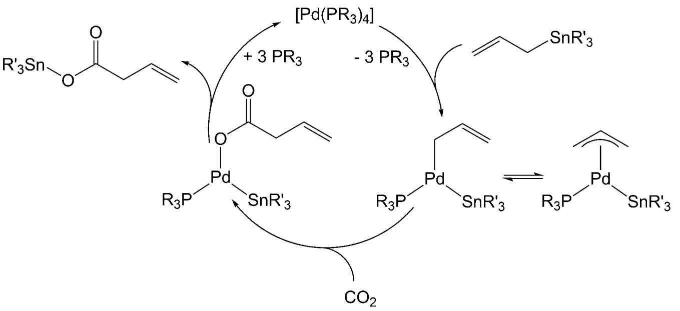
The insertion of carbon dioxide into metal–carbon σ bonds is a long-known reaction. One CO_2 molecule inserts into the M–C bond of a (coordination) compound, which results in the formation of a carboxylate species. This is either bound to the metal through an oxygen atom (normal) or through the carboxylate carbon atom (abnormal). The latter case is quite exotic and only a few examples are known to date. Originally, research focused on investigating this reaction by using oxophilic metals. Ziegler and co-workers had already reported in 1960 that triethylaluminum readily reacts with CO_2 to give the compound $Et_2Al(OOC\text{-}Et)$, which can—depending on the stoichiometry—further react with $AlEt_3$. Subsequent hydrolysis leads to a mixture of carboxylic acids and alcohols.[110] Later, the research groups of Zweifel, Eisch, and Giannini investigated the reaction of unsaturated hydrocarbons with aluminum-, titanium-, and zirconiumalkyl compounds and CO_2.[111–113] Acid hydrolysis leads to the corresponding carboxylic acids and $[Al(H_2O)_6]^{3+}$. The first report on CO_2 insertion into transition-metal–carbon bonds was reported by Vol'pin and co-workers, who treated $[(Ph_3P)_3RhPh]$ with CO_2 to obtain the benzoate complex $[(Ph_3P)_3Rh(OOCPh)]$.[114] Since then, numerous reports on the insertion of CO_2 into M–C bonds have been published and summarized in several reviews.[4,7,9,50,115,116]



Scheme 22. General route for the catalytic conversion of CO_2 into carboxylic acids by insertion into a M–C σ bond.

In general, the catalytic transformation of CO_2 by this route requires two steps (Scheme 22). In the first step, insertion takes place and in a second step the transformed carboxylate is cleaved and the metal catalyst regenerated. This is usually—as is in the cases described in the previous sections—intricate and often requires hydrolysis, which destroys the metal complex and hence the catalysis.

One of the first reports on the catalytic conversion of CO_2 by insertion into a M–C bond was published by Fujiwara and co-workers in 1984.[117] Treatment of simple palladium acetates with aromatic compounds led to activation of the Ar–H bond to yield [Ar-Pd-H] species. Subsequent treatment with 1–30 bar CO_2 gave aromatic carboxylic acids in yields between 2 and 66%. However, the authors also observed—not unusual for palladium complexes— biphenyl cross-coupling products in yields of up to 60%. Some years later, Shi and Nicholas reported the reaction of $[Pd^0(PR_3)_4]$ (8 mol%) with allylstannanes, which gave the oxidative addition products $[(allyl)Pd(SnR'_3)(PR_3)]$.[118] The addition of CO_2 (33 bar, 70 °C, THF) led to insertion into the palladium–allyl bond, thereby creating a carboxylate ligand, which is cleaved from the palladium center by the oxophilic R'_3Sn species (Scheme 23). The authors unfortunately comment neither on product separation or hydrolysis of the stannyl carboxylate to the corresponding acid, nor on the catalyst efficiency (activity, reusability, etc.). Later, Wendt and co-workers reported on the insertion of CO_2 into the Pd–CH_3 bond of the compound $[(PCP)Pd(CH_3)]$ (PCP = 2,6-bis[(R_2P)methyl]phenyl or resorcinolbis(R_2PO)).[119,120] Subsequently, they revisited the work of Shi and Nicholas and treated allylstannanes with CO_2 in the presence of palladium pincer catalysts (5.5–10.5 mol% catalyst, 4 bar CO_2, THF,

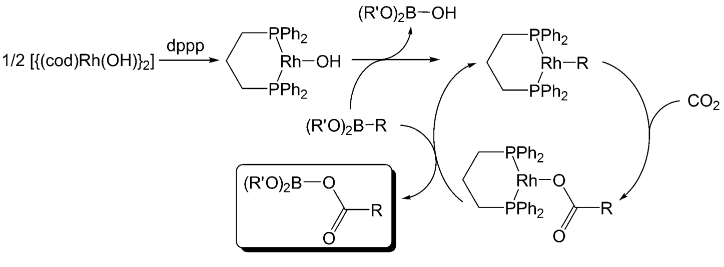


Scheme 23. Synthesis of carboxylstannanes from allylstannanes and CO_2, catalyzed by palladium(0).

80 °C), which afforded stannyl carboxylates in yields between 75 and 80 %.[121] The authors found that the catalyzed process occurs by the same mechanism as shown in Scheme 23. Very recently, Wu and Hazari reported on the carboxylation of allylstannanes and -boranes with [LPd(methylallyl)$_2$] catalysts (5 mol %, 1 bar CO_2, benzene, 25 °C, L = phosphines, NHCs) with yields up to 91 %.[122]

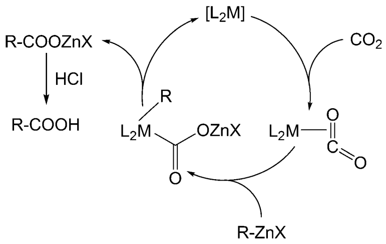
The insertion of CO_2 into M−C bonds is, as many examples in the literature show, a quite straightforward reaction. Cleavage of the transformation product and regeneration of the catalyst is, however, difficult. As seen in the examples of Shi and Nicholas as well as Wendt and co-workers, the concept of cleaving carboxylates with oxophiles (see Section 3.2.2.) is so far the most convenient method. In the last couple of years, several research groups have, therefore, used either boronic esters or zinc/aluminum alkyl compounds. In 2006, Iwasawa and co-workers reported the synthesis of various carboxylic acids from CO_2 (1 bar) and aryl- and alkenylboronic esters in yields of 59–95 %, by using a [(dppp)Rh(OH)] catalyst.[123] The mechanism, shown in Scheme 24, was confirmed by DFT calculations of Dang, Lin, and Marder.[124] In the first step, $RB(OR')_2$ adds to the catalyst (3 mol %, 1,4-dioxane, 60 °C) to form the catalytically active species [(dppp)RhR] and $HOB(OR')_2$. In the following step, CO_2 (1 bar) inserts into the Rh−R bond, thereby transforming the ligand R into a carboxylate. Finally, another equivalent $RB(OR)_2$ cleaves the carboxylate and transfers the R group back to the rhodium center. The authors found that the alkylation of the catalyst was accelerated upon addition of CsF. The carboxylic acids were obtained by acid hydrolysis of the reaction mixture and subsequent chromatography on silica gel. Hence, the catalyst could not be reused. Additionally, it was found that the rhodium catalyst showed only limited tolerance toward functional groups on the aryl/alkenyl moiety. Soon after, Iwasawa and co-workers used [(bisoxazoline)Cu^II)] complexes as catalysts for the carboxylation of aryl- and alkenylboronic esters, and obtained yields of up to 74 %.[125] The catalysis mechanism is analogous to that with the rhodium catalyst; however, the copper complexes are somewhat more stable toward substrates with different functional groups.

On the basis of the studies by Iwasawa and co-workers, Hou and co-workers examined the catalytic properties of copper halide complexes bearing NHC ligands for the reaction of CO_2 with organoboronic esters to afford carboxylic acids.[126] The authors used KO*t*Bu to exchange the halide in a salt metathesis reaction to generate [(NHC)Cu(O*t*Bu)] (THF, 25 °C, 30 min), which then reacts with aryl- or alkenylboronic esters to form the active species [(NHC)CuR)], with $(R'O)_2$BO*t*Bu as a by-product. The subsequent CO_2 insertion is performed at 1 bar pressure in THF (−78 to 25 °C). Numerous substrates were tested, and afforded carboxylic acids (after workup with aq HCl) in yields of 73 to 99 %.



Scheme 24. Synthesis of carboxylic acids from CO_2 and $RB(OR')_2$ with rhodium catalysts.

