The First Catalytic Synthesis of an Acrylate from CO_2 and an Alkene—A Rational Approach

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Dedicated to Professor Dieter Seebach on the occasion of his 75th birthday

Abstract: For more than three decades the catalytic synthesis of acrylates from the cheap and abundantly available C_1 building block carbon dioxide and alkenes has been an unsolved problem in catalysis research, both in academia and industry. Herein, we describe a homogeneous catalyst based on nickel that permits the catalytic synthesis of the industrially highly relevant acrylate sodium acrylate from CO_2, ethylene, and a base, as demonstrated, at this stage, by a turnover number of greater than 10 with respect to the metal.

Keywords: C_1 building blocks · carbon dioxide fixation · carboxylation · homogeneous catalysis · nickel

Introduction

The exploitation of CO_2 for the production of organic chemicals on a global scale is of huge industrial interest because CO_2 is a cheap and abundantly available C_1 building block.[1,2,3] Nevertheless, there is only a very limited number of known reactions and catalysts that enable the efficient and straightforward catalytic incorporation of CO_2 into industrially relevant target molecules.[4] This is why over recent decades a considerable amount of research and money has been invested into the realization of these, so far unknown, reactions—often called "dream reactions".

The direct synthesis of acrylates from CO_2 and alkenes is one of the most economically attractive, but also one of the most challenging, dream reactions: Na acrylate is one of the most industrially important acrylates, with a global market volume of approximately 4 million tons and is frequently used as a monomer in the manufacture of partially neutralized superabsorber polymers. These are ubiquitous in daily life and are found, for example, in modern diapers. In contrast to the state-of-the art, two-step oxidation processes, which are based on fossil-fuel-derived C_3-hydrocarbons (propylene, propane), an efficient synthesis based on ethylene (e.g., from bioethanol) and CO_2 would translate, today, to the utilization of up to 7.3 million tons of CO_2 along this novel value-added chain. This could pave the way to a "green" superabsorber polymer in which all carbon atoms originate from renewable sources.

The metal-catalyzed oxidative coupling of CO_2 with alkenes and alkynes has been intensively studied over three decades. Hoberg et al. and others[5,6,7,8] have revealed metallalactones, in particular nickelalactones ("Hoberg complexes"),[9] to be stable and isolable intermediates of the potential catalytic coupling of ethylene and CO_2, but it has never been possible to assemble the elementary reactions of the putative catalytic cycle proposed by Walther et al.,[10] nor has it been possible to actually close the catalytic cycle itself. Despite the development of a catalytic route to the structurally similar acrylamides from alkenes and isocyanates (isoelectronic to CO_2),[11] and an intensive search for other catalytically active metals from the nickel (Pd, Pt)[12,13] and iron triads,[14] the basic obstacles for a catalytic transformation have not been overcome; the prohibitive overall thermodynamic situation for the production of acrylic acid ($\Delta G = +42.7$ kJ mol^{-1}),[15] the limitation to a small set of ligands, the unproductively low reaction temperatures (down

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to −70 °C), and the failure of the Hoberg-type complexes (and of other metallalactones) to undergo a productive cleavage (believed to occur, for example, through a β-hydride elimination) have made this reaction a difficult object to study.[16]

Results and Discussion

Nickelalactone formation: In his pioneering studies Hoberg et al. reported the direct coupling of CO_2 and ethylene at a nickel center only with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[9,17] and bipyridine ligands.[18] These ligands lead to poorly soluble metallalactones with various stabilities.[19] Bisphosphine ligands, such as 1,2-bis(dicyclohexylphosphino)-ethane (dcpe),[18] not only yield nickelalactones with good solubility in common solvents, but also carry a convenient ^{31}P NMR spectroscopic handle for mechanistic studies.[18]

Thus, we first systematically studied the influence of the length of the carbon bridge [-CH$_2$(CH$_2$)$_n$- ($n = 0$–2)] in the backbone of bisphosphine ligands **1a–f**, containing either phenyl or *tert*-butyl substituents at the phosphorus atoms, on the selectivity of the oxidative coupling to yield nickelalactones **2a–f** (Table 1). Although complexes based on bis(di-

Table 1. Direct synthesis of nickelalactones **2a–f**, η^2-ethylene complexes **3a–f**, and tetracoordinate bisphosphine complexes **4a–f** from CO_2 and ethylene (cod = 1,5-cyclooctadiene).

Entry	1a–f	R	n	Yield 2a–f [(%)][a]	Yield 3a–f [(%)][a]	Yield 4a–f [(%)][a]
1	**1a**	dppm	Ph	0	0	0	0
2	**1b**	dppe	Ph	1	0	0	65
3	**1c**	dppp	Ph	2	0	0	24
4	**1d**	d*t*bpm	*t*Bu	0	60 (0)[b,c]	0[b,c]	0
5	**1e**	d*t*bpe	*t*Bu	1	35	62	0
6	**1f**	d*t*bpp	*t*Bu	2	0	97	0

[a] Yield by ^{31}P NMR spectroscopy at $p(CO_2)/p(C_2H_4) = 6$ bar/2 bar, [D$_8$]THF, 50 °C, 72 h. [b] Yield by ^{31}P NMR spectroscopy after release of CO_2/C_2H_4 pressure is given in parentheses. [c] Yield by ^{31}P NMR spectroscopy at $p(CO_2)/p(C_2H_4) = 6$ bar/2 bar, [D$_8$]THF, 25 °C, 19 h.

phenylphosphino)methane (dppm, **1a**) formed aggregates,[20] those based on the homologues 1,2-bis(diphenylphosphino)-ethane (dppe, **1b**)[21] and 1,3-bis(diphenylphosphino)propane (dppp, **1c**)[22] rapidly formed the tetracoordinate Ni^0 species [Ni(dppe)$_2$] (**4b**)[23,24] and [Ni(dppp)$_2$] (**4c**)[25,26] in 65 and 24 % yield, respectively. Even after a reaction time of 72 h, none of the nickelalactones [Ni{(CH$_2$)$_2$CO$_2$}(dppe)] (**2b**) and [Ni{(CH$_2$)$_2$CO$_2$}(dppp)] (**2c**) had formed, as shown by ^{31}P NMR spectroscopy. We rationalized that this coordinative saturation of the metal might be avoided by switching to more bulky *tert*-butyl substituents at the phosphorus atoms because DFT calculations (by using COSMO-RS theory for chlorobenzene (PhCl) as the solvent under stand-

ard conditions; see the Supporting Information)[27] predicted the formation of **4d–f** to be noticeably endergonic ($\Delta G > 50$ kJ mol^{-1}). The formation of lactones **2d–f** from ethylene complexes **3d–f** and CO_2 was calculated to be almost thermoneutral under ambient conditions for ligands **1d–f** by analysis of the corresponding energy profiles (ΔG, see Figure 2a below for d*t*bpe), and the energy barriers increase with the ligands' bite angle [d*t*bpm (**1d**): 102 kJ mol^{-1},[28] d*t*bpe (**1e**): 101 kJ mol^{-1}, and d*t*bpp (**1f**): 112 kJ mol^{-1}]. Thus, d*t*bpe (**1e**) was found to be the optimal ligand for further reactivity studies because [Ni{(CH$_2$)$_2$CO$_2$}(d*t*bpe)] (**2e**) formed reasonably quickly at higher temperatures under CO_2 pressure and is stable at ambient temperature because the back-reaction is frozen at ambient temperature.

