Top Organomet Chem (2016) 53: 199–224
DOI: 10.1007/3418_2015_111

Ni-Catalyzed Synthesis of Acrylic Acid Derivatives from CO_2 and Ethylene

Sebastian Kraus and Bernhard Rieger

Abstract The story of nickelalactones finally ends well. Over three decades after their discovery, catalytic processes have been successfully established to synthesize acrylate derivatives from ethylene and abundantly available carbon dioxide. The performed research during this time in the CO_2 utilization via C–C bond formation with olefins is presented within this review. It gives detailed insights starting from the initial milestones in the 1980s up to modern strategies through cleavage auxiliaries. Different approaches are examined from an experimental and theoretical point of view as the choice of cleavage agent and the corresponding ligand is crucial for the reaction control and suppression of undesired pathways. Methylation of the lactone species led to a first successful liberation of methyl acrylate in stoichiometric amounts. These results led to a vast progress in research with auxiliaries afterward. Upon addition of Lewis acids or strong sodium bases, finally the first two different catalytic routes have been established which are discussed in detail.

Keywords Acrylate · C1 olefin · Nickelalactone · Oxidative coupling

Contents

S. Kraus and B. Rieger (✉)
Technische Universität München, Wacker-Lehrstuhl für Makromolekulare Chemie,
Lichtenbergstraße 4, 85747 Garching bei München, Germany
e-mail: rieger@tum.de

Abbreviations

Ar^F	3,5-Bis(trifluoromethyl)phenyl
bpy	2,2′-Bipyridine
BenzP*	(*R*,*R*)-(+)-1,2-Bis(*tert*-butylmethylposphino)benzene
BTPP	(*tert*-Butylimino)tris(pyrrolidino)phosphorane
cdt	1,5,9-Cyclododecatriene
cod	1,5-Cyclooctadiene
Cy	Cyclohexyl
dcpe	1,2-Bis(dicyclohexylphosphino)ethane
dcpp	1,3-Bis(dicyclohexylphosphino)propane
d*i*ppf	1,1′-Bis(di-*iso*-propylphosphanyl)ferrocene
dppb	1,4-Bis(diphenylphosphino)butane
dppe	1,2-Bis(diphenylphosphino)ethane
dppf	1,1′-Bis(diphenylphosphanyl)ferrocene
dppm	Bis(diphenylphosphino)methane
dppp	1,3-Bis(diphenylphosphino)propane
d*t*bpe	1,2-Bis(di-*tert*-butylphosphino)ethane
d*t*bpm	Bis(di-*tert*-butylphosphino)methane
d*t*bpp	1,3-Bis(di-*tert*-butylphosphino)propane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DFT	Density functional theory
D*I*PEA	*N*,*N*-Di-*iso*-propylethylamine
IR	Infrared
L	Ligand
Lac	2-Oxacyclopentan-3-one
MMA	Methyl methacrylate
NMR	Nuclear magnetic resonance
p.a.	Per year
PAA	Poly(acrylic acid)
PANa	Sodium poly(acrylate)
PMMA	Poly(methyl methacrylate)
rt	Room temperature
thf	Tetrahydrofuran
tmeda	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine
TOF	Turnover frequency
TON	Turnover number

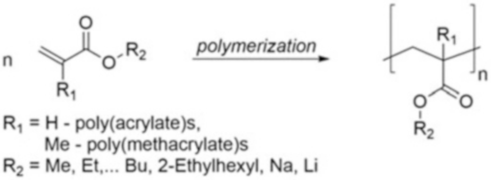
1 Introduction

Acrylic acid and its derivatives, i.e., organic esters and alkali salts, are widely used as monomers for the synthesis of polymeric materials (Fig. 1). One of the most famous examples is poly(acrylic acid) (PAA) with its unique properties as a superabsorber [1]. Depending on the degree of neutralization to sodium poly (acrylate) (PANa), this polymer is able to absorb water up to 300 times of its own mass. Besides the application in modern diapers, a huge variety of household and daycare products in cosmetics contain PAA as thickener or film-forming substance, adhesives, coatings, and paints. Due to its ability to bind earth alkali elements like calcium and magnesium, it is utilized in sequestering agents. The applications become even more versatile by using blends or copolymers from a variety of poly (acrylate)s [2].

One of the most commonly used derivatives is methyl methacrylate (MMA) in its polymerized form, poly(methyl methacrylate) (PMMA). The translucency and resistance to acids and bases make it a suitable substitute to common glass materials applied mainly in construction, the automotive sector, and medical technology. Today's production volume of acrylic acid and its derivatives reach ~4 Mt p.a. with a further increase in the future, especially due to a rising demand in emerging countries. To accommodate this demand, efficient and keen production pathways are requested by the chemical industry [3].

An overview of the abandoned production processes is drawn in Fig. 2 [1]. The cyanohydrin method (i) was established first in industrial scale. Starting from ethylene oxide, the corresponding 3-hydroxypropionitrile is formed by addition of highly toxic HCN. Treatment with H_2SO_4 leads to acrylic acid; however, huge amounts of NH_4HSO_4 are formed as undesired side product. The *Reppe* synthesis (ii) was introduced in 1939 and used coal-based acetylene and CO to undergo a heterogenic nickel-catalyzed C–C bond formation. Major disadvantages of this route are the toxicity and corrosivity of the catalyst $Ni(CO)_4$ as well as the huge energy consumption of the overall process. Similar problems occur from the pyrolysis of acetic acid to the corresponding ketene (iii). Again, the high toxicity and demand of energy forced the industry to investigate new strategies toward acrylates. The first established synthesis with a C3 building block was the *Sohio* process (iv) for the synthesis of acrylonitrile via ammoxidation. Subsequent acidic hydrolysis with sulfuric acid yields the desired product. In common with the cyanohydrin route, huge amounts of NH_4HSO_4 waste are produced.

Fig. 1 Typical polymerization of acrylic acid and some of its important derivatives



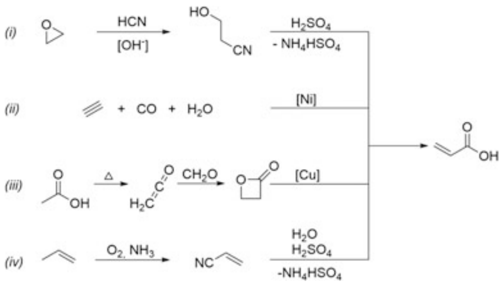


Fig. 2 Abandoned industrial synthesis pathways to acrylic acid via (*i*) cyanohydrin, (*ii*) Reppe synthesis, (*iii*) pyrolysis, and (*iv*) Sohio process [1].

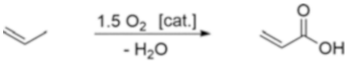


Fig. 3 Today's industrial process for the synthesis of acrylic acid through oxidation of propylene

Fig. 4 Ni(0)-catalyzed synthesis of acrylic acid from ethylene and CO_2

Today's acrylic acid is synthesized from propylene by direct oxidation with O_2 over molybdenum/bismuth catalysts, leading to acrolein as intermediate compound. In a subsequent second step, it is oxidized over molybdenum/vanadium catalysts to acrylic acid [2]. This process has largely replaced any other industrial method nowadays because of the increased selectivity, less undesired by-products, and hence higher profitability (Fig. **3**) [1]. However, this pathway is limited to propylene as a substrate and thus to unsubstituted acrylic acid. Additional modifications of the carboxylic group need to be performed separately.

The finiteness of oil reserves accompanied by the imbalance of supply and demand for fossil fuel leads to fluctuating market prices. Thus, novel routes to acrylic acid replace crude oil-based C3 resources with cheap, renewable, and abundantly available C2 and C1 building blocks as raw materials [4]. Besides the oxycarbonylation of ethylene with CO and water, the nickel-catalyzed direct carboxylation of ethylene with CO_2 (Fig. 4) represents one promising approach for industrial application [2]. The C–C coupling of CO_2 and ethylene with Ni (0) was discovered by Hoberg in the early 1980s [5, 6]. However transformations of nickelalactones were limited to stoichiometric reactions. Postulations about the catalytic employment of nickelalactone intermediates toward acrylic acid in 2006 [7] aroused huge attention in science leading to a dramatic increase of investigations in this topic. Within this review, we want to give an insight into the beginning of this story 30 years ago up to the latest advances in research about the catalytic formation of acrylates from carbon dioxide and ethylene (Fig. 4).

2 Formation and Reactivity of Nickelalactones

2.1 Pioneering Work

The initial milestones date back to the year 1980 when Yamamoto et al. published the first cyclic Ni(II) complexes with a nickelalactone motif [8]. The Ni(0) precursor $Ni(cod)_2$ was treated with acrylic acid and acrylamide in an excess of phosphine ligand. The resulting cyclic amide and ester complexes were confirmed by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy (Fig. 5).

They postulated a pathway involving a bond rearrangement triggered by the *Michael* reaction type shift of the acidic proton to the β-carbon of the π-system (Fig. 6). The influence of the phosphine's steric demand and basicity on the reaction path was also revealed. While PCy_3 and $PEt(^tBu)_2$ favorably form the cyclic compound, a less basic P-ligand (PEt_3, PPh_3) promotes the reaction to the air-sensitive Ni(0) π-complexes.