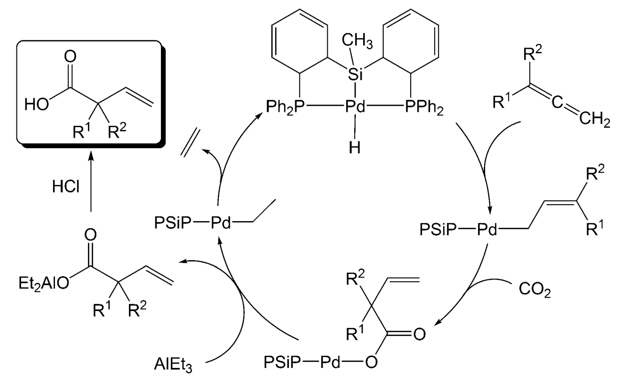
In 2008, the research groups of Oshima and Dong almost simultaneously published their investigations of the reaction of the in situ formed Aresta complex $[(Cy_3P)_2M(\eta^2\text{-}CO_2)]$ (Oshima: M = Ni; Dong: M = Ni, Pd) with alkyl- and arylzinc halides.[127] Oxidative addition affords a (CO_2)MR intermediate, which undergoes a CO_2 insertion (1 bar, THF, 0-25 °C) into the Ni−R bond (Scheme 25). The catalyst concentration varied between 5 and 20 mol %. Takaya and Iwasawa modified this concept by using PSiP pincer palladium hydride complexes.[128]



Scheme 25. General catalytic mechanism for the carboxylation of organozinc halides.

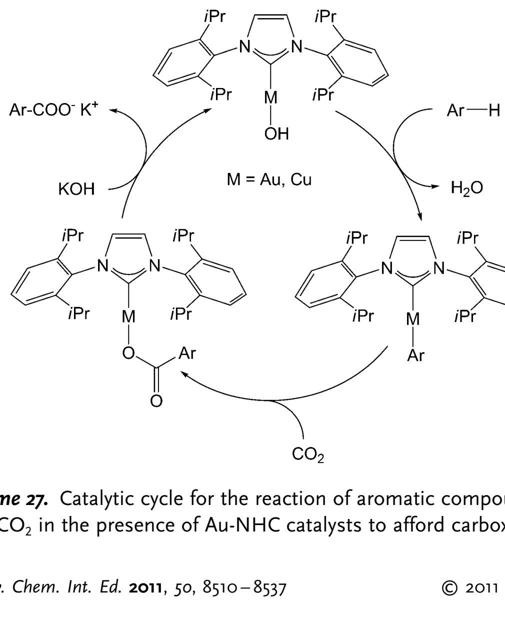
The treatment of allenes with catalytic amounts of [(PSiP)Pd-H] (0.5—1 mol %) affords palladium allyl species. Treatment with CO_2 (1 bar, DMF, 25 °C) results in insertion taking place, with formation of a palladium allyl carboxylate intermediate. The addition of triethylaluminum transfers one ethyl group to the palladium center (thus recovering the palladium hydride by β-H elimination) and cleaves the allyl carboxylate in yields of 88 % (Scheme 26). Interestingly, this reaction is highly regioselective: CO_2 does not insert into the α position of the palladium–allyl bond, but rather enforces a rearrangement and inserts in the γ-C bond that bears the substituents R^1 and R^2. Shortly after, Correa and Martin applied a similar strategy.[129] They treated aryl halides with $[(NHC)_2Pd^0]$ catalysts, which led to an oxidative addition product $[(NHC)_2Pd^{II}(Ar)(X)]$, which was treated with CO_2 (1 bar, diethylacetamide, 40 °C) to afford a palladium benzoate. Subsequent treatment with $ZnEt_2$ led to transmetalation of the carboxylate to the zinc center, and transfer of one ethyl group to the palladium(II) center, which underwent reductive elimination. The carboxylic acid was isolated by acid hydrolysis in almost all cases in nearly quantitative yields.

More recently, the research groups of Nolan and Larrosa used highly basic gold(I) catalysts with NHC ligands for the activation of aryl–hydrogen bonds.[130] The C−H activation is regioselective, since the catalyst attacks the most acidic C−H bond. Boogaerts and Nolan transferred this concept to the synthesis of



Scheme 26. Palladium-catalyzed reaction of CO_2 and allenes to give β,γ-unsaturated carboxylic acids.

carboxylic acid by the in situ formation of Au–Ar bonds by the C–H activation of aromatic substrates with [(NHC)Au(OH)] catalysts and the subsequent insertion of CO_2 into the Au–Ar bond (Scheme 27).[131] In an initial study, they showed that oxazoles can be carboxylated with the gold catalyst by first cleaving the C–H bond (3 mol% catalyst, KOH, THF, 45°C) and subsequent treatment with CO_2 (1.5 bar, 20°C, 12 h). The formed carboxylate ligand is cleaved by the KOH to afford the potassium carboxylate in 94% yield. Although the TOFs are very low and the workup of the carboxylic acid proceeds by acid hydrolysis, this reaction bears some advantages over the other systems presented in this section. First, the catalyst can be separated from the product by extracting the potassium carboxylate with water, without decomposition of the catalyst, thus allowing the catalyst to be reused. Second, a large variety of different aromatic compounds with functional groups can be used, without greatly affecting the catalytic performance. Very recently, Nolan and co-workers showed that the Au-NHC catalysts used for the carboxylation of Ar–H bonds can also be used to decarboxylate benzoic acid derivatives, which suggests that the CO_2 insertion might, depending on the substrate, be reversible.[132]



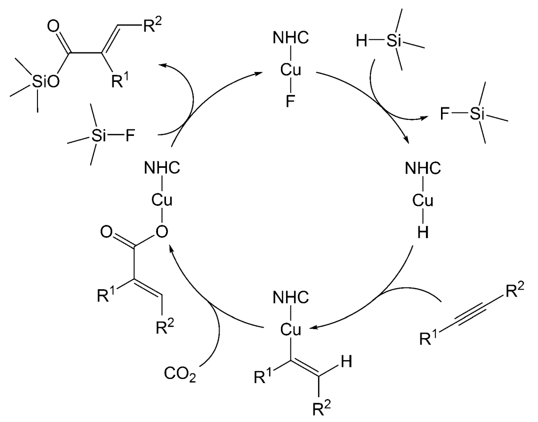
Scheme 27. Catalytic cycle for the reaction of aromatic compounds with CO_2 in the presence of Au-NHC catalysts to afford carboxylates.

Furthermore, Nolan and co-workers showed that analogous copper catalysts exhibit similar activities, and extended their studies to other substrates with acidic element–hydrogen bonds, such as imidazoles, and were able to demonstrate an N-carboxylation of N-heterocyclic compounds.[133] Several other research groups are currently working on the synthesis of carboxylic acids by the route established by Nolan and co-workers. Hou and co-workers, who previously used [(NHC)Cu] catalysts for the synthesis of RCOOH from organoboronic esters and CO_2,[126] synthesized numerous alkyl benzoxazole-2-carboxylates (1 bar CO_2, THF, 80°C) according to the route of Nolan and co-workers presented in Scheme 27.[134] KO*t*Bu was used instead of KOH as the base. A rather high catalyst concentration of 10 mol% was used. Interestingly, the authors managed to characterize some [(NHC)Cu(oxazolyl)] intermediates by means of X-ray single-crystal diffraction, thus confirming both the C–H bond activation by the copper catalyst and the catalytic mechanism shown in Scheme 27. The authors observed, however, decarboxylation when the potassium carboxylate was worked up with HCl. Hence, they selected alkyl iodide to obtain the final ester product and KI. The yields vary between 53 and 70% depending on the catalyst. Interestingly, treatment of CO_2 with similar catalysts in the presence of bis(pinacolato)diboron leads to the reduction of CO_2 to CO.[135]

Gooßen et al. focused on the synthesis of propiolic acids, which are useful synthetic reagents, but rather difficult to synthesize. The authors approached the synthesis from terminal alkynes and CO_2 by using [(phenanthroline)Cu-(PR_3)] catalysts. Deprotonation of the alkyne by Cs_2CO_3 and subsequent insertion of CO_2 into the copper–alkynyl bond affords copper carboxylates, which are transformed to carboylic acids by HCl.[136] Yields between 62 and 99% are reached on treating various alkyne substrates with 2 mol% catalyst, 1 bar CO_2, and 1.2 mol% Cs_2CO_3 (DMF; 35–50°C, 16 h). In a very similar publication, Yu and Zhang reported the use of [(NHC)CuCl] catalysts for the carboxylation of various terminal alkynes, with very good to excellent yields obtained.[137]

Analogously, Tsuji and co-workers synthesized novel [(NHC)CuF] complexes, which were used as precatalysts for the hydrocarboxylation of alkynes.[138] As shown in Scheme 28, in the first step, the fluoride ligand of the catalyst (1 mol%) is abstracted by silanes (2 equiv per substrate) to yield a Cu–H species and a fluorosilane. In the following step, similar to the mechanism proposed by Iwasawa and co-workers (Scheme 26), the Cu–H complex is treated with an alkyne to form a copper vinyl complex. Thereupon, CO_2 (1 bar, 1,4-dioxane, or *n*-hexane, 70–100°C, 4–14 h) inserts into the Cu–C bond to generate an α,β-unsaturated carboxylate ligand. The carboxylate ligand is cleaved by the fluorosilane, which leads to recovery of the catalyst and formation of a silyl ester, which is hydrolyzed to the corresponding carboxylic acid.