In fact, ligands **1d–f** immediately formed the corresponding ethylene complexes **3d–f** in good to excellent yield (62–97 %), which, in a subsequent step of the reaction with CO_2, were converted to the desired nickelalactones **2d–e** (35–97 % yield). These complexes vary greatly in stability; whereas [Ni{(CH$_2$)$_2$CO$_2$}(d*t*bpe)] (**2e**) was stable enough to be isolated and stored as a solid for several months without decomposition, [Ni{(CH$_2$)$_2$CO$_2$}(d*t*bpm)] (**2d**) was stable only under a CO_2 atmosphere ($p(CO_2)/p(C_2H_4) = 6$ bar/ 2 bar), conditions under which a 60 % yield was formed, but it decomposed quickly upon pressure release. The free ligand d*t*bpm (**1d**) was liberated from **2d** quantitatively.

The highly air-sensitive ethylene complex [Ni(η^2-C$_2$H$_4$)(d*t*bpe)] (**3e**) was independently prepared in 45 % yield by reacting d*t*bpe, [Ni(cod)$_2$], and ethylene (19 bar) in an autoclave (^{31}P NMR: $\delta = 92.8$ ppm).[29] Crystals of **3e** suitable for X-ray analysis were grown from Et$_2$O at −35 °C,[30] whereas crystals of [Ni(η^2-C$_2$H$_4$)(d*t*bpp)] (**3f**) were grown from THF at room temperature (Figure 1). In **3e** and **3f** the geometry around the Ni atom is approximately square-planar, but the bite angle of d*t*bpp is significantly larger than for d*t*bpe (104.700(15)° vs. 93.89(8)°). The C−C bond lengths of the η^2-bound ethylene ligands point to stronger Ni-to-ethylene back-bonding for the bisphosphine with the smaller bite angle.

The yield of nickelalactone **2e** was found to be highly temperature dependent and reaches a maximum of 54 % in THF after 6 h at 50 °C ($p(C_2H_4)/p(CO_2) = 5$ bar/40 bar). At a lower temperature, the reaction slowed significantly (31, 18, and 9 % yield at 45, 35, and 25 °C, respectively, all after 6 h). Although, at temperatures above 55 °C [Ni{(CH$_2$)$_2$CO$_2$}(d*t*bpe)] (**2e**) was formed in reasonable yield (50 % after 6 h at 55 °C), significant amounts of d*t*bpe dioxide and its monoxide counterpart formed.[31] As we worked under strictly anaerobic conditions, these most likely originate from decomposition pathways starting from an η^2 side-on-bound CO_2 complex of the catalytically active {Ni(d*t*bpe)} fragment,[31] which is at best innocent and unproductive,[19,32] with a free energy of 36 kJ mol^{-1} relative to **3e**.

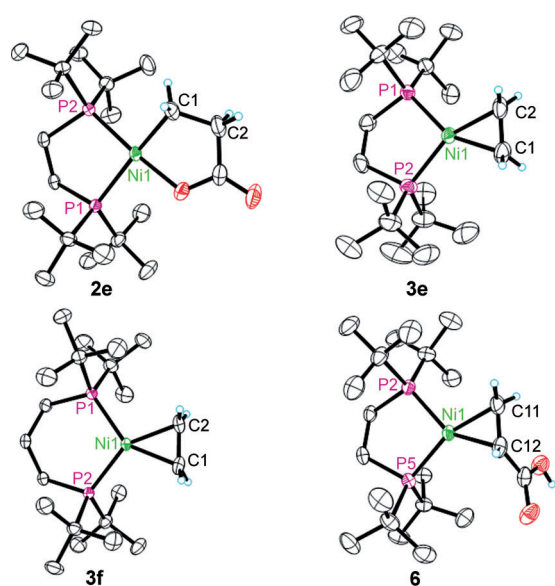Figure 1. Solid-state (X-ray) molecular structures of [Ni{(CH₂)₂CO₂}-(d*t*bpe)] (**2e**), [Ni(η²-C₂H₄)(d*t*bpe)] (**3e**), [Ni(η²-C₂H₄)(d*t*bpp)] (**3f**), and [Ni(η²-CH₂=CHCO₂H)(d*t*bpe)] (**6**), with ellipsoids drawn at the 50% probability level. Hydrogen atoms of the phosphine ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2e**: P−Ni 2.1681(8) and 2.2409(8), C1−C2 1.512(5); P-Ni-P 90.74(3), C-Ni-O 84.74(13); **3e**/ **3f**: Ni−P1 2.1654(18)/2.1749(4), Ni−P2 2.1659(18)/2.1839(4), Ni−C1 1.961(6)/1.9720(19), Ni−C2 1.970(6)/1.9807(17), C−C 1.416(9)/1.392(3); P-Ni-P 93.89(8)/104.700(15), C-Ni-C 42.2(3)/41.24(8); **6**: P−Ni 2.1579(6) and 2.1954(6), C1−C2 1.417(3), Ni−C 1.942(2) and 1.988(2); P-Ni-C 93.49(2), C-Ni-C 42.24(9).

A significant increase in reaction rate was observed in PhCl (91% after 6 h at 60°C). Temperatures of 60°C gave lactone **2e** in a clean reaction (90% conversion, 72% yield of isolated product after 2 h of reaction time). The superiority of PhCl over THF as the solvent might be a consequence of its lower coordinating ability, which facilitates interaction of nickel with CO₂ and has already been observed in cross-coupling reactions that involve weakly coordinating substrates.[33] Kinetic experiments in PhCl show that [Ni(η²-C₂H₄)(d*t*bpe)] (**3e**) forms quantitatively in the initial phase of the reaction as the sole species. Its reaction with CO₂ to form [Ni{(CH₂)₂CO₂}(d*t*bpe)] (**2e**) follows straight first-order kinetics (see the Supporting Information), as determined by ³¹P NMR spectroscopy (PhCl, 60°C, 40 bar CO₂).

Nickelalactone cleavage: The cleavage of nickelalactones [Ni{(CH₂)₂CO₂}(ligand)] to form acrylate π-complexes of the form [Ni(η²-CH₂=CHCO₂R)(ligand)] had to be considered to be the most challenging step in the hypothetical catalytic cycle (Table 2).[15,34] Although an equilibrium between a nickelalactone and an η²-coordinated acrylic acid complex (R=H) has been proposed by Walther et al.,[10] reliable experimental evidence for this step has so far been completely missing. Furthermore, the cleavage of nickelalactone complexes [Ni{(CH₂)₂CO₂}(ligand)] has hitherto only been observed through decomposition of the ligand,[10] or in a stoichiometric, low yield reaction to form [Ni(η²-CH₂=

Table 2. Base-mediated transformation of [Ni{(CH₂)₂CO₂}(d*t*bpe)] (**2e**) into [Ni(η²-CH₂=CHCO₂Na)(d*t*bpe)] (**5**).
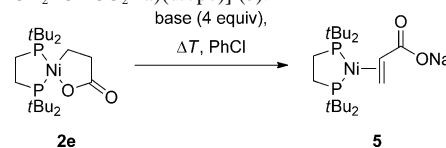
Entry	Base	Additive	Time [h]	Temperature [°C]	Yield **5** [%]
1	NaO*t*Bu	–	0.25	25	90
2	NaHMDS	–	0.25	25	87
3	NaOMe	–	24	50	51 (71)[a]
4	NaOH	–	24	50	0 (70)[b]
5	NaOPh	–	72	70	0
6	NBu₄OMe	–	72	50	0
7	NBu₄OMe	NaBAr_F	72	50	47
8	DBU	–	72	70	0
9	DBU	NaBAr_F	72	70	0
10	P1	–	72	50	0
11	P1	NaBAr_F	72	50	40

[a] The value in parentheses corresponds to a reaction carried out in a PhCl/MeOH (1:1) solvent mixture. [b] The value in parentheses corresponds to a reaction carried out in a MeOH/H₂O (1:1) solvent mixture.