Although the cyclic structures demand more space around the metal center, a larger cone angle of the phosphine ligand affords the lactone or lactam preferably. A bulky phosphine coordinates only via one equivalent, while less sterically crowded ligands form a nickel complex with two equivalents of phosphine. This leads to an even more occupied ligand sphere and therefore promotes the π-complex formation. An interconversion from the Ni(0) π-complex to the cyclic Ni(II) species can be observed for $(PCy_3)Ni$ by refluxing the reaction mixture in thf.

In 1982, Burkhart and Hoberg presented the first synthesis of a nickelalactone based on a C1 carbon source and an alkyne [9]. The reaction of Ni(cdt) with tmeda and CO_2 causes a disproportion to $Ni(CO)_4$ and $(tmeda)Ni(CO_3)$. In the presence of 2-butyne, this pathway is suppressed and affords the five-membered oxanickelacyclopentene derivative instead. Indirect proof of the structure was given upon hydrolysis or CO addition which leads to 2-methylcrotonic acid and dimethylmaleic anhydride, respectively (Fig. 7).

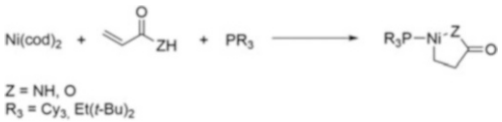


Fig. 5 First published synthesis of nickelalactones and nickelalactams through addition of acrylic substrates by Yamamoto et al. [8]

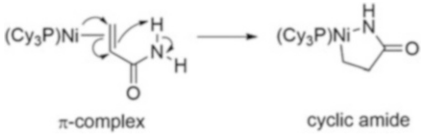


Fig. 6 Postulated interconversion mechanism for the nickelalactam formation [8]

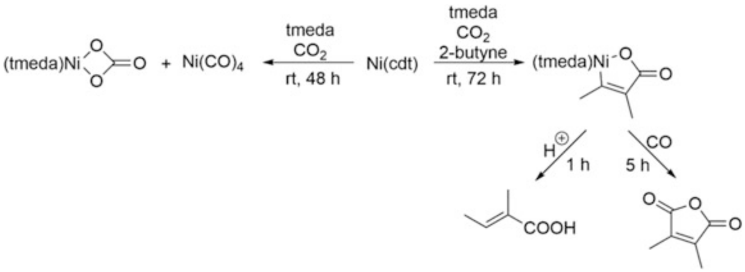


Fig. 7 Reactivity of Ni(0) complexes toward CO_2 in the absence and presence of an alkyne [9]

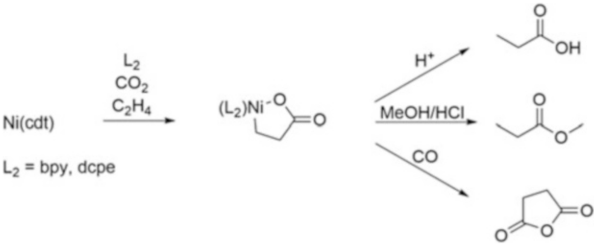


Fig. 8 The first oxidative coupling with ethylene and CO_2 and subsequent conversion to organic compounds [5]

These findings were further investigated and extended to a vast variety of alkynes and subsequently to alkenes [10–13]. Activated alkenes like norbornene easily undergo a nickel-induced C–C bond formation [14]. The cyclic intermediate was not entirely characterized, but the saturated product *exo*-norbornane-2-carboxylic acid formed when HCl was added. To extend the library of utilized olefins, Hoberg employed chelating σ-donor ligands (i.e., 2,2′-bipyridine (bpy), 1,2-bis (dicyclohexylphosphino)ethane, (dcpe)) which are suitable for nonactivated alkenes like ethylene [5, 6]. In this case, the lactone formation occurs if $Ni(cod)_2$ is replaced by the more reactive $16e^-$ precursor Ni(cdt) in the absence of additional tmeda. Tmeda promotes the alternative pathway to the reductive disproportion of carbon dioxide as depicted in Fig. 7. Subsequent acidic hydrolysis of the cyclic compounds affords propionic acid and its methyl esters, whereas CO insertion liberates succinic anhydride (Fig. 8). Already in 1983, Hoberg declared these findings as a first groundbreaking step toward nickel-catalyzed reactions of ethylene and its homologues with CO_2 to a huge variety of organic compounds [5].

2.2 *Utilization of Nickelalactones*

The research on the nickel-induced C–C coupling with CO_2 expanded tremendously in the following years. A wide range of linear [6] and cyclic olefins [15, 16], 1,2-dienes [13], 1,3-dienes [17–19], alkynes [10], imines, and aldehydes have been studied. Furthermore, the addition of specific promotors (electrophiles, acids, alkyl halides, CO) affords highly selective products from one nickelalactone intermediate, which makes them a versatile tool for organic compounds [20, 16]. The C–C bond formation of alkenes and its homologues affords saturated compounds; alkynes lead to products with an olefinic moiety. Depending on the auxiliary, the deactivation of the Ni complex or hydrolytic workup inhibits a catalytic approach though. Intramolecular reactions like β-H elimination and followed reductive elimination could avoid the use of promotors, but have been elusive so far. An exception is the depicted oxidative coupling of $(DBU)_2Ni(0)$, styrene, and CO_2 [21]. Depending on the reaction temperature, the isomers 2-phenylpropionic acid (A), 1-phenylpropionic acid (B), and additionally cinnamic acid (C) are isolated after hydrolysis. Oxidative coupling at 60°C promotes the formation of the saturated acids ($A + B/C = 32/1$), whereas a temperature increase to 85°C mainly yields cinnamic acid ($A + B/C = 1/7$). Derived from the product structure, a thermal β-H elimination is most likely initiated to afford the unsaturated alkyl species upon hydrolysis (Fig. 9). It was the first published synthesis of an α,β-unsaturated carboxylic acid from an olefin and CO_2. A catalysis has not been achieved as the regeneration of $(DBU)_2Ni(0)$ through reductive elimination was not observed. Hoberg assumed that H-migration to the ligand occurs and deactivates the nickel compound for recycling.

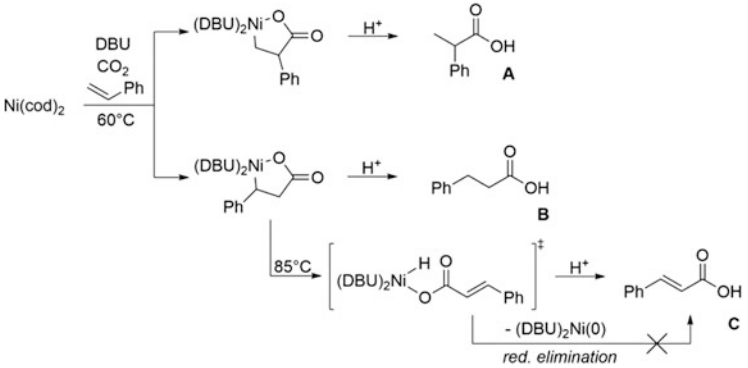


Fig. 9 Synthesis of cinnamic acid from styrene via thermal β-H elimination by Hoberg et al. [21]

Besides the utilization of carbon dioxide, isoelectronic isocyanates have been explored, which react with C=N, C=O, or C=C double bonds in analogous manner affording imines, amides, carbamates, and ureas [22–29]. In contrast to the use of CO_2, catalytic conversions with isocyanates are possible.

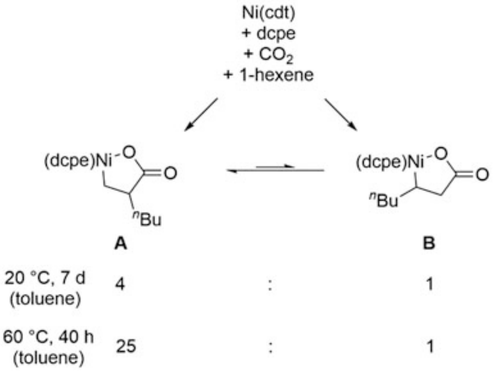
2.3 Regioselectivity, Ring Contraction, and Expansion

The first mechanistic studies regarding the regioselectivity of monosubstituted alkenes in nickelalactones were reported for 1-hexene by Hoberg in 1984 [6]. The oxidative coupling for the two different occurring isomers was studied at 20 and 60°C (Fig. 10). Due to the higher stability of a metal–C_{prim} bond, the lactone formation reveals a preference of product A over B. At 20°C an isomeric ratio of A/B = 4/1 is reached. With rising temperatures, the equilibrium shifts further to the thermodynamically favored product A (A/B = 25/1).