The reaction is regioselective in terms of the *cis* position of the substituents R^1 and R^2, most probably as a consequence of the steric demand of the NHC ligand at the copper atom, which directs the substituent into the *cis* position. In the cases

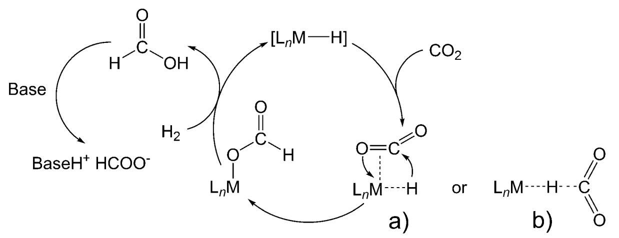


Scheme 28. Hydrocarboxylation of alkynes with copper catalysts according to Tsuji et al.

where $R^1 = R^2$, the yields are 58–78%. In the cases where $R^1 \neq R^2$, moderate to good stereoselectivities were obtained, with the sterically less-demanding substituent usually directed next to the carboxylate group. However, the authors did not comment on the catalyst activity, lifetime, or reusability.

5. Insertion of CO_2 into M–H Bonds—Synthesis of Formic Acid

Formic acid and its salts are used for a plethora of applications, mainly as a base chemical in organic synthesis (esters, alcohols, aspartame, pharmaceuticals etc.), as a silage agent, dyeing additive, in the leather industry, and for the deicing of airplanes and runways. Formic acid is produced industrially by four different methods:[139] 1) the hydrolysis of methyl formate, which is synthesized from methanol and CO, 2) carbonylation of hydroxides and subsequent acid hydrolysis, and—to a lesser extent—3) oxidation of hydrocarbons and 4) hydrolysis of formamide. Most of the processes require toxic carbon monoxide or syngas, whose production by steam reforming is an energy-demanding synthesis. The synthesis of formic acid from the far less toxic and far more abundant CO_2 is, however, not easy without catalysts, since the reaction of CO_2 and H_2 to HCOOH is endergonic ($\Delta G^{\circ}_{298} = +33\ \mathrm{kJ\,mol^{-1}}$). The hydrogenation of carbon dioxide to formic acid by insertion of CO_2 into the metal–hydrogen bond of the catalyst is one of the best-studied catalytic reactions of CO_2 in a homogeneous phase. The development of this reaction and the state-of-the art catalyst systems are well described in the literature and are the subject of several comprehensive reviews.[140–144] Therefore, this section will focus on the most active catalysts used so far and the reaction media. Additionally, the transition-metal-catalyzed hydrogenation of CO_2 to formate esters, formamides, or silyl formates has also been reported.[140,145–147] These studies, however, are not the focus of this Review, since the basic mechanism principle is very similar to that of the catalyzed synthesis of formates.



Scheme 29. General reaction mechanism for the catalytic hydrogenation of CO_2 to formic acid or formates.

From a mechanistic point of view (Scheme 29), the insertion of CO_2 into the M–H bond can proceed in two possible ways: a) the η^2 coordination of CO_2 to the metal center and subsequent migration of the hydrogen atom to the carbon atom to give a formate ligand, or b) a weak $H\cdots CO_2$ interaction, which leads to cleavage of the M–H bond and formation of the formate ligand. Although mechanism (a) is commonly accepted,[148] the mechanism can vary, depending on the catalyst and its coordination environment: theoretical studies have shown that the second mechanism is also possible.[149] Inoue et al. had already reported in 1976 the catalytic fixation of CO_2 to HCOOH by using various catalysts bearing mono- or bisphosphine ligands, including the well-known Wilkinson catalyst $[(Ph_3P)_3RhCl]$.[150] They found that the best catalyst is $[(Ph_3P)_4RuH_2]$, which afforded 87 mol HCOOH per mol catalyst in the presence of triethylamine after 20 h at 25 °C in benzene (25 bar H_2, 25 bar CO_2, 0.1 mol% catalyst). Since the reaction of CO_2 and H_2 to generate HCOOH is thermodynamically unfavorable, a base has to be added to form stable formate salts. In organic media, amines are preferred, whereas in water, NaOH or carbonates are used (see below). This makes catalyst reusability easier, since in some cases (in nonpolar solvents) the salts can be precipitated and separated from the catalyst. Since the finding by Inoue et al., numerous research groups have studied this reaction by using late transition metal catalysts (Ru, Rh, Ir, Ni, and Pd). From all the subsequent reports published, those by the research groups of Noyori, Jessop, Leitner, Joó, and Himeda will be highlighted in particular.[152–155,157–165]

In 1992, Tsai and Nicholas[151] as well as Graf and Leitner[152] reported the direct formation of HCOOH from CO_2 and H_2 by using molecular rhodium phosphine catalysts. Leitner and co-workers used a mixture of $[\{(cod)RhCl\}_2]$ and dppb, which proved to be an active catalyst at ambient temperature (the activities are presented in Table 1, entries 1–3). Based on this, the authors determined the catalytically active species to be the complex $[(dppb)_2RhH]$, which is formed by the hydrogenation of the cod and Cl ligands and coordination of the phosphine moieties, thereby preventing precipitation of metallic rhodium.[153] Formic acid was not observed in the absence of phosphines. The authors stated that the addition of NaOH enabled the rhodium species to be precipitated and reused as a catalyst for 10 more runs without notable loss of activity. Subsequently, they used several rhodium precatalysts, such as $[\{(cod)RhH\}_4]$ [154] or $[(hfac)Rh(diphosphine)]$[155] (hfac = hexafluoroacetylacetonate). Lau and Chen et al. used $[(Cl_2bipy)_2Ru(OH_2)_2][OTf_2]$ for the catalytic CO_2 hydrogenation, and obtained TONs of up to 5000 (Table 1, entry 7).[156]

In 1994, Noyori and co-workers used supercritical CO_2 ($scCO_2$) as the solvent for the hydrogenation of CO_2,

Table 1: Overview of selected transition-metal catalysts for the hydrogenation of CO_2 or HCO_3^- to formates.

Entry	(Pre)catalyst	Solvent	Additives	p H_2/CO_2 [bar]	T [°C]	t [h]	TOF [h^{-1}]	TON	Ref.
1	[{(cod)RhCl}$_2$]	DMSO	NEt_3, dppb	20/20	25	22	52	1150	[152]
2	[{(cod)RhH}$_4$]	DMSO	NEt_3, dppb	40	25	18	122	2200	[152]
3	[{(cod)RhCl}$_2$]	DMSO	NEt_3, dppe	40	25	18	11	205	[152]
4	[$(Me_3P)_4RuH_2$]	$scCO_2$	NEt_3, H_2O	85/120	50	1	1400	1400	[157]
5	[$(Me_3P)_4RuCl_2$]	$scCO_2$	NEt_3, H_2O	85/120	50	47	150	7200	[157]
6	[$(Me_3P)_4$(OAc)RuCl]	$scCO_2$	NEt_3, C_6F_5OH	70/120	50	–	95000	–	[159]
7	[$(Cl_2bipy)_2Ru(OH_2)_2$][OTf_2]	EtOH	NEt_3	30/30	150	8	–	5000	[156]
8	[{(cod)RhCl}$_2$]	H_2O	$NHMe_2$, tppts[a]	20/20	25	12	287	3439	[160]
9	[{$(tppms)_2RuCl$}$_2$][b]	H_2O	$NaHCO_3$	35/5	25	2	262	524	[161]
10	[{$(tppms)_2RuCl$}$_2$]	H_2O	$NaHCO_3$	60/35	80	–	9600	–	[162]
11	[(C_6Me_6)Ru(dhbipy)][c]	H_2O	KOH	30/30	120	8	4400	13620	[164a]
12	[Cp*Ir(dhbipy)Cl]	H_2O	KOH	30/30	120	57	42000	190000	[166]
13	[Cp*Ir(dhpt)Cl][d]	H_2O	KOH	30/30	120	48	33000	220000	[166]
14	[$(NHC)_2RuCl$][PF_6]	H_2O	KOH	20/20	200	75	–	23000	[167]
15	[(PNP)IrH_3]	H_2O	KOH	30/30	120	48	73000	3500000	[168]
16	[(dppm)Ru(H)(Cl)]	H_2O	dppm, $NaHCO_3$	50/0	70	2	687	1374	[169]
17	$Fe(BF_4)_2\cdot 6\,H_2O$	H_2O	PP_3[e]	60/0	80	20	–	610	[170]

[a] tppts = trisodium-3,3′,3″-phosphinidynetris(benzenesulfonate). [b] tppms = 3-sulfonatophenyldiphenylphosphine. [c] dhbipy = 4,4′-dihydroxy-2,2′-bipyrdine. [d] dhpt = 4,7-dihydroxy-1,10-phenantroline. [e] $PP_3 = P(CH_2CH_2PPh_2)_3$.

catalyzed by [$(Me_3P)_4RuX_2$] (X = H, Cl).[157] The authors found that the reaction is more efficient when $scCO_2$ is the solvent than in organic media (for TOFs, see Table 1, entries 4 and 5); this was the most active system at that time. The high activity was ascribed to the high miscibility of H_2 in $scCO_2$, rather than to the high CO_2 concentration.