CHCO₂Me)(ligand)], as described by Rieger et al.[6] and subsequently by Kühn et al.[7] Interestingly, the reverse reaction of [Ni(η²-CH₂=CHCO₂H)(ligand)] to form a nickelalactone [Ni{(CH₂)₂CO₂}(ligand)] has been proposed by Yamamoto et al.[35] for PCy₃ (Cy=cyclohexane) as a ligand; however, the species assigned to be an acrylic acid π-complex based on IR spectroscopy, should more accurately be regarded as an oligomeric nickelalactone ($\tilde{\nu}=1567$ cm⁻¹).[36]

Because the coordination geometry around Ni in **2e** is square-planar, a productive, low-barrier β-hydride elimination from the flat 5-membered nickelalactone ring system is unlikely for stereoelectronic reasons (see the tetrahedral C2 in **2e** in Figure 1). This has been noted in an earlier DFT study by Buntine et al.,[15] who were unable to find any reasonable reaction pathway (simplified DBU as the ligands). If an intramolecular β-elimination mechanism of nickelalactone **5** involving a nickel hydride is nevertheless considered to be a viable pathway towards a [Ni(η²-CH₂=CHCO₂R)-(d*t*bpe)] species, an increasing Ni−O bond length should correlate with the tendency to undergo this transformation. In fact, [Ni{(CH₂)₂CO₂}(d*t*bpe)] (**2e**) has one of the longest Ni−O bonds (see Figure 1) amongst a set of crystallized nickelalactones (1.889(2) Å vs. 1.890(2) Å for dcpe,[18] 1.8448(1) Å for 2,2′-bipyridine,[37] 1.8655(13) Å for pyridine,[38] and 1.868(3) Å for DBU[9]). Not surprisingly, neither heating a sample of **2e** in [D₈]THF or PhCl to 80°C gave any product that would indicate the intermediacy of a β-hydride elimination product, nor did the reaction from [Ni(η²-CH₂=CHCO₂H)(d*t*bpe)] (**6**) to **2e** take place under those conditions.

Among the manifold of mechanistic scenarios considered for the nickelacycle to nickel acrylate transformation, the aforementioned DFT investigations of Buntine et al.[15] also discarded pathways involving deprotonation at the nickela-

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lactone's C1 and C2 carbon atoms by a base like DBU because these reactions were calculated to be energetically inaccessible. Experimentally we found that in our hands strong anionic alkali-metal bases, such as alkoxides (NaOtBu) or hexamethyldisilylamides (e.g., sodium hexamethyldisilazide (NaHMDS)), converted [Ni{(CH$_2$)$_2$CO$_2$}-(dtbpe)] (**2e**) in PhCl at room temperature into [Ni(η^2-CH$_2$=CHCO$_2$Na)(dtbpe)] (**5**) in 90% yield within minutes (see Table 2). A similar reaction of **2e** with NaOMe or aqueous NaOH required prolonged reaction times and elevated temperatures, whereas less basic reagents, like NaOPh, did not lead to conversion of lactone **2e**.

This reaction is most likely effected by abstraction of one of the lactone's fairly acidic α-protons next to the carbonyl group by a base. Interestingly, the cation was found to play a crucial role in this transformation; when the quarternary ammonium salt [NBu$_4$OMe] was used instead of NaOMe, [Ni-{(CH$_2$)$_2$CO$_2$}(dtbpe)] (**2e**) was not converted even after a significantly longer reaction time of 72 h. However, by adding an alternative sodium source to [NBu$_4$OMe], such as sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr$_F$), the reaction again led to a fast cleavage of **2e** to form [Ni(η^2-CH$_2$=CHCO$_2$Na)(dtbpe)] (**5**; 47% yield in 72 h). The Lewis acidity and coordination ability of the sodium cation seems to be necessary to stabilize the carboxylate that is formed during the course of the elimination reaction. Significant activity of neutral bases was only observed in the case of the the phosphazene superbase *tert*-butyliminotri(pyrrolidino)phosphorane (P1; pK_a = 28.35)[39] in combination with NaBAr$_F$ as an external Na$^+$ source (40% yield after 72 h).