A subsequent treatment of a 4/1 mixture at 60°C affords a final ratio of A/B = 25/1, indicating that the C–C bond formation is a reversible step in the overall reaction. Various monosubstituted alkenes (e.g., propylene) reveal analogous regioselectivity, whereas specific ligands (i.e., (2-diethylaminoethyl)-dicyclohexylphosphine) are capable to invert the regioselectivity toward isomer B. Due to the electronic interactions of the precursors, the electrophilic CO_2 carbon favors the C–C bond formation with the nucleophilic C1 carbon of the alkene. The electronic effects play a bigger role than the thermodynamically favored formation of a M–C_{prim} bond and are in good accordance with the observed regioselectivity in the coupling reaction of imines and aldehydes with CO_2 [30, 31]. Yamamoto et al. discovered similar M–C_{sec} isomers [32] when ring contractions of six-membered nickelalactones occur (Fig. 11). The stability of six-membered nickelacycles is highly influenced by the employed auxiliary ligand.

Bulky ligands like 1,2-bis(diphenylphosphino)ethane (dppe) and its propyl-bridged homologue (dppp) cause a rapid isomerization to the methyl-substituted

Fig. 10 Regioselectivity and reversibility of the C–C bond formation with monosubstituted alkenes, Ni(cdt), and dcpe [6]



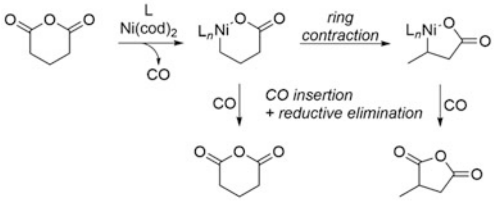


Fig. 11 Ligand-induced ring contraction of six-membered nickelalactones [32]

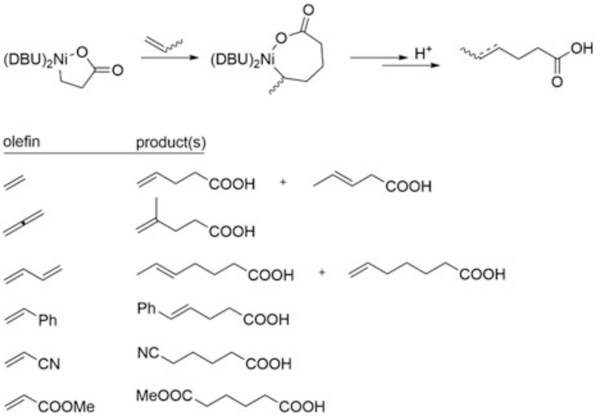


Fig. 12 Reactions of $(DBU)_2NiLac$ with C=C-containing substrates via ring expansion [34]

five-membered lactones, while less sterically demanding ligands like bpy in contrast do not induce a ring contraction. A similar trend can be observed for monodentate phosphines ($PPh_3 > PEtPh_2 > Pet_2Ph > PMePh_2 > PEt_3 > PMe_2Ph$) with regard to the Tolman's cone angle. In conclusion, a higher bulkiness of the ligand promotes the ring contraction. The degree of contraction was determined by the ratio of the respective methyl succinic anhydride and glutaric anhydride after treatment with CO. Approaches to perform the backward ring expansion were unsuccessful indicating an irreversible process due to the high stability of five-membered lactone species.

Ring expansions are accessible via insertion of olefinic compounds into the M–C bond of saturated nickelalactones bearing two 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) ligands [33, 34]. The widely used phosphines and bpy suppress this reaction pathway; respective products have not been isolated. By contrast, DBU promotes the subsequent incorporation of a second C=C double bond (Fig. 12). The five-membered lactone precursor expands to the seven-membered lactone and can be cleaved hydrolytically to obtain elongated and functionalized acids. In certain cases, β-H elimination occurs, resulting in the cleavage of the ring, formation of a Ni–H species, and regeneration of the olefinic function. The reductive elimination to the free acid and $(DBU)_2Ni(0)$ does not take place and therefore prevents a catalytic run. The same phenomenon was observed for the C–C coupling of styrene (Sect. 2.2) [21].

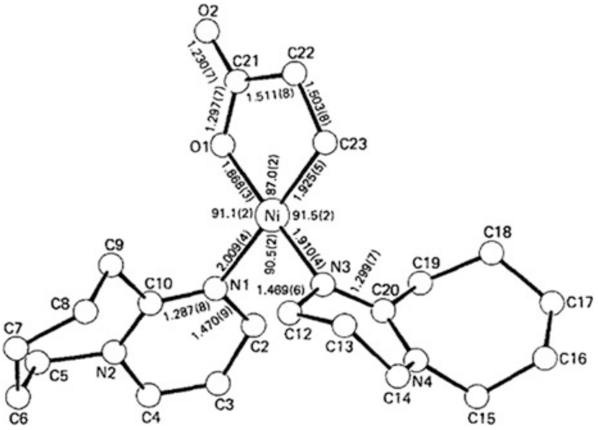


Fig. 13 Crystal structure of $(dbu)_2NiLac$ with a square-planar coordination sphere [34]

With the employment of DBU, a first successful X-ray crystal structure analysis was obtained for the five-membered nickelalactone consisting of CO_2 and ethylene (Fig. 13) [34]. The $16e^-$ complex revealed a square-planar coordination of the Ni atom, which is bound to the imine nitrogen of two DBU units. Due to the planar orientation, a nonbinding interaction of the metal with the hydrogen of C_α was excluded.

2.4 Preliminary Studies Toward Acrylic Acid

The interest in the topic of nickelalactone utilization decreased in the 1990s leaving the question if a catalytic conversion for CO_2 could ever be realized. Despite a huge variety of synthetic methods, promotors, and ligands, each approach was limited to stoichiometric conversions at some point. Either the crucial β-H elimination or the reductive elimination did not occur. For this reason, alternative metal centers (Fe [35, 36], Pd [37, 38], Pt [39, 40], Ti [41], Zr [42], Rh [43], Mo [44, 45]) have been investigated. Nevertheless, Ni seemed to be the most versatile metal center in the C–C bond formation with olefins. In 2006, Walther et al. revived the vision of the catalytic conversion to acrylic acid. They postulated a theoretical catalytic cycle of the "dream reaction" (Fig. 14) [7]. The first step involves the oxidative coupling of a Ni(0) with ethylene and CO_2 and subsequent generation of an acrylate species via β-hydride elimination of the five-membered lactone. The reductive elimination of the Ni(II) center affords the π-coordinated acid which is released by ligand exchange with ethylene and hence closes the catalytic cycle.

One of the key steps in this catalytic cycle is the β-H elimination that has been elusive so far except for styrene (Sect. 2.2) [21]. Walther investigated phenyl-substituted bis(phosphine)s with different bridge lengths. They revealed that the reaction pathway upon addition of ligand to (tmeda)NiLac is strongly dependent on

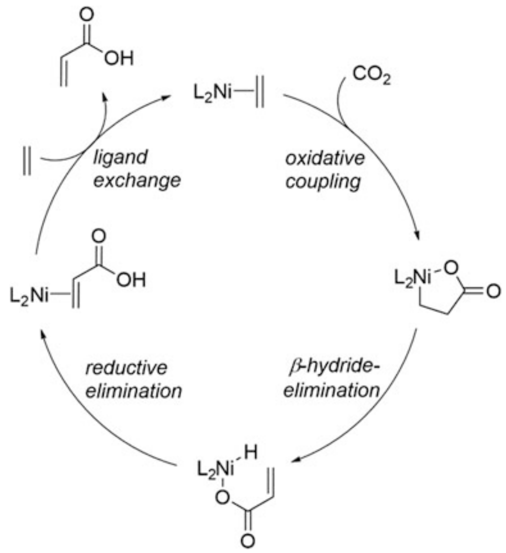


Fig. 14 Hypothetical catalytic cycle to the formation of acrylic acid from ethylene and CO_2 via nickelalactone intermediates by Walther et al. [7]

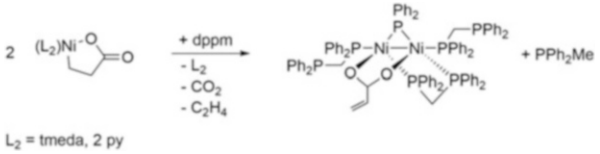


Fig. 15 Synthesis of a bridged binuclear nickel-acrylate complex through β-H elimination [7]

the bridge length. Longer backbones either afford stable complexes (dppe), or a reductive decoupling (dppp, dppb) is induced, whereas the methylene-bridged ligand 1,1′-bis(diphenylphosphino)methane (dppm) promotes a β-H elimination and subsequent dimerization with the decoupled species $(dppm)_3Ni(0)$ to an acrylate-bridged compound (Figs. 15 and 16). However, reductive elimination from the complex to release the acrylate does not occur. Due to its stability and the sacrificial cleavage of one dppm ligand to form a phosphido bridge ($PPh2^-$), it cannot be utilized in further syntheses.