Noyori and co-workers expanded this reaction to the conversion of CO_2 into alkyl formates and formamides.[158] Later, Jessop and co-workers described a new catalyst which is very efficient in $scCO_2$ (Table 1, entry 6).[159] The authors found that addition of water or acidic alcohols promotes the formation of formates, unlike the case of the rhodium complexes described by Leitner et al., who found that water inhibits the reaction. It is assumed that the beneficial effect of alcohols is the coordination of ROH to the metal center and interaction of CO_2 with the M−H or alcohol proton.[142] However, the high pressure required to form liquid CO_2 results in the reaction conditions being quite drastic and thus difficult to apply on a large scale.

Very early, research focused on the question as to whether the hydrogenation of CO_2 with homogeneous catalysts could be carried out in aqueous media. Gassner and Leitner used in situ formed [(tppts)RhCl], the soluble derivative of the Wilkinson catalyst, to probe the reaction.[160] They found that good activities were obtained under relatively moderate conditions (Table 1, entry 8). Joó et al. performed comprehensive studies on the catalytic activity of various water-soluble ruthenium and rhodium complexes for the aqueous hydrogenation of CO_2 in the presence of hydrogen carbonates, which exhibit a beneficial effect on the catalyst activity. The complex [{$(tppms)_2RuCl$}$_2$] was found to be the most active catalyst, with a TOF of 9600 h^{-1} (Table 1, entries 9 and 10).[161,162] It was shown that bicarbonates can be reduced by the catalyst to formate without addition of amines. Computational mechanistic studies by Joó and co-workers showed that in basic aqueous solution, most probably, metal dihydride complexes react with HCO_3^- to form water, CO_2, and {M−H}. Subsequently, a metal formate complex is formed, which is followed by cleavage of the formate ligand and coordination of H_2O to the metal. The addition of H_2 regenerates the active species.[163]

The resesrch groups of Himeda and Gonsalvi presented metal-Cp* complexes (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) bearing N-donor ligands as active catalysts for the hydrogenation of CO_2.[164–166] Himeda et al. studied the activity of [(C_6Me_6)RuCl] and [Cp*IrCl] complexes with dhbipy and 4,7-dihydroxy-1,10-phenanthroline (dhpt) ligands. They found that these complexes exhibit significantly higher activities than was reported before, with TOFs of formate formation of 13620, 42000, and 33000 h^{-1} (Table 1, entries 11–13). Himeda et al. stated that the hydroxy groups on the aromatic bipyridine and phenanthroline ligands have an enormous effect on the Lewis basicity of the ligand and, hence, on the metal center and its catalytic activity—when the ligand is protonated, the catalyst is inactive. The deprotonated hydroxypyridine ligand, for example, forms a pyridinolate, which is a much stronger σ donor than the protonated pyridinol, which can be tuned by changing the pH value of the reaction solution.[141] The pH-dependent activation and deactivation of the catalyst also has an effect on the reusability of the catalyst: in acidic media, the catalyst precipitates and can thus be separated from the reaction mixture. The analogous [Cp*Ir(pta)Cl] (pta = 1,3,5-triaza-7-phosphaadamantane) catalysts of Gonsalvi and co-workers are, however, significantly less efficient compared to other water-soluble catalysts, which nicely shows how important the ligand design is on the catalyst performance. Peris and co-workers examined the catalytic properties of [$(C_6Me_6)RuCl]^+$ and $[Cp^*IrCl]^+$ complexes with bis(NHC) ligands in the production of formate from CO_2 and H_2.[167] The authors found that TONs of up to 23000 can be achieved with the ruthenium catalysts (Table 1, entry 14), but only at reaction temperatures of 200 °C. The authors also investigated the formation of formates from CO_2 by transfer hydrogenation using isopropanol, but low very yields were obtained.

More recently, several research groups have been examining other transition-metal catalysts for the synthesis of formic acid from CO_2 and H_2. Nozaki[168] and co-workers studied the catalytic activity of iridium hydride complexes bearing PNP pincer ligands. This water-soluble iridium complex exhibits both a remarkable TOF (73 000 h^{-1}) and TON (3 500 000; Table 1, entry 15), which are the highest values for this reaction reported to date. Beller and co-workers studied the activity of ruthenium and iron catalysts towards the hydrogenation of bicarbonates in aqueous media without addition of CO_2. The in situ formed complex [(dppm)Ru(H)(Cl)] reacts with H_2 to give the corresponding formate complex and a 55 % yield of sodium formate (Table 1, entry 16).[169] Later, the same research group reported on the first iron-catalyzed synthesis of formate from bicarbonate, again without the extra application of CO_2 pressure.[170] The mixture of $Fe(BF_4)_2{\cdot}6\,H_2O$ and the tetradentate ligand $P(CH_2CH_2PPh_2)_3$ yields the complex $[(PP_3)FeH]$ (catalyst concentration 0.14 mol %), which leads to a 88 % yield of sodium formate (Table 1, entry 17). Furthermore, the authors studied the activity of $[(PP_3)FeH]$ for other CO_2 transformation products (60 bar H_2, 30 bar CO_2, NEt_3, 100 °C, 20 h), with methyl formate and dimethylformamide, for example, formed in moderate to good yields.

Although there are numerous reports on the catalytic formation of formates from CO_2 and H_2 in a homogeneous phase, a large-scale application still suffers from the rather harsh reaction conditions, such as high temperature and pressure. It is definitely very unfavorable for a sustainable process, that is, using formic acid or formates as energy carriers. Thus, future work will surely have to concentrate on the development of catalysts which convert H_2 and CO_2 into formates under mild conditions. The development of such processes goes hand in hand with alternative, large-scale, and cost-efficient methods to produce hydrogen, which is a rather expensive chemical. Apart from the case of Himeda's catalyst, catalyst recycling is quite difficult. In this respect, many reports lack a statement on the conversion values of CO_2.

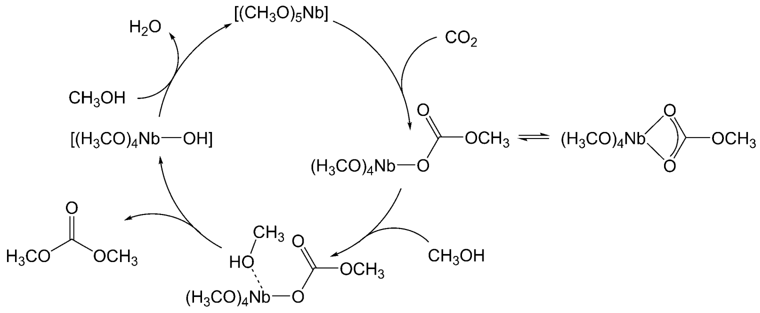
6. Insertion of CO_2 into M–O Bonds—Synthesis of Organic Carbonates from CO_2

The insertion of CO_2 into M–O bonds leads to the formation of carbonate species at the metal center. Technically, this reaction leads to three possible products: linear or cyclic carbonates, and polycarbonates, which are all important products in the chemical industry. In a catalytic process, the M–O bond is formed in situ from alcohols or epoxides. The product distribution largely depends on the nature of the catalyst as well as the reaction conditions and media, as will become clear in Section 6.

6.1. Synthesis of Linear Carbonates

The synthesis of linear carbonates—dimethyl carbonate (DMC) and its derivatives—is besides cyclic carbonates, and especially polycarbonates, an important reaction. DMC can be used as a basic chemical in organic synthesis, as well for various applications (solvents, lubricants etc.).[171,172] The most common industrial route to DMC is the reaction of alcohols/phenols with phosgene, which certainly has no future in industrial processes.

Therefore, the question as to whether carbonates can be accessed from CO_2 on a large scale is highly relevant.[173] Aresta et al. showed that niobium alkoxide catalysts lead to DMC and other carbonates.[174] However, the yields and catalyst activity are very low and the mechanism is so far unclear. The proposed mechanism (Scheme 30) appears to be more complex and involves several side reactions.[175] Other research groups reported that $[Sn(R_2(OR')_2]$ catalysts gave moderate to good yields.[176] However, toxic stannanes are certainly not an alternative to produce carbonates.



Scheme 30. Proposed mechanism for the synthesis of DMC from methanol and CO_2 with $[Nb(OCH_3)_5]$.

6.2. Synthesis of Cyclic Carbonates

Cyclic carbonates are primarily used as polymer synthons, as intermediates for the synthesis of fine chemicals and other organic reactions such as transesterification,[171] or as solvents and electrolytes in lithium ion batteries.[172,177] So far, there are two routes to obtain cyclic carbonates from carbon dioxide by using homogeneous transition-metal catalysts: with (propargylic) alcohols or with epoxides (oxiranes).

6.2.1. Cyclic Carbonates from CO_2 and Epoxides

Cyclic carbonates are also important chemical products in industry, being mainly used for the production of polycarbonates and linear carbonates. Similar to dialkyl- and aryl carbonates, cyclic carbonates were synthesized from phosgene and diols. Nowadays, this route has been replaced by the reaction of CO_2 and epoxides, which are either isolated or produced in situ. The most desired and thus most investigated product is propylene carbonate (PC), which is a frequently used solvent, electrolyte, and plastics softener.