Quantum mechanical (QM) calculations on reactions involving alkali alkoxides are challenging because solvent effects are strong and the actual basic species present in solution are often not precisely known. This is why all calculations were carried out with the COSMO-RS model to account for the solvent effects of PhCl (see above). For very reactive species like alkoxide monomers or dissociated Na$^+$ and RO$^-$ ions, deprotonation next to the lactone carbonyl group is clearly feasible. The formation of this type of ion, however, is endergonic by more than 100 kJ mol^{-1} and cubane-like alkoxide tetramers[40] have a computed free binding energy of approximately 90 kJ mol^{-1} per monomer. The mechanism was investigated in detail for NaOMe, and the most stable located structure before lactone cleavage is the nickelalactone coordinated to a (NaOMe)$_4$ tetramer (**7**, Figure 2a). Possible reactions are discussed relative to this species (for details, see
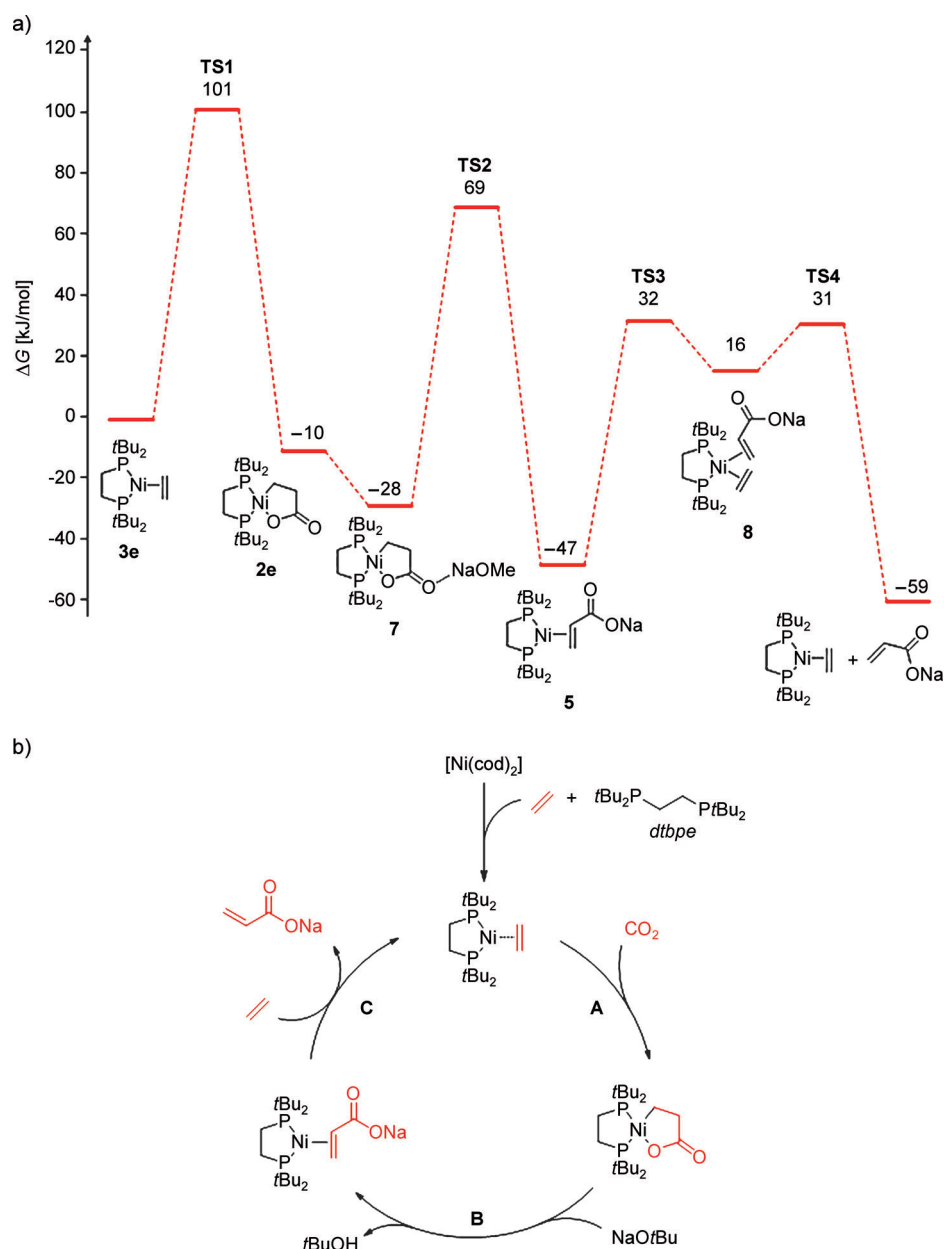

Figure 2. a) A DFT-computed ΔG profile of the complete catalytic cycle. TS2 is the highest barrier in the stepwise α-deprotonation reaction. Free energies are given for reactions in PhCl with (NaOMe)$_4$ tetramers, although only monomers are displayed for clarity. b) Catalytic cycle for the formation of Na acrylate from CO$_2$, ethylene, and a base.
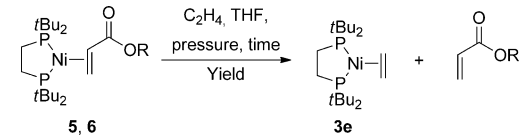
the Supporting Information). Concerted deprotonation α to the carbonyl group and formation of [Ni(η^2-CH$_2$= CHCO$_2$Na)(d$t$bpe)] (**5**) occurs through a relative barrier of 105 kJ mol^{-1}. Exchange of one OMe oxygen atom of the (NaOMe)$_4$ cubane structure for a lactone oxygen atom leads to an activated lactone[40] that can then be deprotonated at the α position by the still-coordinated, exchanged alkoxide. The subsequent rearrangement to form **5** has the highest barrier (98 kJ mol^{-1}) of this step-wise process.

The activated lactone could also react through β-hydride elimination, as proposed by Aresta et al.[13] for activated palladalactones. The high energy of the first barrier (approximately 122 kJ mol^{-1} for d$t$bpe) and the instability of the formed intermediate towards deprotonation make even this type of activated β-hydride elimination unlikely. This fundamental thermodynamic limitation is overcome by switching to Na acrylate **5** ($\Delta G = -59$ kJ mol^{-1}, see Figure 2a), which also significantly reduces the kinetic barrier for metallacycle cleavage (98 kJ mol^{-1}). Lactone cleavage could, in principle, also be induced by formation of an alkoxide-O−Ni bond and by breaking of the nickelalactone-O−Ni bond. The resulting intermediate is of reasonable stability with NaOMe (49 kJ mol^{-1}) and much less stable with NaOtBu (78 kJ mol^{-1}) for steric reasons (whereas other intermediates are of comparable energies for the two alkoxides). Because we could not find data supporting the formation and favorable subsequent reactions of this intermediate, its relevance is not clear at this point. It is important to realize that, depending on solvation, different clusters of alkoxides might be present that may lead to a multitude of possible reaction pathways. We therefore conclude 1) that the base (both the alkali metal and the alkoxide) plays an important role in all lactone-cleavage reactions studied so far, 2) that the energy barriers are lower than those for β-hydride elimination mechanisms as well as for nickelalactone formation and, therefore, 3) that lactone formation and deprotonation α to the lactone carbonyl group appears to be the most viable route from CO$_2$ and ethylene to coordinated acrylate.

Acrylate/ethylene exchange: The final step required for the desired catalytic cycle must be a ligand exchange reaction of in situ formed [Ni(η^2-CH$_2$=CHCO$_2$Na)(d$t$bpe)] (**5**) with ethylene to liberate Na acrylate and to deliver [Ni(η^2-C$_2$H$_4$)-(d$t$bpe)] (**3e**) to reinitiate the catalytic cycle (Table 3). To study this reaction, we prepared [Ni(η^2-CH$_2$=CHCO$_2$H)-(d$t$bpe)] (**6**), a π complex with η^2-coordinated acrylic acid in 94% yield by following the procedure by Yamamoto et al.[41] Crystals suitable for X-ray analysis were obtained by slow diffusion of Et$_2$O into a saturated solution of **6** in THF at room temperature (Figure 1). In the solid state, compound **6** forms a dimer with H bridges between two carboxylic acid units. If compared with the Yamamoto η^2-bound ethyl methacrylate complex [Ni(η^2-CH$_2$=CMeCO$_2$Et)(PCy$_3$)$_2$],[42] the Ni−C bonds in **6** are significantly shorter (1.988(2) and 1.942(2) Å vs. 2.029(7) and 1.976(8) Å). This could point to significantly greater back-bonding in **6**. [Ni(η^2-CH$_2$= CHCO$_2$Na)(d$t$bpe)] (**5**) was isolated in 32% yield by depro-

tonation of **6** with NaOtBu, although by NMR spectroscopy the yield was quantitative. Whereas **5** underwent an exchange reaction to give, by ^{1}H NMR spectroscopy, an almost equimolar amount of Na acrylate at only 8 bar of ethylene, compound **6** mainly remained unreacted even at a pressure of as high as 30 bar (Table 3).[43]

Table 3. Liberation experiments for Na acrylate from [Ni(η^2-CH$_2$= CHCO$_2$Na)(d$t$bpe)] (**5**) and for acrylic acid from [Ni(η^2-CH$_2$=CHCO$_2$H)-(d$t$bpe)] (**6**).