Further investigations by Walther focused on the ligand modification [46]. They obtained model compounds of the different postulated intermediates in the catalytic cycle employing rigid and bulky 1,1′-bis(di-*iso*-propylphosphanyl)ferrocene (d*i*ppf) and 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) (Fig. 17). Depending on the substituents at the phosphorous atom and the synthetic strategy, a stable Ni (0) π-complex with coordinated acrylic acid, the corresponding nickelalactone, or the $Ni(0)(C_2H_4)$ π-complex is formed. Conversion of the cyclic compound to the ethylene complex was observed by CO_2 liberation; however, no isomerization of the lactone to the acrylic acid occurs.

Buntine et al. performed detailed computational calculations on the desired catalytic C–C coupling between CO_2 and ethylene mediated by the $(DBU)_2Ni$

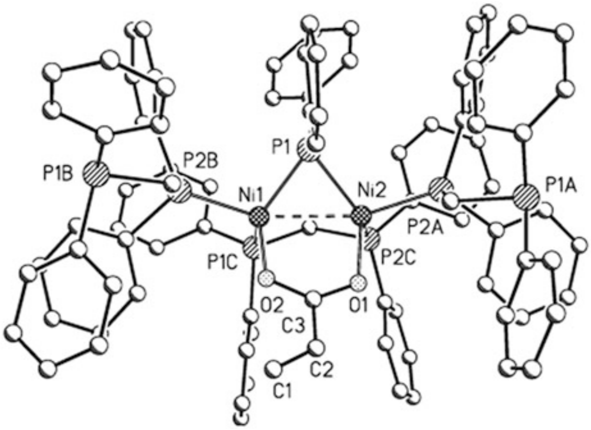


Fig. 16 X-ray analysis of the binuclear Ni species with the acrylate-bridged ligand motif [7]

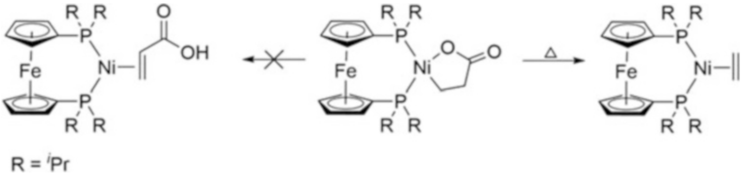


Fig. 17 Synthesized model compounds bearing a rigid d*i*ppf ligand [46]

(0) catalyst [47]. The quantum mechanical data was elaborated using the model ligand (*m*DBU) in which the seven-membered ring was substituted by two methyl groups. It decreased the computational effort. The data reveals three main barriers in the catalytic reaction: (1) the oxidative coupling (+121.8 kJ/mol), (2) β-H elimination (+147.4 kJ/mol), and (3) the reductive elimination (+104.1 kJ/mol) through a most likely "five-center three-ligand" transition state. A transition structure for the β-H elimination in the five-membered nickelacycle proved unsuccessful due to the restricted geometry in the ring. Through an elongation of the Ni–O bond, the abstraction of the hydride may occur. With regard to the values, these barriers do not hinder the catalytic process at moderate reaction conditions; however, the overall endergonic reaction (+42.7 kJ/mol) of the catalytic cycle is most likely the biggest obstacle to overcome from a thermodynamic point of view. The deactivation pathway through H-migration of Ni–H to the N=C double bond of DBU has a moderate barrier (+150.2 kJ/mol), but the instability of the product (+102.1 kJ/mol) makes it negligible, in contrast to theories of Hoberg (Sects. 2.2 and 2.3) [34]. Prospective solutions have to improve the overall thermodynamics by removal of the acrylic acid and shift the equilibrium to the product site or modify the desired acrylic acid to improve the overall energy balance.

3 Liberation of Acrylates

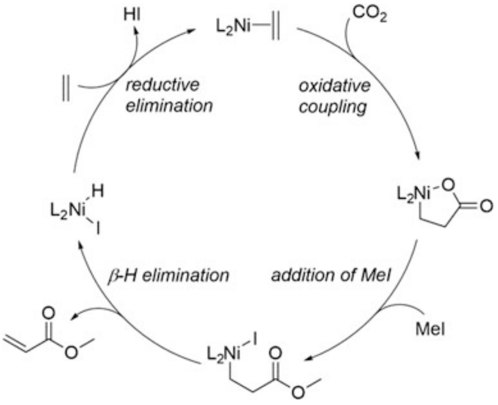
3.1 Methylation of Nickelalactones

Previous studies and DFT-based calculations lowered the expectations to realize a Ni(0)-catalyzed process to acrylic acid [47]. Therefore, novel approaches and strategies were required. In 2010, Rieger et al. reported the first liberation of an acrylate derivative via methylation of nickelalactones [48]. Upon addition of 2–100 equiv. of MeI to the reaction mixture of (dppp)NiLac in CH_2Cl_2, the respective methyl acrylate is obtained in yields up to 29%. Neat MeI increases the yield by 4%. The replacement of MeI with LiI yields 6% Li(acrylate) due to its low solubility and weaker interaction with the Ni–O bond. Other methylating agents like methyl triflate and trimethyloxonium tetrafluoroborate afford only traces of acrylate. Although only stoichiometric amounts of methyl acrylate were formed, a new hypothetic catalytic cycle was postulated (Fig. 18). After the oxidative coupling, the cleavage of the Ni–O moiety by MeI promotes the β-H elimination to release the desired methyl acrylate. The reductive elimination of the side product HI finally regenerates the Ni(0) catalyst.

Analogous to reactions of platina- [40] and palladalactones [49] with MeI, the methylation induces the elongation of the Ni–O bond, so that subsequent β-H elimination is promoted. Furthermore, the unfavored reductive elimination of a stable Ni–O bond is circumvented. Closure of the catalytic cycle was not achieved due to the formation of methyl propionate as by-product and unsuccessful recovery of the active species.

Limbach et al. performed deeper experimental and theoretical studies on the methylation with the d*t*bpe ligand (Fig. 19) [50]. They found out that the methylation most likely occurs at the carbonyl oxygen and proceeds via S_N2-type reaction with a low barrier. The methylated species equilibrates between a cationic four- and five-membered intermediate via β-H elimination. The final formation of methyl acrylate offers two possible pathways. Either a second nickelalactone deprotonates

Fig. 18 Postulated catalytic cycle for the formation of methyl acrylate from nickelalactones by Rieger et al. [48]



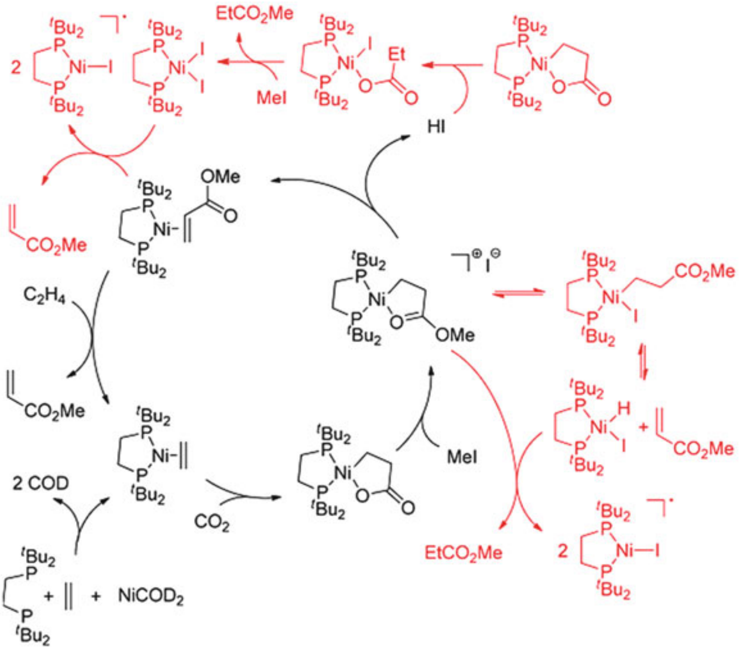


Fig. 19 Hypothetic catalytic cycle forming methyl acrylate (*black*) and examined side reactions to methyl propionate (*red*) by Limbach et al. [50]

the cationic intermediate and affords the Ni(acrylate) π-complex, or the postulated β-H elimination occurs and liberates methyl acrylate from the complex. Furthermore, they identified unfavorable pathways, which inhibit a catalytic approach due to the formation of HI.

Due to the unselective reaction with MeI, a range of alternative methylating agents have been examined for various nickela- and palladalactones by Kühn [51, 52]. In contrast to results of Rieger and Limbach, methyl triflate turned out to be the most suitable cleavage agent under the chosen reaction conditions, independent of the auxiliary ligand. A fast transformation of the cyclic ester to the nickel hydride and the ring opening intermediate was observed via in situ H-NMR spectroscopy. A catalytic conversion was not performed though.

3.2 Lewis Acid-Induced β-H Elimination

The spontaneous β-H elimination from a five-membered nickelalactone has not been observed so far, except for one styrene-based lactone [21]. However, the use of Lewis acids reveals a promoting effect on β-H elimination. When we take a look back, Hoberg added $BeCl_2$ to various substituted and unsubstituted nickelalactones

[53]. An immediate ring contraction occurs, most likely via β-H elimination and subsequent 2,1-insertion. Due to the ring strain and the Ni–C_{sec} bond, the formed β-lactone structures exhibit a higher reactivity than their five-membered congeners and readily insert a second substrate to expand to a six-membered ring (Fig. 20). Therefore, the four-membered intermediate was not isolated. Via this route, geminal dicarboxylic acids are accessible by the addition of a second carbon dioxide. Again, the stability of the Ni–O moiety prevents a catalytic approach; hence, the acidic hydrolysis is essential to liberate the organic products.