In the last 30 years, much effort has been devoted to the development of molecular single-site catalysts for the reaction of CO_2 with epoxides in the homogeneous phase. The first report by Takeda and Inoue on the catalyzed synthesis of polycarbonates with nearly quantitative conversions from CO_2 and epoxides involved aluminum porphyrin catalysts; however, the reaction times were extremely long (> 2 weeks).[178] Other ligands were subsequently studied as well. Nowadays, the most frequently used catalysts are mononuclear salen complexes of Al^{III}, Cr^{III}, and Co^{III}, with amines, or ammonium or phosphonium halides as co-catalysts,[179,180] as well as bimetallic salen-based catalysts.[181] Since then, a plethora of different catalysts and the influence of the ligand modification on the product yield and polymer properties have been published. Figure 2 gives an overview of the most common catalysts.

The results are summarized in a series of reviews by Darensbourg,[196,197] Sakakura,[172,173] and more recently by Kleij.[179] In Table 2, the most active catalysts for the formation of cyclic carbonates from CO_2 and epoxides are presented. In some cases, the reaction time is quite long, and the epoxide conversion and cyclic carbonate yields are not reported. Furthermore, other coordination compounds, such as $[M(PR_3)X_2]$ (M = Ni,[198] Zn[199]), $[(dppp)Mn(CO)_3X]$,[200] various copper complexes with macrocyclic ligands,[201] $[(OC)CpRu(\mu\text{-dppm})Mn(CO)_4]$,[202] and $[(acac)_2VO]$[203] are active in the synthesis of cyclic carbonates from CO_2 and epoxides. However, they are of less relevance compared to the complexes of types **A**–**E** shown in Figure 2.

Several groups also reported the immobilization of complexes of type **A** on silica or polymer materials.[172] The ring closure competes with the copolymerization of the reactants. However, it was shown that cyclic carbonates are the thermodynamically favored products. The catalysts for the copolymerization are often the same as for the cyclization (see below). Hence, from the viewpoint of polymerization chemists, the cyclization is an undesired side reaction on the way to polymers. The general mechanism for the formation of cyclic carbonates from epoxides and CO_2 in the presence of molecular catalysts is shown in Scheme 31. In the first step, the epoxide coordinates to the metal center through the oxygen atom, and is thus activated. The ring opening is

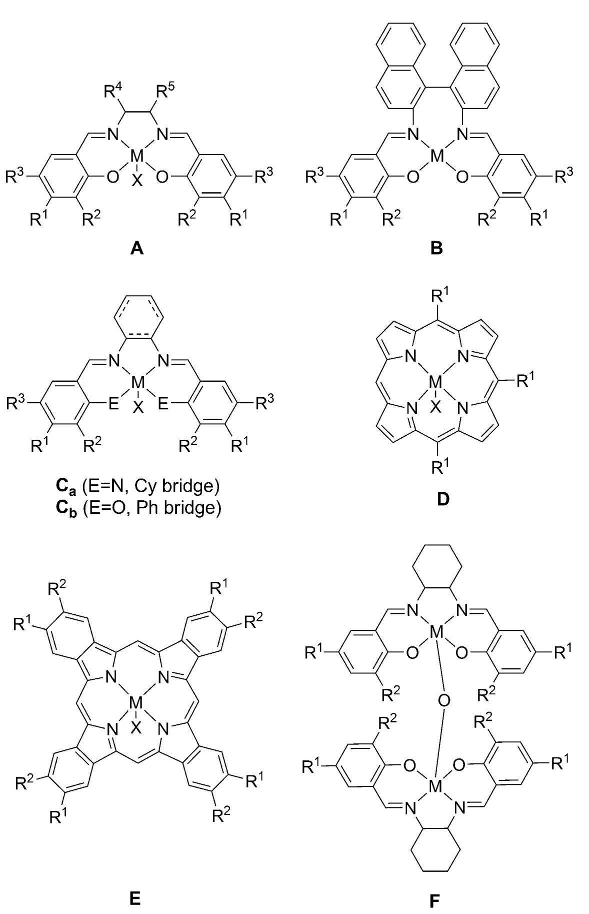
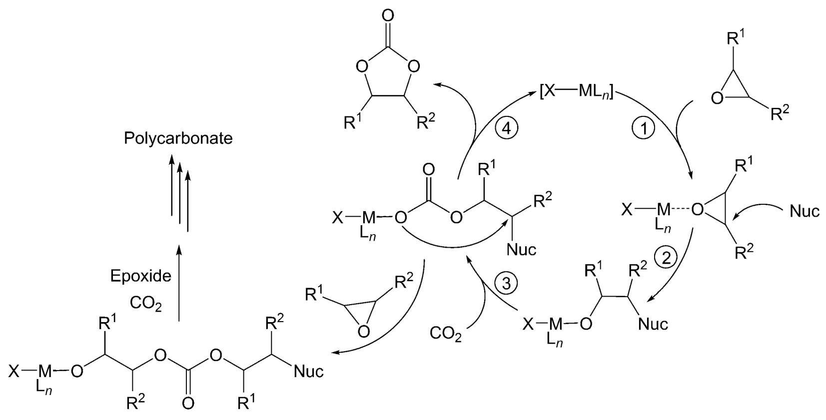


Figure 2. The most efficient metal complexes for the synthesis of cyclic carbonates from CO_2 and epoxides.

Table 2: Selected transition-metal catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides.

Metal	Ligand type	X	Substituents[f]	Co-catalyst	Solvent	Epoxide	Cat. conc. [mol %]	pCO_2 [bar]	T [°C]	t [h]	TOF [h^{-1}]	Ref.
Al	**A**	Br	all H	[18]crown-6-KI	CH_3CN	PO[a]	0.125	6	25	8	62	[182]
Al	**A**	Cl	all H	$(n\text{Bu}_4\text{N})\text{I}$	–	PO	0.125	6	35	8	84	[183]
Al	**A**	Cl	all H	$(n\text{Bu}_4\text{N})\text{Br}$	$scCO_2$	EO[b]	0.02	160	120	1	2360	[184]
Cr	**A**	Cl	$R^2 = R^3 = \text{Ph}$	dmap[c]	CH_2Cl_2	PO	0.075	7	100	1	916	[185]
Co	**A**	Ts	$R^2 = R^3 = t\text{Bu}$	$(n\text{Bu}_4\text{N})\text{Br}$	–	PO	0.1	35	45	16	316	[186]
Co	**A**	–	$R_3 = CH_2PPh_2Cl$	–	–	PO	0.5	40	100	4	–	[187]
Sn	**A**	Br_2	$R^2 = R^3 = \text{Br}$	dmap	CH_2Cl_2	PO	0.025	7	120	5	531	[188]
Zn	**B**	–	all H	NEt_3	CH_2Cl_2	PO	0.1	35	100	16	56	[189]
Co	**B**	–	all H	NEt_3	CH_2Cl_2	PO	0.1	35	100	16	57	[185]
Cr	**D**	Cl	$R^1 = 4\text{-tolyl}$	dmap	–	PO	0.01	50	80	64	–	[190]
Al	**E**	OAc	$R^1 = t\text{Bu}$	tehpa[e]	$CHCl_3$	PO	0.5	1	25	6	–	[191]
Al	**E**	Cl	all H	PPh_3	–	PO	0.1	50	140	2	–	[192]
Fe	**C$_a$**	2 Cl	$R^1 = R^2 = \text{cyclo-}C_4H_4$	–	CH_2Cl_2	PO	1.5	15	100	8		[193]
Al	**F**	–	$R^1 = R^2 = t\text{Bu}$	Bu_4NBr	–	PO	2.5	1	0	3	–	[194]
Zn	**C$_b$**	–	$R^2 = t\text{Bu}$	Bu_4NI	2-butanone	HO	2.5	2	25	18	–	[195]

[a] PO = propylene oxide. [b] EO = ethylene oxide. [c] 1-hexene oxide. [d] dmap = (4-dimethylamino)pyridine. [e] tehpa = triethyl(2-hydroxypropyl)ammonium iodide. [f] When not otherwise specified, the substituent is H.



Scheme 31. Simplified two-component mechanism for the formation of cyclic carbonates from CO_2 and epoxides. Nuc = nucleophile.

facilitated in the presence of halides (or other bases) to yield an alkoxy ligand. Subsequently, CO_2 inserts into the M—O bond to form the five-membered ring. The exact reaction mechanism is, however, so far not clearly understood. The question remains as to what exactly induces the ring opening. One of the hypotheses is that one catalyst molecule binds to the epoxide, while the base substitutes the halide ligand from the second one. The free coordination site is occupied by one CO_2 molecule, which acts as the nucleophile and leads to ring opening. This would involve a bimetallic intermediate. The two-component mechanism is regarded as the most probable one.[182,190]

Analogous to the synthesis of cyclic carbonates, cyclic carbamates can be obtained from the reaction of aziridines with carbon dioxide in the presence of chromium salen catalysts.[204] However, an industrial application of this reaction appears to be hardly possible, because of the high toxicity of aziridines.