Entry	Complex	R	Pressure [bar]	Time [h]	Yield **3e** [%]
1	**5**	Na	8	18	93
2	**5**	Na	30	0.25	95
3	**6**	H	8	18	6

QM calculations indicate that the reactivity difference between **5** and **6** towards ethylene is likely a consequence of the endergonic character of this reaction in the case of [Ni(η^2-CH$_2$=CHCO$_2$H)(d$t$bpe)] (**6**; $\Delta G = 24$ kJ mol^{-1}) due to a stronger stabilization by metal-to-ligand back-donation. In contrast, the acrylate-to-ethylene exchange is exergonic ($\Delta G = -12$ kJ mol^{-1}) for the ionic complex [Ni(η^2-CH$_2$= CHCO$_2$Na)(d$t$bpe)] (**5**), with computed barriers of 79 and 78 kJ mol^{-1} for **5** versus 88 and 99 kJ mol^{-1} for **6** and, according to our calculations occurs through the tetrahedral intermediate **8** (Figure 2a).

Assembly of a catalytic cycle: Having each elementary reaction **A**–**C** in place, as a last step in our study, the compatibility of the nickelalactone cleavage (**A**) with the other steps had to be proven (Figure 2b) because the alkoxides used in step **B** are known to irreversibly form fairly stable carbonic acid half esters with CO$_2$.[44] Therefore, the catalytic cycle had to be divided into two halves: a CO$_2$-rich regime (step **A**) and a CO$_2$-poor regime (i.e., steps **B** and **C**). Although the conversion of [Ni(η^2-C$_2$H$_4$)(d$t$bpe)] (**3e**) into nickelalactone [Ni{(CH$_2$)$_2$CO$_2$}(d$t$bpe)] (**2e**) proceeds quickly at a fairly high pressure of CO$_2$ (40 bar), the transformation of **2e** into [Ni(η^2-CH$_2$=CHCO$_2$Na)(d$t$bpe)] (**5**) and the final ligand-exchange reaction of **5** with ethylene to form Na acrylate were performed in its absence. Following this procedure in consecutive cycles, we were able to obtain a catalytic turnover of greater than 10. This is the first example of a clearly catalytic reaction for this synthesis. The Na acrylate formed in the reaction was finally separated by simple aqueous extraction and its identity was proven by HPLC-MS and NMR spectroscopy (see the Supporting Information). It is worth noting that the only organic product found in the organic and aqueous phases was the targeted compound, sodium acrylate.

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Conclusion

We have reported the first catalytic synthesis of an acrylate from CO_2 and ethylene. This new reaction is clearly catalytic as illustrated by a turnover number of greater than 10 at this stage for the valuable product sodium acrylate. This is considered to be a very good starting point for further process optimization, which might pave the way for a novel acrylic acid/acrylate value-added chain based on renewable raw materials. Our success has only been possible by careful isolation and characterization of potential intermediates, by a systematic study of the elementary reactions within the catalytic cycle, both experimentally and by calculations at the DFT level.

Experimental Section

Materials and physical methods: All manipulations were performed under an inert atmosphere of dry argon by using Schlenk techniques or by working in a glovebox. Solvents were dried by using a solvent-drying machine (MBraun SPS 800), degassed, and stored over molecular sieves (4 Å) in Teflon-valve ampoules under argon. Tetramethylethylenediamine (TMEDA) and DBU were distilled over CaH_2 prior to use. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker Avance 200, 300, 500, or 600 MHz spectrometers and were referenced to the residual proton (^{1}H) or carbon (^{13}C) resonance peaks of the solvent. Chemical shifts (δ) are reported in ppm. Elemental analyses and mass spectra were recorded by the analytical service of the chemistry department of the University of Heidelberg. Mass spectra were recorded on a Finnigan LCQ with a quadrupole ion trap (positive ion channel). Bis(di-*tert*-butylphosphino)-ethane[45] and bis(di-*tert*-butylphosphino)propane[46] were synthesized by following reported procedures. X-ray structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm by using the SHELXTL (Version 2008/4) software package.[47] Intensities were corrected for Lorentz and polarization effects.[48]

CCDC-869735 (**3e**), CCDC-869736 (**3f**), CCDC-869737 (**2e**), and CCDC-869738 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Bis(di-*tert*-butylphosphino)ethane](ethylene)nickel,   [Ni(η^2-C$_2$H$_4$)-(d*t*bpe)] (3e): A steel autoclave was charged with d*t*bpe (662 mg, 2.10 mmol), [Ni(cod)$_2$] (571 mg, 2.10 mmol), and THF (28 mL). The autoclave was pressurized several times with ethylene (15 bar). Removal of the solvent in a vacuum yielded compound **3e** as yellow-brown crystals (306 mg, 36% yield). Crystals suitable for X-ray analysis were grown at $-35\,°C$ from the reaction mixture upon addition of Et$_2$O. The formed crystals melt rapidly at room temperature. Yellow crystal (plate); dimensions: $0.23 \times 0.22 \times 0.10$ mm^3; crystal system: monoclinic; space group: $P2_1/c$; $Z=8$; $a=14.5382(3)$, $b=23.0028(5)$, $c=13.8463(3)$ Å; $\alpha=90$, $\beta=90.016(1)$, $\gamma=90°$; $V=4630.5(2)$ Å^3; $\rho=1.162$ g cm^{-3}; $T=200(2)$ K; $\theta_{max}=25.01°$; radiation: Mo$_{K\alpha}$, $\lambda=0.71073$ Å; 0.3° ω scans with a CCD area detector, covering a whole sphere in reciprocal space; reflections: 38711 measured, 8166 unique (R(int)$=0.0943$), 6289 observed ($I>2\sigma(I)$); an empirical absorption correction was applied $\mu=0.98$ mm^{-1}; min/max transmission$=0.81/0.91$; 416 parameters refined; hydrogen atoms were treated by using appropriate riding models; goodness of fit: 1.03 for observed reflections; final residual values: $R1(F)=0.054$, $wR(F^2)=0.113$ for observed reflections; residual electron density: -0.48 to 0.54 e Å^{-3}; elemental analysis calcd (%) for C$_{20}$H$_{44}$NiP$_2$ (405.2): C 59.28, H 10.94, P 15.29; found: C 58.88, H 10.85, P 15.11; ^{1}H NMR (500 MHz, C$_6$D$_6$): $\delta=1.14$ (m, 36H; C(CH$_3$)$_3$), 1.46 (m, 4H; PCH$_2$CH$_2$P), 2.42 ppm (s, 4H; $=$CH$_2$); ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$): $\delta=24.2$ (t, $J=16.6$ Hz; PCH$_2$CH$_2$P), 31.1 (t, $J=3.3$ Hz; CH$_3$), 34.3 (t, $J=8.3$ Hz; $=$CH$_2$),

34.7 ppm (t, $J=6.1$ Hz; C(CH$_3$)); ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): $\delta=105.2$ ppm (s); IR (KBr): 2944, 1663, 1477, 1387, 1364, 1179, 1163 cm^{-1}.