Based on these results and observations with Li^+ [48], a similar strategy was published by Bernskoetter [54]. Treatment of nickelalactones, in this case (dppf) NiLac, with the strong neutral Lewis acid $B(C_6F_5)_3$ at rt promotes a rapid β-H elimination. The most likely formed nickel-acrylate hydride intermediate was not detected, but a subsequent 2,1-insertion affords the first stable four-membered β-lactone (Fig. 21). The X-ray analysis exhibits a formally zwitterionic product with the expected ring structure and the Lewis acid attached to the oxygen.

Further utilization of the β-lactone is possible via deprotonation with neutral organic bases. With DBU, unselective side reactions arise, and the Ni species partially decomposes, whereas BTPP selectively affords the deprotonated π-complex at rt after two days. From a mechanistic point of view, the source of the withdrawn proton is not identified. Most likely the deprotonation takes place from the nickel hydride intermediate. Alternative pathways like the proton abstraction from the C_α position in the four-membered ring or from the CH_3 group in β-position seem unlikely but cannot be fully excluded with regard to the pK_a values of

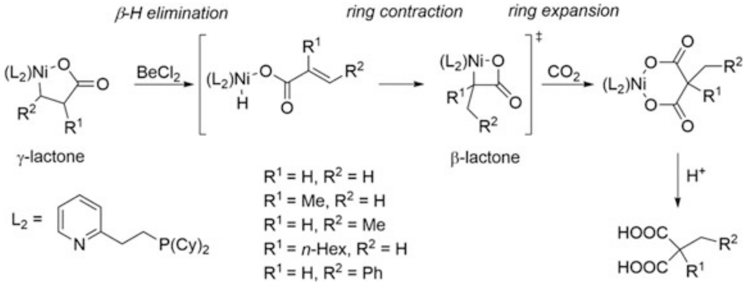


Fig. 20 Postulated pathway to geminal dicarboxylic acids through Lewis acid-induced ring contraction by Hoberg et al. [53]

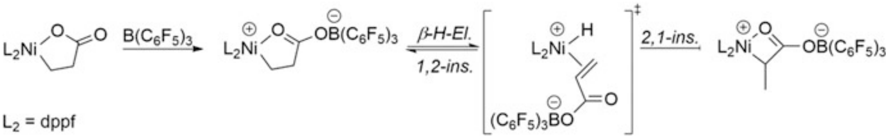


Fig. 21 Lewis acid-induced transformation of a nickelalactone via β-H elimination and subsequent 2,1-insertion to the thermodynamically favored β-lactone [54]

the complex and the base. The subsequent ligand exchange readily occurs by addition of ethylene and expels the formed [BTPPH][(B(C_6F_5)$_3$)(acrylate)]. However, the establishment of the last step of the catalytic cycle remained elusive, due to the fact that dppf does not induce an oxidative coupling with CO_2 under the investigated reaction conditions (Fig. 22).

Recently, Bernskoetter examined a strong influence of the chosen ligand on the lactone's reactivity [55]. Dcpm and its ethyl-bridged congener dcpe both perform the C–C bond formation of CO_2 and ethylene to the *γ*-nickelalactone in average to high yields (47% for dcpm, 88% for dcpe). Upon addition of a weak Lewis acid ($NaBAr^F{}_4$), the Na^+ coordinates to the carboxylic moiety. Subsequent heating to 55°C in thf induces a partial *γ*-to-*β* isomerization ($\beta/\gamma = 1/3.5$ for dcpe, 1/8 for dcpm), verified by NMR spectroscopy and X-ray analysis. In contrast to the dcpm ligand, thf solutions of (dcpe)NiLac even isomerize in the absence of Lewis acid to an unactivated *β*-lactone. The unactivated species is less stable than the sodium adduct; therefore, a higher preference for the five-membered *γ*-lactone can be observed in equilibrium in this case (Fig. 23).

Computational analysis supports the beneficial effect of Na^+ on the *γ*-to-*β* isomerization [55]. It provides a decrease of the ring strain in the formed *β*-lactone and stabilizes the negative charge of the carboxylic moiety in the transition state. The addition of suitable Lewis acids as cocatalysts that can bind reversibly to the carboxylic moiety to promote *β*-H elimination could introduce new strategies toward catalytic reactions.

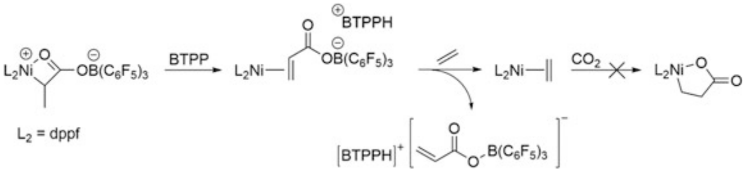


Fig. 22 Deprotonation and subsequent release of the acrylic salt from a 2,1-insertion nickelalactone [54]

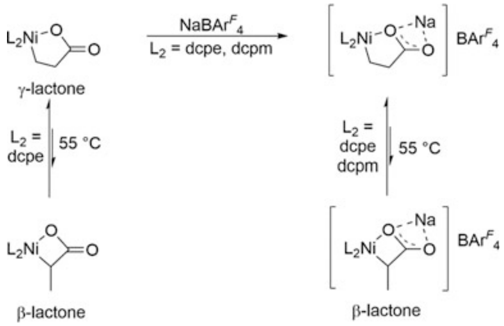


Fig. 23 Lewis acid-assisted and Lewis acid-unactivated thermal isomerization to a *β*-lactone [55]

3.3 Catalytic Routes

The addition of cleavage auxiliaries has been broadly investigated recently. However, the employed electrophiles and Lewis acids do not lead to catalysis. Either one of the elementary steps remained elusive, or side reactions to inactive species occurred. Investigating a different approach, Limbach et al. reported in 2012 the first successful nickel-catalyzed synthesis of an acrylate, derived from carbon dioxide and ethylene (TON = 10) [3]. With the choice of a suitable ligand and the sacrificial use of a strong sodium alkoxide base, a selective catalytic reaction was established. Formation of Na(acrylate) as desired product shifts an overall endergonic reaction (for acrylic acid) [47] to a favorable exergonic process (−59 kJ/mol) (Fig 24) [56].

The initial step of the catalytic cycle represents the oxidative coupling. It reveals a strong influence by the chosen ligand. The literature-known ligands, i.e., bpy and DBU, only offer limited solubilities and stabilities; therefore, Limbach focused on *tert*-butyl and phenyl-substituted bis(phosphine)s with different bridge lengths ((–CH_2−)$_{1-3}$). The phenyl-substituted bis(phosphine)s rapidly form Ni(dppe)$_2$ and Ni(dppp)$_2$ upon addition of Ni(cod)$_2$, even in the presence of ethylene and CO_2. The use of bulky *tert*-butyl groups inhibits the deactivation by two ligands attached to one Ni(0) center. Due to their strong σ-donating properties, they rapidly form the corresponding π-ethylene complexes and subsequently induce the C–C bond formation with CO_2. This is in good accordance with a mechanistic point of view. The reaction is expected to occur through the C–C bond formation of an incoming CO_2

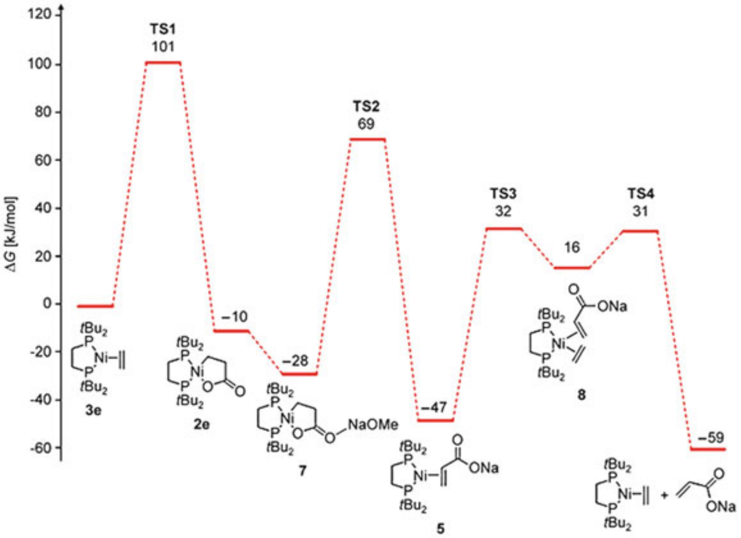


Fig. 24 Quantum mechanical energy profile for the catalyzed synthesis of Na(acrylate) by Limbach et al. [3]

into a Ni–C_2H_4 bond; hence, the formation of a Ni-π-(ethylene) complex is crucial. With regard to the bridge length, only (dtbpe)NiLac forms a stable isolable compound, whereas (dtbpm)NiLac is only detectable under CO_2 pressure via ^{31}P NMR spectroscopy.