6.2.2. Cyclic Carbonates from CO_2 and Alcohols

In 1986, Sasaki reported the synthesis of various carbonates from propargylic alcohols and CO_2 by using the complex $[Ru_3(CO)_{12}]$ as a catalyst.[205] It was observed that cyclic carbonates also formed, but only in poor yields. Soon after, Inoue et al. described the synthesis of cyclic carbonates in yields of up to 87 % from propargylic alcohols and CO_2 catalyzed by cobaltocene (50 bar CO_2, NEt_3, 80 to 100 °C, 5 h).[206] It was suggested that the amine deprotonates the alcohol in the first step, thereby forming an ammonium alcoholate, which reacts with CO_2 to form a carbonate compound. In the second step the alkyne moiety coordinates to the metal center, with a subsequent nucleophilic attack of the carbonate O atom at the alkyne leading to the ring closure. Deng and co-workers showed that simple cooper salts (2 mol %) catalyze the reaction of propargylic alcohols and CO_2 in ionic liquids to give nearly quantitative yields of cyclic carbonates (10 bar CO_2, 120 °C, 8 h).[207] Analogously, Yamada et al. used silver salts (10 mol %) to obtain cyclic carbonates in good yields (10 to 20 bar CO_2, dbu, dichloromethane or toluene, 25 °C).[208] Yamada and co-workers also synthesized enantiopure cyclic carbonates in high yields from bisproparylic alcohols in the presence of chiral ligands.[209] This reaction shows that this route to cyclic carbonates is more suitable for special products than for large-scale reactions with CO_2.

6.3. Synthesis of Polycarbonates

The synthesis of polycarbonates from carbon dioxide and epoxides catalyzed by transition-metal complexes is probably one of the processes that is closest to an industrial application. The physical properties of polycarbonates, such as strength, lightness, durability, biodegradability, heat resistance, easy processability, high transparency, and good electrical insulation render these materials of high industrial importance with applications in the automotive, electronics, optical media, glazing, and sheeting industries, as well as the medical and healthcare sectors. The copolymerization of CO_2 with epoxides has been known since 1969, when Inoue et al. combined $ZnEt_2$, water, CO_2, and propylene oxide to yield a small quantity of polymeric material.[210] However, the active catalyst is not well defined in this case and the polymer yield is poor. Various systems composed of $ZnEt_2$ or ZnO and di- or triprotic alcohols were subsequently investigated, but all suffered from their low activity and undesired by-products (e.g. cyclic carbonates, ether linkages). Later, the same research group reported the use of aluminum porphyrins as the first homogeneous catalysts for this reaction.[178] In the 1990s, several research groups reported the synthesis of other, well-defined homogeneous catalysts, with a focus on new mechanistical insights towards the optimization of the catalyst activity. The development of molecular catalysts and the most efficient systems are well described in several comprehensive reviews.[173,196,197,211–215] The first highly active and well-defined zinc complexes were the zinc phenoxide complexes developed in 1995 by Darensbourg et al. (**N**, Figure 3).[216] This was followed by the report by Coates and co-workers on a series of zinc β-diketiminato complexes (**F**–**I**, Figure 3).[217,230] The most active zinc catalyst for the copolymerization of CHO/CO_2 was found (TOF: 2290 h^{-1}) by systematic variation of the electronic and steric character.[217] Today, the most investigated CO_2/epoxide copolymerization catalysts are those bearing salen ligands (**A**–**C**, Figure 2), originally introduced by the research groups of Darensbourg,[218–220] Coates,[221,222] and others.[223–227]

The addition of co-catalysts to traditional porphyrin and salen complexes can considerably influence the efficiency of the system. Careful modification of the long-established salen ligands led to the development of anchored binary catalytic systems that are able to increase the activity towards polymerization by a factor of several orders of magnitude compared to earlier systems. Recently, several research groups presented single-component metal salen catalysts which bear the co-catalyst salt in the backbone of the salen

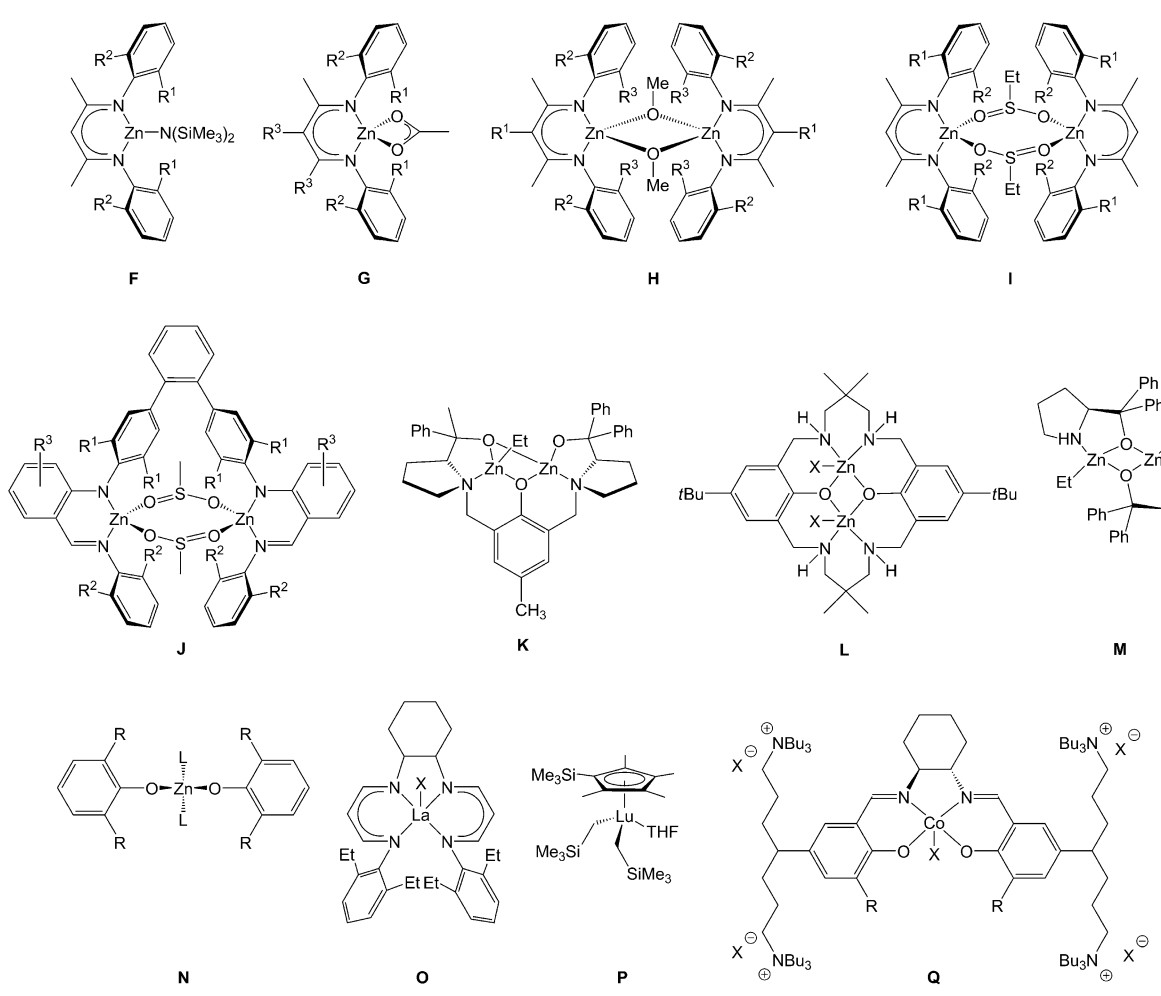


Figure 3. Overview of mono- and bimetallic catalysts for the copolymerization of CO_2 and epoxides to polycarbonates.

ligand (**Q**, Figure 3).[224–226] These complexes are so far the most efficient salen-based catalysts (Table 3). Only very recently, Nozaki and co-workers reported the efficient synthesis of stereogradient poly(propylene carbonate) by using cobalt salen catalysts that resemble the type **Q** catalysts shown in Figure 3.[228] Immobilization of salen systems affords materials with lower activities for copolymerization, but makes separation of the catalyst from the product possible. Investigations on conformationally flexible dimeric salphen complexes enabled the bifunctional character of the copolymerization to be deduced.[229]