[Bis(di-*tert*-butylphosphino)propane](ethylene)nickel,   [Ni(η^2-C$_2$H$_4$)-(d*t*bpp)] (3f): [Ni(CH$_2$CH$_2$COO-κC,κO)(tmeda)][34] (282 mg, 1.10 mmol) and d*t*bpp (380 mg, 1.10 mmol) were mixed in THF (10 mL). The reaction mixture was stirred for 10 d at RT. Filtration of the orange crystals that formed over time and drying them in a vacuum yielded compound **3f** as orange crystals (92 mg, 20%). Orange crystal (polyhedron); dimensions: $0.34 \times 0.30 \times 0.18$ mm^3; crystal system: monoclinic; space group: $P2_1/n$; $Z=4$; $a=14.0230(2)$, $b=9.0870(1)$, $c=18.2757(1)$ Å; $\alpha=90$, $\beta=92.455(1)$, $\gamma=90°$; $V=2326.68(4)$ Å^3; $\rho=1.197$ g cm^{-3}; $T=200(2)$ K; $\theta_{max}=27.49°$; radiation: Mo$_{K\alpha}$, $\lambda=0.71073$ Å; 0.3° ω scans with a CCD area detector, covering a whole sphere in reciprocal space; reflections: 22767 measured, 5345 unique (R(int)$=0.0597$), 4542 observed ($I>2\sigma(I)$); $\mu=0.97$ mm^{-1}; min/max transmission$=0.73/0.84$; 245 parameters refined; hydrogen atoms were treated by using the appropriate riding models, except for the hydrogen atoms of ethylene, which were refined isotropically; goodness of fit: 1.05 for observed reflections; final residual values: $R1(F)=0.033$, $wR(F^2)=0.082$ for observed reflections; residual electron density: -0.65 to 0.53 e Å^{-3}; elemental analysis calcd (%) for C$_{21}$H$_{46}$NiP$_2$ (419.2): C 60.16, H 11.06, P 14.78; found: C 59.70, H 11.19, P 14.68; ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta=1.20$ (m, 36H; CH$_3$), 1.68(m, 8H; CH$_2$), 2.04 ppm (m, 2H; CH$_2$); ^{13}C{^{1}H} NMR (50.3 MHz, [D$_8$]THF): $\delta=22.1$ (t, $J=6.28$ Hz; CH$_2$), 25.0 (t, $J=6.34$ Hz; CH$_2$), 30.5 (t, $J=3.24$ Hz; CH$_3$), 34.3 (t, $J=7.21$ Hz; CH$_2$), 35.8 ppm (t, $J=6.57$ Hz; C-(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (81 MHz, [D$_8$]THF): $\delta=46.9$ ppm (s).

1-Bis(di-*tert*-butylphosphino)ethan-1-ethylenenickela-2-oxacyclopentan-3-one, [Ni(CH$_2$CH$_2$COO-κC,κO)(d*t*bpe)] (2e): [Ni(cod)$_2$] (138 mg, 500 µmol) and d*t*bpe (159 mg, 500 µmol) were suspended in PhCl (10 mL) and stirred until a red solution was formed. The mixture was transferred into an autoclave vessel and diluted with PhCl (10 mL). The autoclave was pressurized with ethylene (20 bar) and the reaction mixture was stirred (600 rpm) at RT for 30 min. Subsequently, the ethylene pressure was reduced (10 bar) and CO_2 was added until a final pressure of 50 bar was reached. Then, the stirring (600 rpm) was continued at $45\,°C$ for 16 h. After cooling to RT, the pressure was released and the mixture was transferred into a glass vial. The solvent was evaporated and the solid residue was dissolved in THF (3 mL). Precipitation by addition of *n*-hexane (50 mL), filtration, and drying under vacuum yielded compound **2e** as a fine, yellow precipitate (164 mg, 73% yield). Orange crystal (plate); dimensions: $0.23 \times 0.19 \times 0.07$ mm^3; crystal system: triclinic; space group: $P\bar{1}$; $Z=2$; $a=9.7498(11)$, $b=10.4305(12)$, $c=12.6578(15)$ Å; $\alpha=88.095(3)$, $\beta=86.519(3)$, $\gamma=66.673(2)°$; $V=1179.8(2)$ Å^3; $\rho=1.265$ g cm^{-3}; $T=200(2)$ K; $\theta_{max}=28.40°$; radiation: Mo$_{K\alpha}$, $\lambda=0.71073$ Å; 0.3° ω scans with a CCD area detector, covering a whole sphere in reciprocal space; reflections: 11090 measured, 11091 unique (R(int)$=0.0000$), 9687 observed ($I>2\sigma(I)$); $\mu=0.97$ mm^{-1}; min/max transmission$=0.81/0.94$; 248 parameters refined; hydrogen atoms were treated by using appropriate riding models; goodness of fit: 1.13 for observed reflections; final residual values: $R1(F)=0.049$, $wR(F^2)=0.116$ for observed reflections; residual electron density: -0.33 to 0.88 e Å^{-3}; elemental analysis calcd (%) for C$_{21}$H$_{44}$NiO$_2$P$_2$ (449.2): C 56.15, H 9.87, P 13.79; found: C 54.80, H 9.88, P 13.32; ^{1}H NMR (500 MHz, C$_6$D$_5$Cl): $\delta=1.19$ (m, 2H; Ni-CH$_2$), 1.37 (d, $J_{HP}=12.5$ Hz, 18H; C(CH$_3$)$_3$), 1.39 (d, $J_{HP}=12.5$ Hz, 18H; C(CH$_3$)$_3$), 1.50 (m, 2H; CH$_2$CH$_2$), 1.80 (m, 2H; CH$_2$CH$_2$), 2.07 ppm (m, 2H; CH$_2$-COO); ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_5$Cl): $\delta=9.6$ (dd, $J=62.9$, 26.4 Hz, Ni-CH$_2$), 18.4 (dd, $J=14.9$, 9.1 Hz; PCH$_2$CH$_2$P), 26.2 (dd, $J=39.3$, 22.1 Hz; PCH$_2$CH$_2$P), 30.2 (d, $J=4.8$ Hz; C(CH$_3$)$_3$), 30.3 (d, $J=3.4$ Hz; C-(CH$_3$)$_3$), 34.6 (d, $J=7.6$ Hz; C(CH$_3$)$_3$), 36.4 (dd, $J=17.8$, 1.9 Hz; C-(CH$_3$)$_3$), 37.4 (dd, $J=5.3$, 1.0 Hz; CH$_2$COO), 187.8 ppm (s, $J=17.3$ Hz; COO); ^{31}P{^{1}H} NMR (81 MHz, CD$_2$Cl$_2$): $\delta=77.8$ (d, $J_{P,P}=7.9$ Hz), 80.6 ppm (d, $J_{PP}=8.9$ Hz); HRMS (FAB+): m/z calcd for C$_{21}$H$_{45}$NiO$_2$P$_2$: 449.2246 [M+H]$^+$; found: 449.2202; IR (KBr): $\tilde{\nu}=2994$, 2953, 2899, 2866, 1627, 1481, 1468, 1313 cm^{-1}.