In the second step, strong sodium alkoxides induce a cleavage to the corresponding acrylate species. The role of the base has not been clearly confirmed yet since different mechanistic procedures seem possible according to the quantum mechanical calculations. This includes the deprotonation in the acidic α-position of the lactone with a subsequent rearrangement to the nickel π-acrylate species or the β-H elimination of an activated intermediate, as suggested for palladalactones by Aresta [38]. NaO^tBu turned out to be the best suitable base under the investigated reaction conditions. Further studies have shown that the sodium cation, as well as the base, is crucial for the transformation to the acrylate. The quaternary ammonium salt NBu_4OMe does not promote a lactone cleavage, whereas the supplementary addition of $NaBAr^F{}_4$ accomplishes the reaction with 47% yield. The last step requires a ligand exchange of the coordinated acrylate with ethylene to regenerate the potential catalyst. Due to a weaker π-back bonding of Na(acrylate) compared to Me(acrylate) or acrylic acid [3, 50, 56], the pressurized ethylene can release Na(acrylate) from the complex and hence close the catalytic route (Fig. 25). As a disadvantage, the presented catalysis has to be performed in two repetitive steps. Alkoxide bases irreversibly form carbonic half esters under CO_2 pressure, which inhibit a deprotonation. Therefore, the overall reaction is divided into a CO_2-rich (oxidative coupling) and CO_2-poor (cleavage and liberation) regime.

In further research, Limbach reported an optimized one-pot-catalysis (Fig. 26) [57]. Firstly, the sacrificial base was replaced by sodium phenoxides, due to their lower nucleophilicity. Hence, they are suitable bases under CO_2 pressure which do not form carbonate half esters. In correlation with the according pK_a values (*ortho* < *meta* < *para*), sodium 2-fluorophenoxide reveals the highest activity of the tested substrates. NaOPh, Na(4-fluorophenoxide), and phenoxides with +I

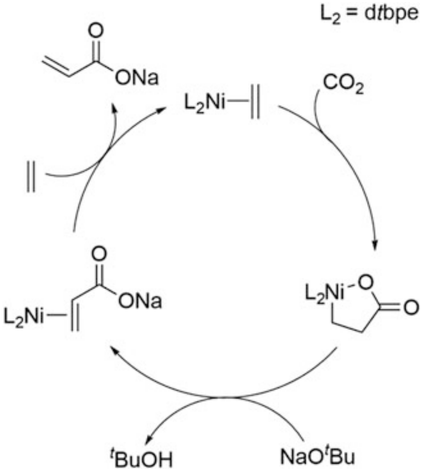


Fig. 25 Ni(0)-catalyzed synthesis of Na(acrylate) from NaO^tBu, CO_2, and ethylene [3]

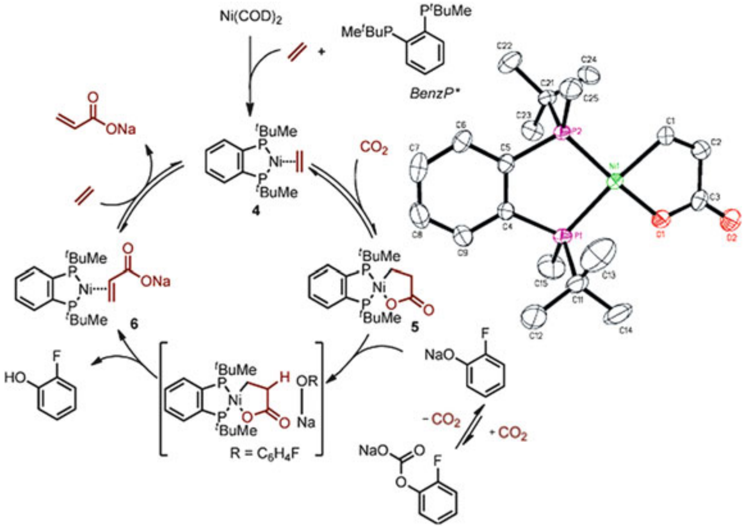


Fig. 26 Advanced catalytic cycle with (BenzP*)Ni(0) as active species and X-ray structure of the lactone intermediate [57]

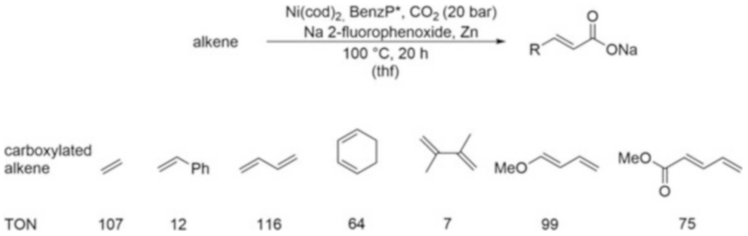


Fig. 27 Excerpt of the carboxylated substrates via one-pot catalysis [57]

substituents exhibit significantly lower TONs. Studies on small-bite angle ligands (dtbpm, dppm), monodentate phosphines (PPh$_3$, P^{t}Bu$_3$), and stereogenic bis(phosphine)s revealed the highest TONs for the chiral ligands (*S*)-BINAPINE, (*S*,*S*,*R*,*R*)-TangPhos, (*R*,*R*,*S*,*S*)-DuanPhos, and (*R*,*R*)-BenzP*. The addition of an excess of zinc has beneficial effects on the TON; however, the specific reason remained unclear.

Additional studies on various substrates have been performed with the BenzP* system at 100°C in thf. The direct carboxylation is applicable to a wide range of olefins including 1,3-dienes, styrenes, cycloalkenes, *Michael* acceptors, and functional group containing olefins; however, it exhibits the highest TONs for ethylene (TON = 107) and 1,3-butadiene (TON = 116) (Fig. 27). In the case of 2-vinylpyridine, styrenes, and 2,3-dimethyl butadiene, the catalytic activity dramatically decreases (TON = 2–12). Summarizing, a one-pot reaction with TONs > 100 was successfully developed, but TOF values up to 6 h^{-1} still prevent this catalysis from applicability in a huge scale.

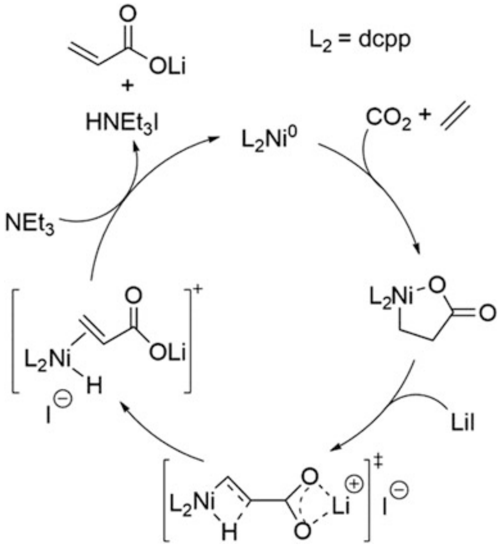


Fig. 28 Proposed catalytic cycle for the acrylate formation upon addition of LiI by Vogt et al. [58]

Vogt et al. recently published an optimized version of Rieger's initial approach with MeI [48, 58]. They realized a catalytic formation from CO_2 and ethylene employing LiI as "hard" Lewis acid (Fig. 28). As examined and calculated for various Lewis acids [56, 55], the Li^+ cation elongates the carboxylic moiety and promotes β-H elimination. According to DFT calculations support the choice of Li^+ over Na^+, since the Gibbs free energy of the transition state (+104 kJ/mol without Lewis acid) is decreased by 20 kJ/mol for Na^+ and +40 kJ/mol for Li^+. Immediate release of the product and regeneration of the catalyst by trapping the formed HI with the base close the catalytic cycle. The role of the iodide remains unclear.

In order to suppress side reactions with the released HI (i.e., propionate), NEt_3 is added. D*I*PEA, K_2CO_3, and Cs_2CO_3 were less efficient. The addition of Zn dust prevented the formation of inactive NiI_2 species reaching a TON = 21 for dcpp after 72 h. Overall, a huge amount of sacrificial auxiliaries (base, Zn) is added to the reaction mixture, and the low TON values are far from a useful application in synthesis. But apart from Limbach's strategy involving sacrificial bases [57], the route by Vogt provides new opportunities to the formation of acrylates with Lewis acids.

4 Conclusion

Since the discovery of the nickel(0)-induced oxidative coupling of CO_2 and ethylene over three decades ago, the formed nickelalactones have been considered as potential intermediates in catalytic approaches. Initial investigations were focused on the stoichiometric conversion to useful organic compounds, e.g., saturated carboxylic acids, esters, and anhydrides. Catalytic strategies however remained elusive. With regard to the synthesis of acrylates, the overall thermodynamics and the missing elimination reactions were pointed out as main obstacles in a catalytic formation.