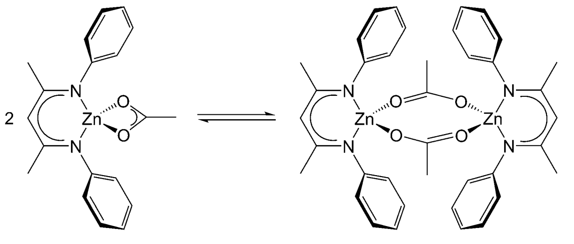
Mono- and bimetallic zinc complexes with different ligands have received considerable attention for the synthesis of polycarboxylates. The monometallic complexes show an equilibrium between a monomeric and a dimeric state (Scheme 32). These catalysts exhibit copolymerization activities at relatively low pressures (1–10 bar CO_2) and moderate temperatures (25–100 °C), as shown by the research groups of Coates,[230–235] Darensbourg,[216,236] Rieger,[237] Ding,[238] Nozaki,[239,240] Lee,[241,242] and Williams.[243] A selection of these catalysts are shown in Figure 3, and their catalytic activities are presented in Table 3. Some lanthanide complexes (**O** and **P**; Figure 3) were also applied as catalysts, but they had low activities and poor polydispersity indices (PDI).[244,245]

Despite intense research in the area of CO_2/epoxide copolymerization, a profound understanding of the underlying mechanism is still lacking and, thus, this field is the subject of ongoing investigations. Without doubt, the first step of the reaction is the coordination of an epoxide to the metal center and a subsequent ring opening. The induction of the ring opening is, however, a subject of debate and was investigated by computational methods by several research groups.[196,197,246] Clearly, the mechanisms for the metal salen complexes and the above described zinc complexes are different, since the latter are often bimetallic and do not require a co-catalyst, as is the case with the salen complexes. After the ring opening, a CO_2 molecule inserts into the M–O bond, thereby forming a carboxylate ligand at the metal center. The chain propagation is a process of alternating epoxide ring opening and CO_2 insertion steps. However, the formation of cyclic carbonates can technically occur in any step ("back-biting"; Scheme 31)—either from the metal alkoxide or the metal carboxylate intermediate—thus, stopping polymer formation. The choice of ligands at the metal center has an enormous impact on this side reaction.

Table 3: Selected transition-metal catalysts for the copolymerization of CO_2 and epoxides to polycarbonates.

Metal	Complex type	X	Substituents[c]	Co-catalyst	Epoxide	Cat. conc. [mol %]	pCO_2 [bar]	T [°C]	t [h]	TOF [h^{-1}]	PDI	Ref.
Cr	**A**	N_3	$R^2=R^3=t$Bu	[PPN]N_3	CHO[b]	0.04	55	80	4	608	1.54	[218]
Co	**C**	$O(C_6F_5)$	$R^2=R^3=t$Bu	[PPN]Cl[a]	PO	0.05	15	25	2	520	1.10	[221]
Co	**C**	$O(C_6H_3(NO_2)_2)$	$R^2=R^3=t$Bu	[PPN]Cl	PO	0.05	15	25	2	530	1.20	[223]
Cr	**C**	N_3	$R^2=t$Bu, $R^3=$OMe	[PPN]N_3	CHO	0.04	35	80	2	1153	1.13	[221]
Zn	**N**	–	–	–	CHO	0.36	55	80	69	3	4.50	[235]
Zn	**F**	–	$R^1=R^2=i$Pr	–	CHO	0.1	7	50	0.5	345	1.10	[234]
Zn	**F**	–	$R^2=R^3=$Et	–	CHO	0.1	7	50	0.5	358	1.16	[234]
Zn	**G**	–	$R^1=$H, $R^2=i$Pr, $R^3=$Et	–	CHO	0.1	7	25	2	235	1.13	[232]
Zn	**H**	–	$R^1=$H, $R^2=i$Pr, $R^3=$Et	–	CHO	0.1	7	50	2	257	1.14	[230]
Zn	**H**	–	$R^1=$CN, $R^2=i$Pr, $R^3=$Me	–	CHO	0.1	7	50	2	2290	1.09	[217]
Zn	**I**	–	$R^1=R^2=$Et	–	CHO	0.1	10	60	2	164	1.13	[236]
Zn	**J**	–	$R^1=$Me, $R^2=i$Pr, $R^3=$H	–	CHO	0.02	12	80	5	312	1.70	[240]
Zn	**J**	–	$R^1=$Me, $R^2=i$Pr, $R^3=$F	–	CHO	0.02	14	80	2	785	2.10	[241]
Zn	**K**	–	–	–	CHO	5	5	60	6	33	1.51	[241]
Zn	**L**	OAc	–	–	CHO	0.1	10	100	24	38	1.20	[242]
Zn	**M**	—	–	–	CHO	2.5	30	40	19	1.4	1.19	[238]
La	**O**	$N(SiMe_3)_2$	–	–	CHO	0.2	1	75	24	13	1.60	[241]
Lu	**P**	–	–	–	CHO	0.25	12	70	24	540	4.03	[244]
Co	**Q**	$O(C_6H_3(NO_2)_2)$	$R^1=R^2=$Me	–	PO	0.004	20	80	0.5	26000	1.20	[226]

[a] PPN = bis(triphenylphosphine)iminium. [b] CHO = cyclohexene oxide. [c] When not otherwise specified, the substituent is H.

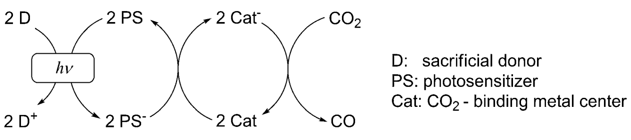


Scheme 32. Equilibrium of the BDI complexes. BDI = β-diketiminato.

Most of the presented systems are model studies in which cyclohexene oxide is used as a co-monomer. They are, apart from the recent system reported by Nozaki and co-workers,[228] however, often incapable of copolymerizing propylene oxide with CO_2, which is of high industrial relevance. Moreover, many of the systems comprise a toxic metal center and a high degree of metal content in the final polymer, which disfavors their industrial application. Furthermore, a rather lengthy synthetic route towards the ligand framework renders most of the complexes unsuitable for industrial purposes.

7. Photocatalytic CO_2 Activation

All the activations of CO_2 discussed above have in common that they overcome the high stability of CO_2 by chemical reaction with highly reactive molecules such as epoxides or olefins. Another very interesting pathway, especially in terms of sustainability, is the photocatalytic reduction of CO_2, in which the activation energy originates from sunlight. The electrochemical reduction of CO_2 to CO without photoirradiation is quite energy consuming and, therefore, much less reported.[247] Summaries of this research are found in two reviews.[248,249] Besides heterogeneous systems for the photocatalytic conversion of CO_2,[250] it is of course a desired goal to develop soluble photocatalysts. Since the first report on the reduction of cobalt(III) to cobalt(II) complexes by irradiation of the complex $[Ru(bipy)_3]Cl_2$ with light in aqueous solution,[251] ruthenium and rhenium complexes bearing chromophoric ligands have become the benchmark in homogeneous photocatalysis. Beside ruthenium- and rhenium-based complexes, there are also some reports on chromophores based on platinum(II),[252] iridium(III),[253] and osmium(II).[254] However, their role in the reduction of CO_2 is negligible. The first reduction of carbon dioxide was described in 1982 by Lehn and co-workers, who used $[Ru(bipy)_3]^{2+}$ as a photosensitizer, $CoCl_2$ as the CO_2-coordinating catalyst, and a sacrificial donor (e.g. triethanolamine) in aqueous solution.[255] One drawback of this catalyst system is its low selectivity towards the formation of CO, as hydrogen, which results from the reduction of water in the aqueous media, is the main product. Replacing $CoCl_2$ by $RhCl_3$, $NiCl_2$, $CuCl_2$, or $K_2[PtCl_4]$} even decreased the CO/H_2 ratio. Despite the low selectivity, this reaction, with turnover numbers of up to 32 for $[Ru(bipy)_3]^{2+}$, is indeed a catalytic process. Mechanistically, this reaction consists of three different electron-transfer steps (Scheme 33). After absorption of a photon, the lowest excited state of the photosensitizer (PS) is quenched by the sacrificial donor (D), thereby forming the one-electron-reduced species (OER) $[Ru(bipy)_3]^{+}$.[256] Subsequently, mediated by a CO_2-coordinating catalyst, the CO_2 is reduced.



Scheme 33. Simplified mechanism for the photocatalytic transformation of CO_2 to CO.

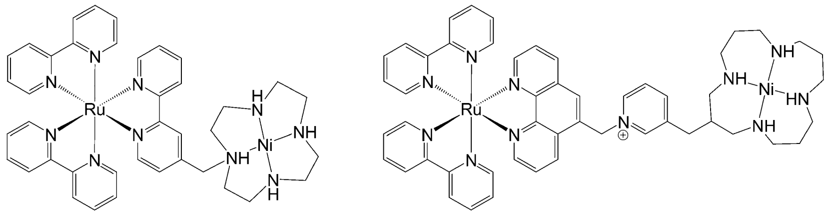


Figure 4. Bimetallic ruthenium/nickel catalysts for the reduction of CO_2.