Formation of nickelalactones 2a–f in an high-pressure (HP) NMR experiment: [Ni(cod)$_2$] (17.9 mg, 65.0 µmol) and the phosphorous ligands **1a–f** (65.0 µmol) were dissolved in [D$_8$]THF (0.6 mL) and placed in an HP NMR tube. The NMR tube was consecutively pressurized with ethyl-

ene (2 bar) and CO_2 (6 bar) to an overall pressure of 8 bar and then heated to 25 (**1d**) or 50 °C (**1a–c**, **e**, and **f**) and the reaction was studied by NMR spectroscopy (^{1}H/^{31}P) after 19 (**1d**) or 72 h (**1a–c**, **e**, and **f**).

Ligand 1a (dppm): Formation of a black precipitate. ^{1}H NMR (200 MHz, [D₈]THF): $\delta = 2.33$ (s, 8H; CH_2 COD, dppm), 5.35 (s, 4 H; C_2H_4), 5.50 ppm (s, 4H; CH COD); ^{31}P{^{1}H} NMR (81 MHz, [D₈]THF): $\delta = 22$ ppm (br s).

Ligand 1b (dppe): ^{31}P NMR spectroscopic yield of **4b**: 65 %. ^{1}H NMR (200 MHz, [D₈]THF): $\delta = 2.07$ (m, 4H; CH_2 dppe), 2.33 (s, 8H; CH_2 COD), 5.35 (s, 4 H; C_2H_4), 5.50 (s, 4H; CH COD), 6.98 (m, 8H; CH), 7.39 ppm (m, 12H; CH); ^{31}P{^{1}H} NMR (81 MHz, [D₈]THF): $\delta = 43.9$ (s; **4b**), 50.9 ppm (s).

Ligand 1c (dppp): ^{31}P NMR spectroscopic yield of **4c**: 24 %. ^{1}H NMR (200 MHz, [D₈]THF): $\delta = 1.70$. (m, 4H; CH_2 dppp) 2.17 (br s, 2H; CH_2 dppe), 2.33 (s, 8H; CH_2 COD), 4.96 (s, 4 H; C_2H_4), 5.50 (s, 4H; CH COD), 7.05 (m, 2H; CH), 7.24 (m, 10H; CH), 7.51 ppm (m, 8H; CH); ^{31}P{^{1}H} NMR (81 MHz, [D₈]THF): $\delta = 12.0$ (s; **4c**), 17.4 (s), 20.8 ppm (s).

Ligand 1d (dtbpm): ^{31}P NMR spectroscopic yield of **2d**: 60 %; **1d**: 40 %. ^{1}H NMR (200 MHz, [D₈]THF): $\delta = 0.91$ (m, 2H; **2d** NiCH₂), 1.20 (m, 36 H; **1 d** CH_3), 1.49 (m, 18H; **2d** CH_3), 1.56 (m, 2, 18H; **1 d**, **2d** CH_2, CH_3), 1.75 (s), 2.12 (s,), 2.33 (s, 8H; CH_2 COD), 2.62 (m, 2H; **2d** CH_2CO), 3.60 (br s), 4.32 (s) 5.36 (s, 4 H; C_2H_4), 5.50 ppm (s, 4H; CH COD); ^{31}P{^{1}H} NMR (81 MHz, [D₈]THF): $\delta = 16.3$ (d, $J = 22.8$ Hz, **2d**), 21.8 (s, **1 d**), 36.1 ppm (d, $J = 22.8$ Hz, **2 d**).

Ligand 1e (dtbpe): ^{31}P NMR spectroscopic yield of **2e**: 35 %; **3e**: 62 %. ^{1}H NMR (200 MHz, [D₈]THF): $\delta = 1.21$ (m, 2, 36H; **2 e**, **3e** CH_2, CH_3), 1.40 (m, 36H; **2e** CH_3), 1.77 (m, 6, 8H; **2e**, **3d**), 2.33 (s, 8H; CH_2 COD), 5.36 (s, 4H; C_2H_4), 5.50 ppm (s, 4H; CH COD); ^{31}P{^{1}H} NMR (81 MHz, [D₈]THF): $\delta = 78.5$ (d, $J = 8.9$ Hz; **2e**), 81.0 (d, $J = 8.9$ Hz; **2e**), 91.9 ppm (s; **3e**).

Ligand 1f (dtbpp): ^{31}P NMR spectroscopic yield of **3f**: 97 %. Single crystals suitable for X-ray diffraction were isolated from the HP NMR experiment. Orange crystal (polyhedron); dimensions: $0.27 \times 0.25 \times 0.21$ mm³; crystal system: monoclinic; space group: $C2/c$; $Z = 4$; $a = 18.1611(14)$, $b = 13.1964(10)$, $c = 19.8885(15)$ Å; $\alpha = 90$, $\beta = 109.6810(10)$, $\gamma = 90°$; $V = 4488.1(6)$ Å³; $\alpha = 1.308$ g cm⁻³; $T = 200(2)$ K; $\theta_{max} = 28.32°$; radiation: Mo$_{K\alpha}$, $\lambda = 0.71073$ Å; 0.3° ω scans with a CCD area detector, covering a whole sphere in reciprocal space; reflections: 23 309 measured, 5566 unique ($R(\text{int}) = 0.0241$), 5129 observed ($I > 2\sigma(I)$); $\mu = 0.61$ mm⁻¹; min/max transmission = 0.85/0.88; 267 parameters refined; hydrogen atoms were treated by using appropriate riding models; goodness of fit: 1.04 for observed reflections; final residual values: $R1(F) = 0.029$, $wR(F^2) = 0.075$ for observed reflections; residual electron density: 0.20 to 0.40 e Å⁻³; ^{1}H NMR (200 MHz, [D₈]THF): $\delta = 1.21$ (m, 36H; **3f** CH_3), 1.44 (m), 1.73 (s, 8H; **3f** CH_2), 2.05 (m, 2H; **3f** CH_2), 2.33 (s, 8H; CH_2 COD), 5.36 (s, 4H; C_2H_4), 5.50 ppm (s, 4H; CH COD); ^{31}P{^{1}H} NMR (81 MHz, [D₈]THF): $\delta = 47.4$ ppm (s; **3f**).

Formation of nickelalactone 2e at various temperatures: [Ni(cod)₂] (138 mg, 500 μmol), d$t$bpe (159 mg, 500 μmol), and the internal standard tetrabutylphosphonium tosylate (108 mg, 250 μmol) were dissolved in THF (15 mL) and added to an autoclave (60 mL) by using a charger. The autoclave was pressurized with ethylene at RT (5 bar, 15 min equilibration time), CO_2 was added until a pressure of 40 bar was reached. After 15 min, the reaction was heated to the temperature given in the main text and a sample was taken from the reaction by syringe and characterized by ^{31}P NMR spectroscopy.

Kinetic experiments for formation of nickelalactone 2e in PhCl: [Ni(cod)₂] (138 mg, 500 μmol), d$t$bpe (159 mg, 500 μmol) and the internal standard tetrabutylphosphonium tosylate (108 mg, 250 μmol) were dissolved in PhCl (15 mL) and added to an autoclave by using a charger. The autoclave was pressurized with ethylene at RT (5 bar, 15 min equilibration time), CO_2 was added until a pressure of 40 bar was reached. After 15 min, the reaction was heated to 60 °C. Samples were taken from the reaction by syringe and characterized by ^{31}P NMR spectroscopy after the indicated time periods (see the Supporting Information).