After more than 25 years of research, the methylation of a nickelalactone with MeI afforded the first successful liberation of a methyl acrylate species. The methyl group elongates the Ni–O moiety and facilitates a subsequent β-H elimination to release the product. This route is accompanied by the formation of inactive Ni (II) compounds and by-products that can only be suppressed to a certain amount. Although limited to stoichiometric conversion, it was the basis for further experimental investigations and computational studies. Hence, a wide range of potential cleaving agents (i.e., electrophiles, Lewis acids) have been examined recently. Finally, two different catalytic pathways have been developed. In the presence of LiI, a catalytic conversion to Li(acrylate) with a $\mathrm{TON} = 21$ was achieved. The Li^+ ion serves as Lewis acid and promotes the Ni–O bond dissociation. However the reaction is slow and occurring side reactions were suppressed upon stoichiometric addition of base and reducing agent. Sacrificial sodium alkoxide bases offer an alternative catalytic route via deprotonation of the lactone intermediate and subsequent transformation to sodium acrylate. By ligand modification, exploration of suitable bases, and optimization of the reaction conditions, one-pot catalysis with a $\mathrm{TON} > 100$ was achieved. Further examinations will focus on the acceleration and versatility of the catalysis, since this system is not limited to ethylene only. In order to compete with the current oil-based industrial processes one day, the catalyst activities have to improve dramatically. With respect to the recent breakthrough in this field, one can be excited about prospective developments in the nickelalactone utilization. Due to the rising demand for fossil resources, novel and modern strategies like the catalytic CO_2-based C–C coupling with olefins to basic chemicals are highly demanded in the future.

References

1. Behr A, Agar W, Joerissen J (2010) Einführung in die Technische Chemie. Spektrum Akademischer Verlag, Heidelberg
2. Aresta M, Dibenedetto A, Angelini A (2014) Catalysis for the valorization of exhaust carbon: from CO2 to chemicals, materials, and fuels. Technological use of CO_2. Chem Rev 114(3): 1709–1742. doi:10.1021/cr4002758
3. Lejkowski ML, Lindner R, Kageyama T, Bódizs GÉ, Plessow PN, Müller IB, Schäfer A, Rominger F, Hofmann P, Futter C, Schunk SA, Limbach M (2012) The first catalytic synthesis of an acrylate from CO2 and an alkene—a rational approach. Chem Eur J 18(44): 14017–14025. doi:10.1002/chem.201201757
4. Cokoja M, Bruckmeier C, Rieger B, Herrmann WA, Kühn FE (2011) Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? Angew Chem Int Ed 50(37):8510–8537. doi:10.1002/anie.201102010

5. Hoberg H, Schaefer D (1983) Nickel(0)-induced C-C bonding between carbon dioxide and ethylene as well as monosubstituted and disubstituted alkenes. J Organomet Chem 251(3): C51–C53. doi:10.1016/s0022-328x(00)98789-8
6. Hoberg H, Schaefer D, Burkhart G, Krüger C, Romão MJ (1984) Nickel(0)-induzierte C–C-verknüpfung zwischen kohlendioxid und alkinen sowie alkenen. J Organomet Chem 266(2): 203–224. doi:10.1016/0022-328X(84)80129-1
7. Fischer R, Langer J, Malassa A, Walther D, Gorls H, Vaughan G (2006) A key step in the formation of acrylic acid from CO2 and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex. Chem Commun 23:2510–2512
8. Yamamoto T, Igarashi K, Komiya S, Yamamoto A (1980) Preparation and properties of phosphine complexes of nickel-containing cyclic amides and esters [(PR3)nNiCH2CH(R1) COZ (Z = NR2, O)]. J Am Chem Soc 102(25):7448–7456. doi:10.1021/ja00545a009
9. Burkhart G, Hoberg H (1982) Oxanickelacyclopentene derivatives from nickel(0), carbon-dioxide, and alkynes. Angew Chem Int Ed 21(1):76. doi:10.1002/anie.198200762
10. Hoberg H, Schaefer D (1982) Model complexes of nickel for the $2 + 2 + 2'$-cycloaddition of alkynes with carbon-dioxide. J Organomet Chem 238(4):383–387. doi:10.1016/s0022-328x(00)83800-0
11. Hoberg H, Apotecher B (1984) Alpha, omega-diacids from butadiene and carbon-dioxide on nickel(0). J Organomet Chem 270(1):C15–C17. doi:10.1016/0022-328x(84)80346-0
12. Hoberg H, Schaefer D (1983) Sorbic acid from piperylene and CO2 through C-C coupling on nickel. J Organomet Chem 255(1):C15–C17. doi:10.1016/0022-328x(83)80185-5
13. Hoberg H, Oster BW (1984) Nickel(0)-induced C-C bonding between 1,2-dienes and carbon-dioxide. J Organomet Chem 266(3):321–326. doi:10.1016/0022-328x(84)80145-x
14. Hoberg H, Schaefer D (1982) Nickel(0) induced C-C linkage between alkenes and carbon-dioxide. J Organomet Chem 236(1):C28–C30. doi:10.1016/s0022-328x(00)86765-0
15. Hoberg H, Ballesteros A (1991) Ni0-induzierte Herstellung cyclischer C8-Carbonsäuren aus Cyclooctenen und Kohlendioxid. J Organomet Chem 411(1–2):C11–C18. doi:10.1016/0022-328x(91)86033-m
16. Hoberg H, Ballesteros A, Sigan A, Jegat C, Milchereit A (1991) Durch (Lig)Ni(0) induzierte Herstellung von mono- und di-Carbonsäuren aus Cyclopenten und Kohlendioxid. Synthesis 1991(05):395,398. doi:10.1055/s-1991-26475
17. Hoberg H, Barhausen D (1989) Nickel(0)-induced CC coupling of CO2 with 1,3-butadiene for preparing linear C-13-acids. J Organomet Chem 379(1–2):C7–C11. doi:10.1016/0022-328x(89)80043-9
18. Hoberg H, Gross S, Milchereit A (1987) Nickel(0)-catalyzed production of a functionalized cyclopentanecarboxylic acid from 1,3-butadiene and CO2. Angew Chem Int Ed 26(6): 571–572. doi:10.1002/anie.198705711
19. Hoberg H, Schaefer D, Oster BW (1984) Diene carboxylic-acid from 1,3-dienes and CO2 through C-C bonding on nickel. J Organomet Chem 266(3):313–320. doi:10.1016/0022-328x(84)80144-8
20. Fischer R, Walther D, Braunlich G, Undeutsch B, Ludwig W, Bandmann H (1992) Nickelalactone als Synthesebausteine: Sonochemische und Bimetallaktivierung der Kreuzkopplungsreaktion mit Alkyl-halogeniden. J Organomet Chem 427(3):395–407. doi:10.1016/0022-328x(92)80077-b
21. Hoberg H, Peres Y, Milchereit A (1986) C-C coupling of alkenes with Co_2 in nickel(0) - production Of cinnamic acid in styrene. J Organomet Chem 307(2):C38–C40. doi:10.1016/0022-328x(86)80487-9
22. Hoberg H, Summermann K, Milchereit A (1985) CC bond formation of alkenes with isocyanates on NI-0 complexes - a new synthesis of acrylamides. Angew Chem Int Ed 24(4): 325–326
23. Hoberg H, Summermann K, Milchereit A (1985) C-C bond forming of alkenes with isocyanates on nickel(0). J Organomet Chem 288(2):237–248. doi:10.1016/0022-328x(85)87282-x