It must be mentioned here that because of the high reduction potential of the one-electron reduction (−1.9 V versus the normal hydrogen electrode), multielectron reduction processes are more favorable.[257] To meet these requirements, MacDonnell and co-workers developed a ruthenium photocatalyst that is capable of storing up to four electrons.[258] However, this idea was not followed up in further investigations of CO formation. The efficiency of a photocatalytic process is, besides the yield and turnover numbers, characterized by its quantum yield Φ, which is defined as the number of times a CO_2 molecule is transformed per photon absorbed by the photosensitizer. The system developed by Lehn and co-workers reaches a quantum yield of 0.012. Later, the same research group introduced the complex $[Re(bipy)(CO)_3X]$ ($X = Cl$, Br), which acts as both photosensitizer and catalyst to afford quantum yields of up to 0.14.[259,260] Again, the reductive quenching of the ^{3}MLCT (triplet metal-ligand charge-transfer) excited state of the photosensitizer by triethanolamine is the starting process, which was verified by laser spectroscopy.[261] This gives an unstable 19-electron species in which a coordination site becomes available by ligand dissociation.[260] The question as to which ligand dissociates was discussed in the literature and its mechanistic aspects are summarized in a recently published review.[262] It is strongly indicated that the dissociation of the ligand X from the OER is an important process in the photocatalytic reduction of CO_2. Another mechanistic question is the origin of the second electron, as two electrons are required for the reduction of CO_2. In this context, Fujita and co-workers identified the binuclear [Re-C(O)O-Re] moiety as a key intermediate of this reduction pathway.[263]

Subsequently, Ishitani and co-workers modified this system to produce $[Re(bipy)(CO)_3\{P(OEt)_3\}]^+$, which is the most efficient photocatalyst to date, reaching a quantum yield of up to 0.38, but strongly depends on the light intensity.[264] The use of a mixture of $[Re(bipy)(CO)_3(MeCN)]^+$ and $[Re\{4,4'-(MeO)_2bipy\}(CO)_3(POEt)_3)]^+$ leads to an increase in the quantum yield to 0.59.[265] Despite the high activity of rhenium-based catalysts, one problem with a view of utilizing solar light as an energy source is that most of the emissive rhenium complexes do not strongly absorb in the visible region.[262]

A solution to this problem is to use CO_2-coordinating catalysts covalently linked to a ruthenium complex as a visible-light absorber.[266] Kimura et al. developed a series of nickel cyclam catalysts for the photocatalytic reduction of CO_2 (Figure 4). However, because of the lack of selectivity for the production of CO over H_2 and other unidentified competing processes in the catalytic cycle, these complexes exhibit very low yields. The amount of formed CO in all the investigated cases is less than stoichiometric with respect to the complex.[267]

Ishitani and co-workers reported the use of covalently linked multinuclear ruthenium/rhenium complexes for the reduction of CO_2 that led to a great enhancement in the photocatalytic response to light in the visible region and a greatly improved photocatalytic activity (Figure 5).[268] This was attributed to an intermolecular electron transfer. Decisive for the activity of these intramolecular complexes is the nature of the covalent bridge between the photosensitizer and the CO_2-coordinating subunit, which defines the electrochemical and spectroscopic properties of the supramolecular system.[269] Strong electronic communication through the bridging ligand decreases the photocatalytic activity, despite accelerating the electron transfer between the metal centers.[270] Alkyl-bridged complexes have, despite the weak interactions between the subunits, exhibit significantly higher turnover numbers (Figure 5).

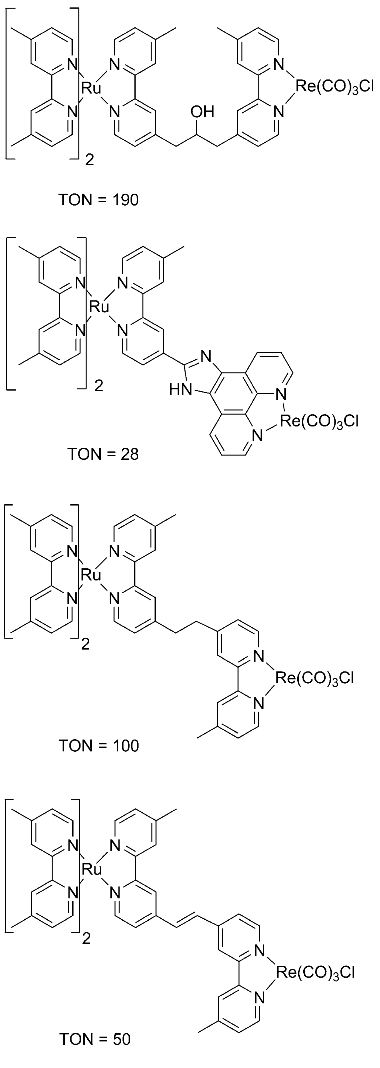
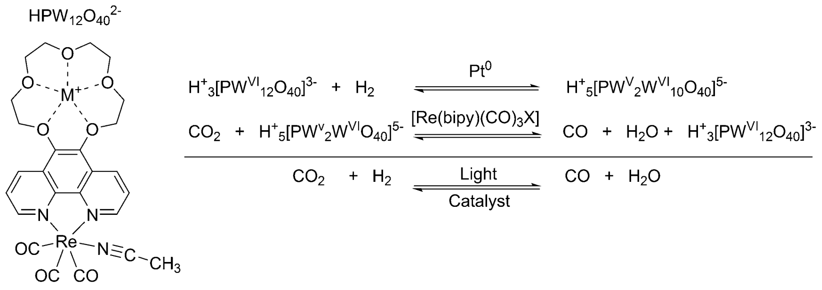


Figure 5. Bimetallic photocatalysts for the reduction of CO_2 to CO.

However, it must be noted that besides the electron transfer between the photosensitizer and the CO_2-coordinating units, there is another important electron-transfer step: the quenching of the excited state of the photosensitizer (Scheme 33). In most reported studies, the electrons for this reduction step originate from a sacrificial donor (mainly triethanolamine). In a very recent report, Neumann and coworkers replaced the sacrificial donor by hydrogen, thereby leading to a reverse water-gas shift reaction (Scheme 34).[271] The possibility of oxidizing H_2 with polyoxometalates in the presence of platinum(0) is known.[272] By complexing a Keggin-type polyoxometalate with a crown ether group linked to a rhenium(I) phenanthroline complex it was possible to combine the oxidation of hydrogen (catalyzed by the polyoxometalate) with the reduction of CO_2 (catalyzed by the rhenium(I) phenanthroline complex).



Scheme 34. Photoreduction of CO_2 with H_2 catalyzed by a rhenium(I) phenanthroline polyoxometalate hybrid complex.

As the maximum intensity of sunlight lies at a wavelength of 500 nm, future research efforts will focus on connecting the outstanding properties of $[Ru(bipy)_3]^{2+}$ moieties as a photosensitizer (e.g. ^{3}MLCT in the visible region, long-lived excited state, stable against aqueous media …) with a highly active CO_2-coordinating catalyst (e.g. rhenium(I) catalysts). The next step will be the combination of this half-cell reaction with oxidation reactions that do not have sacrificial character. A first example is the reaction pathway shown in Scheme 34. The long term goal will be the simultaneous light-driven reduction of CO_2 and oxidation of H_2O with molecular catalysts in a homogeneous phase, thus approaching artificial photosynthesis.

8. Conclusion

Does today's research offer a molecular solution to a global problem—the shortage of carbon resources? Heterogeneous catalysis is still the state-of-the-art for the large-scale transformation of CO_2 to basic bulk chemicals. However, the processes are not selective enough for the transformation of CO_2 to more sophisticated molecules (fine chemicals, pharmaceutical agents etc.). Most of the catalytic conversions of CO_2 in a homogeneous phase highlighted in this Review involve highly energetic reactants (olefins, acetylenes, epoxides, etc.). Despite the plethora of publications in this field, it has to be noted that only a few have the potential to be used on a large scale. Some of the concepts are more than 30 years old, and a real breakthrough has not yet been achieved; many reactions involve extremely air- and moisture-sensitive compounds, and the product distribution is not selective. The insertion of CO_2 into metal–element bonds is already a well-established procedure. However, it appears to be interesting for special organic products for fine chemical synthesis, rather than for a broad use on scales of many tons per year. It still remains to be seen in which direction the research will turn, and which new methods for using CO_2 as a starting material will emerge in the nearer future.

In terms of sustainability it is of course highly desirable to use sunlight energy, as in the photocatalytic reduction of CO_2. However, it must be taken into account that the formation of CO in that reaction pathway is so far not efficient enough; in most cases it still depends on sacrificial donors and it is currently easier and cheaper to produce in industry-relevant yields by steam reforming with methane.

In our opinion, the hydrogenation of CO_2 to form bulk compounds such as methanol or methane is definitely one of the future challenges in homogeneous catalysis. Both reactions are in fact exothermic (-91 and $-74\ \text{kJ mol}^{-1}$, respectively); however, they require a high activation energy because of C=O bond cleavage, and result in the formation of stable and thus undesired by-products (CO, formates, etc). With respect to this energy barrier, both homogeneous and heterogeneous systems are still in a rather early stage of development. To date, there are only a handful of reports in which homogeneous metal or metal-free catalysts are used, and then only with rather poor conversions.[273] However, the idea of a catalytic system that transforms the all-abundant CO_2 to CH_3OH or CH_4 is a highly attractive target, especially with a view for alternative carbon sources and fuels.

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