24. Hoberg H, Hernandez E (1985) Nickel(0)-catalyzed synthesis of sorbanilide from 1,3-pentadiene and phenyl isocyanate. Angew Chem Int Ed 24(11):961–962. doi:10.1002/anie.198509611
25. Hoberg H, Summermann K (1983) Diazanickelacyclopentanones synthesized from nickel(0), imines and isocyanates. J Organomet Chem 253(3):383–389. doi:10.1016/s0022-328x(00)99233-7
26. Hoberg H, Summermann K (1984) Nickel(0) catalyzed synthesis of imines from isocyanates and aldehydes. Z Naturforsch B 39(8):1032–1036
27. Hoberg H, Summermann K (1984) Nickel(0)-induced couples of benzaldehyde with isocyanates in nickel heterocycles. J Organomet Chem 264(3):379–385. doi:10.1016/0022-328x(84)85082-2
28. Hoberg H, Nohlen M (1991) Ni(O)-induced CC coupling of phenylisocyanate with cyclic 5-membered alkenes, catalytic preparation of beta, gamma-unsaturated carboxylic-acid anilides. J Organomet Chem 412(1–2):225–236. doi:10.1016/0022-328x(91)86057-w
29. Hoberg H, Hernandez E (1986) Intermolecular C-C bond-formation of azanickelacyclopentanone alpha, omega-diacid amides from alkenes and phenyl isocyanate. J Organomet Chem 311(3):307–312. doi:10.1016/0022-328x(86)80252-2
30. Kaiser J, Sieler J, Braun U, Golič L, Dinjus E, Walther D (1982) Aktivierung von Kohlendioxid an Übergangsmetallzentren: Kristall- und molekulstruktur von 2,2′-dipyridyl-nickela-5-methyl-2,4-dioxolan-3-on, einem Kopplungsprodukt von Kohlendioxid und Acetaldehyd am Zentralatom Nickel (0). J Organomet Chem 224(1):81–87. doi:10.1016/S0022-328X(00)82569-3
31. Walther D, Dinjus E, Sieler J, Kaiser J, Lindqvist O, Anderson L (1982) Aktivierung von kohlendioxid an übergangsmetallzentren: nickela(II)-heterocyclen aus kohlendioxid und azaolefinen am elektronenreichen nickel(0)-komplexrumpf. J Organomet Chem 240(3):289–297. doi:10.1016/S0022-328X(00)86795-9
32. Yamamoto T, Sano K, Yamamoto A (1987) Effect of ligand on ring contraction of six-membered nickel-containing cyclic esters, LnNiCH2CH2CH2COO, to their five-membered-ring isomers, LnNiCH(CH3)CH2COO. Kinetic and thermodynamic control of asymmetric induction by chiral diphosphines in the ring contraction. J Am Chem Soc 109(4):1092–1100. doi:10.1021/ja00238a017
33. Hoberg H, Peres Y, Milchereit A (1986) C-C coupling of alkenes with CO2 in nickel(0) - N-pentanoic acids in ethene. J Organomet Chem 307(2):C41–C43. doi:10.1016/0022-328x(86)80488-0
34. Hoberg H, Peres Y, Krüger C, Tsay Y-H (1987) A 1-oxa-2-nickela-5-cyclopentanone from ethene and carbon dioxide: preparation, structure, and reactivity. Angew Chem Int Ed 26(8):771–773. doi:10.1002/anie.198707711
35. Hoberg H, Jenni K, Angermund K, Krüger C (1987) C–C-linkages of ethene with CO2 on an iron(0) complex—synthesis and crystal structure analysis of [(PEt3)2Fe(C2H4)2]. Angew Chem Int Ed 26(2):153–155. doi:10.1002/anie.198701531
36. Hoberg H, Jenni K, Kruger C, Raabe E (1986) CC coupling of CO2 and butadiene on iron(0) complexes - a novel route to alpha-omega-dicarboxylic acids. Angew Chem Int Ed 25(9):810–811. doi:10.1002/anie.198608101
37. Osakada K, Doh MK, Ozawa F, Yamamoto A (1990) Catalytic and stoichiometric carbonylation of beta, gamma-unsaturated carboxylic acids to give cyclic anhydrides through intermediate palladium-containing cyclic esters. Organometallics 9(8):2197–2198. doi:10.1021/om00158a010
38. Aresta M, Pastore C, Giannoccaro P, Kovács G, Dibenedetto A, Pápai I (2007) Evidence for spontaneous release of acrylates from a transition-metal complex upon coupling ethene or propene with a carboxylic moiety or CO2. Chem Eur J 13(32):9028–9034. doi:10.1002/chem.200700532
39. Yamamoto T, Sano K, Osakada K, Komiya S, Yamamoto A, Kushi Y, Tada T (1990) Comparative studies on reactions of alpha, beta- and beta, gamma-unsaturated amides and

acids with nickel(0), palladium(0), and platinum(0) complexes. Preparation of new five- and six-membered nickel- and palladium-containing cyclic amide and ester complexes. Organometallics 9(8):2396–2403. doi:10.1021/om00158a041

40. Aye KT, Colpitts D, Ferguson G, Puddephatt RJ (1988) Activation of a.beta.-lactone by oxidative addition and the structure of a platina(IV)lactone. Organometallics 7(6): 1454–1456. doi:10.1021/om00096a039
41. Cohen SA, Bercaw JE (1985) Titanacycles derived from reductive coupling of nitriles, alkynes, acetaldehyde, and carbon dioxide with bis(pentamethylcyclopentadienyl)(ethylene) titanium(II). Organometallics 4(6):1006–1014. doi:10.1021/om00125a008
42. Burlakov VV, Arndt P, Baumann W, Spannenberg A, Rosenthal U (2006) Simple functionalizations of pentamethylcyclopentadienyl ligands by reactions of decamethylzirconocene complexes with carbon dioxide. Organometallics 25(5):1317–1320. doi:10.1021/om051063z
43. Aresta M, Quaranta E (1993) Synthesis, characterization and reactivity of [Rh(bpy)(C2H4)Cl]. A study on the reaction with C1 molecules (CH2O, CO2) and NaBPh4. J Organomet Chem 463(1–2):215–221. doi:10.1016/0022-328x(93)83420-z
44. Alvarez R, Carmona E, Cole-Hamilton DJ, Galindo A, Gutierrez-Puebla E, Monge A, Poveda ML, Ruiz C (1985) Formation of acrylic acid derivatives from the reaction of carbon dioxide with ethylene complexes of molybdenum and tungsten. J Am Chem Soc 107(19):5529–5531. doi:10.1021/ja00305a037
45. Alvarez R, Carmona E, Galindo A, Gutierrez E, Marin JM, Monge A, Poveda ML, Ruiz C, Savariault JM (1989) Formation of carboxylate complexes from the reactions of carbon dioxide with ethylene complexes of molybdenum and tungsten. X-ray and neutron diffraction studies. Organometallics 8(10):2430–2439. doi:10.1021/om00112a026
46. Langer J, Fischer R, Görls H, Walther D (2007) Low-valent nickel and palladium complexes with 1,1′-Bis(phosphanyl)ferrocenes: syntheses and structures of acrylic acid and ethylene complexes. Eur J Inorg Chem 2007(16):2257–2264. doi:10.1002/ejic.200601051
47. Graham DC, Mitchell C, Bruce MI, Metha GF, Bowie JH, Buntine MA (2007) Production of acrylic acid through nickel-mediated coupling of ethylene and carbon dioxide—a DFT study. Organometallics 26(27):6784–6792. doi:10.1021/om700592w
48. Bruckmeier C, Lehenmeier MW, Reichardt R, Vagin S, Rieger B (2010) Formation of methyl acrylate from CO2 and ethylene via methylation of nickelalactones. Organometallics 29(10): 2199–2202. doi:10.1021/om100060y
49. Kakino R, Nagayama K, Kayaki Y, Shimizu I, Yamamoto A (1999) Formation of a palladalactone complex by C–O bond cleavage of diketene promoted by a zerovalent palladium complex. Chem Lett 28(7):685–686
50. Plessow PN, Weigel L, Lindner R, Schäfer A, Rominger F, Limbach M, Hofmann P (2013) Mechanistic details of the nickel-mediated formation of acrylates from CO2, ethylene and methyl iodide. Organometallics 32(11):3327–3338. doi:10.1021/om400262b
51. Lee SYT, Cokoja M, Drees M, Li Y, Mink J, Herrmann WA, Kühn FE (2011) Transformation of nickelalactones to methyl acrylate: on the way to a catalytic conversion of carbon dioxide. ChemSusChem 4(9):1275–1279. doi:10.1002/cssc.201000445
52. Lee SYT, Ghani AA, D'Elia V, Cokoja M, Herrmann WA, Basset J-M, Kuhn FE (2013) Liberation of methyl acrylate from metallalactone complexes via M-O ring opening (M = Ni, Pd) with methylation agents. New J Chem. doi:10.1039/c3nj00693j
53. Hoberg H, Ballesteros A, Sigan A, Jégat C, Bärhausen D, Milchereit A (1991) Ligandgesteuerte Ringkontraktion von Nickela-fünf- in Vierringkomplexe—neuartige startsysteme für die präparative chemie. J Organomet Chem 407(3):C23–C29. doi:10.1016/0022-328x(91)86320-p
54. Jin D, Schmeier TJ, Williard PG, Hazari N, Bernskoetter WH (2013) Lewis acid induced β-elimination from a nickelalactone: efforts toward acrylate production from CO2 and ethylene. Organometallics 32(7):2152–2159. doi:10.1021/om400025h

55. Jin D, Williard PG, Hazari N, Bernskoetter WH (2014) Effect of sodium cation on metallacycle β-hydride elimination in CO2–ethylene coupling to acrylates. Chem Eur J 20(11):3205–3211. doi:10.1002/chem.201304196
56. Plessow PN, Schäfer A, Limbach M, Hofmann P (2014) Acrylate formation from CO2 and ethylene mediated by nickel complexes: a theoretical study. Organometallics. doi:10.1021/om500151h
57. Huguet N, Jevtovikj I, Gordillo A, Lejkowski ML, Lindner R, Bru M, Khalimon AY, Rominger F, Schunk SA, Hofmann P, Limbach M (2014) Nickel-catalyzed direct carboxylation of olefins with CO2: one-pot synthesis of α, β-unsaturated carboxylic acid salts. Chem Eur J 20(51):16858–16862. doi:10.1002/chem.201405528
58. Hendriksen C, Pidko EA, Yang G, Schäffner B, Vogt D (2014) Catalytic formation of acrylate from carbon dioxide and ethene. Chem Eur J. doi:10.1002/chem.201404082