[Bis(di-*tert*-butylphosphino)ethane](prop-2-enoic acid)nickel, [Ni(η²-C₂H₃COOH)(d$t$bpe)] (6): [Ni(cod)₂] (1.50 g, 5.45 mmol) and d$t$bpe

(1.74 g, 5.45 mmol) were dissolved in THF (20 mL). The reaction mixture was cooled to 0 °C and then acrylic acid (390 μL, 5.70 mmol) was added slowly. After stirring at 0 °C for 3 h, the solvent was removed by evaporation and the crude mixture was washed with Et₂O (2×10 mL). Filtration and drying under vacuum yielded compound **6** as a yellow powder (2.31 g, 94 %). Crystals suitable for X-ray analysis were grown at RT by slow diffusion of Et₂O into a saturated solution in THF. Yellow crystal (polyhedron); dimensions: $0.23 \times 0.14 \times 0.05$ mm³; crystal system: monoclinic; space group: $P2_1/c$; $Z = 4$; $a = 11.0623(16)$, $b = 16.941(3)$, $c = 14.043(2)$ Å; $\alpha = 90$, $\beta = 112.762(3)$, $\gamma = 90°$; $V = 2426.8(6)$ Å³; $\rho = 1.230$ g cm⁻³; $T = 200(2)$ K; $\theta_{max} = 28.33°$; radiation: Mo$_{K\alpha}$, $\lambda = 0.71073$ Å; 0.3° ω scans with a CCD area detector, covering a whole sphere in reciprocal space; reflections: 25 344 measured, 6021 unique ($R(\text{int}) = 0.0325$), 5032 observed ($I > 2\sigma(I)$); $\mu = 0.94$ mm⁻¹; min/max transmission = 0.81/0.95; 238 parameters refined; hydrogen atoms were treated by using appropriate riding models, except for H15 (in the carboxy group), which was refined isotropically; goodness of fit: 1.07 for observed reflections; final residual values: $R1(F) = 0.041$, $wR(F^2) = 0.091$ for observed reflections; residual electron density: -0.22 to 0.49 e Å⁻³; ^{1}H NMR (600 MHz, C₆D₆): $\delta = 0.98$ (d, $^3J_{PH} = 12$ Hz, 9H; $(CH_3)_3C$), 1.10 (d, $^3J_{PH} = 12$ Hz, 9H; $(CH_3)_3C$), 1.14 (d, $^3J_{PH} = 12$ Hz, 9H; $(CH_3)_3C$), 1.22 (d, $^3J_{PH} = 12$ Hz, 9H; $(CH_3)_3C$), 1.33 (m, 4H; CH_2), 2.27 (br m, 1H; CHH=HCCO₂H), 2.76 (br m, 1H; CHH=HCCO₂H), 3.36 (br m, 1H; CHH=CHCO₂H), 13.56 ppm (br s, 1H; OH); ^{13}C{^{1}H} NMR (151 MHz, C₆D₆): $\delta = 23.6$ (m; CH_2), 30.5 (m; $(CH_3)_3C$), 33.0 (d, $^2J_{PC} = 23$ Hz; CH_2=CHCO₂H), 34.6 (m; $(CH_3)_3C$), 35.4 (m; $(CH_3)_3C$), 42.7 (d, $^2J_{PC} = 14$ Hz; CH_2=CHCO₂H), 182.7 ppm (s; CH_2=CHCO₂H); ^{31}P{^{1}H} NMR (243 MHz, C₆D₆): $\delta = 86.1$ (d, $^3J_{PP} = 53$ Hz), 94.9 ppm (d, $^3J_{PP} = 53$ Hz); IR (KBr): $\tilde{v} = 431$, 454, 495, 529, 564, 578, 609, 664, 690, 792, 814, 838, 849, 899, 950, 989, 1022, 1055, 1095, 1140, 1180, 1279, 1367, 1392, 1452, 1479, 1561, 1637, 1659, 1685, 1908, 2718, 2867, 2900, 2948, 2979, 3041, 3085, 3407 cm⁻¹.

[Bis(di-*tert*-butylphosphino)ethane](sodium prop-2-enoate)nickel, [Ni(η²-C₂H₃COONa)(d$t$bpe)] (5): [Ni(η²-C₂H₃COOH)(d$t$bpe)] (**6**) (503 mg, 1.12 mmol) and sodium bis(trimethylsilyl)amide (209 mg, 1.12 mmol) were dissolved in THF (10 mL) and stirred at RT for 14 h. A yellow precipitate formed. Filtration and washing with THF yielded compound **5** (197 mg, 37 %). ^{1}H NMR (600 MHz, CD₃OD): $\delta = 1.26$ (m, 36H; $(CH_3)_3C$), 1.76 (m, 4H; CH_2), 1.89 (br m, 1H; CHH=HCCO₂Na), 2.28 (br m, 1H; CHH=HCCO₂Na), 2.86 ppm (br m, 1H; CHH=CHCO₂Na); ^{13}C{^{1}H} NMR (151 MHz, CD₃OD): $\delta = 24.6$ (m; CH_2), 31.2 (m; $(CH_3)_3C$), 35.0 (d, $^2J_{PC} = 22$ Hz; CH_2=CHCO₂Na), 35.5 (m; $(CH_3)_3C$), 47.9 (d, $^2J_{PC} = 17$ Hz; CH_2=CHCO₂Na), 187.3 ppm (s; CH_2=CHCO₂Na); ^{31}P{^{1}H} NMR (243 MHz, CD₃OD): $\delta = 87.2$ (d, $^3J_{PP} = 61$ Hz), 93.5 ppm (d, $^3J_{PP} = 61$ Hz); IR (KBr): $\tilde{v} = 431$, 454, 495, 529, 564, 578, 609, 664, 690, 792, 814, 838, 849, 899, 950, 989, 1022, 1055, 1095, 1140, 1180, 1279, 1367, 1392, 1452, 1479, 1561, 1637, 1659, 1685, 1908, 2718, 2867, 2900, 2948, 2979, 3041, 3085, 3407 cm⁻¹.

Ligand exchange of [bis(di-*tert*-butylphosphino)ethane](sodium prop-2-enoate)nickel, [Ni(η²-C₂H₃COONa)(d$t$bpe)], with ethylene: [Ni(η²-C₂H₃COOH)(d$t$bpe)] (**6**; 32.4 mg, 72.1 μmol) and sodium bis(trimethylsilyl)amide (69.7 mg, 369 μmol) were dissolved in [D₈]THF (0.60 mL) and stirred at RT for 6 h. The reaction mixture was transferred to a high-pressure NMR tube and the tube was filled with ethylene (8 bar). The reaction mixture was heated at 60 °C for 20 h. ^{31}P{^{1}H} NMR analysis revealed the product to be mainly [Ni(η²-C₂H₄)(d$t$bpe)] (**3e**, 95.9 %; $\delta = 91.9$ ppm (s)), along with minor amounts of d$t$bpe (4.1 %; $\delta = 35.9$ ppm (s)).

Ligand exchange of [bis(di-*tert*-butylphosphino)ethane](prop-2-enoic acid)nickel, [Ni(η²-C₂H₃COOH)(d$t$bpe)], with ethylene: [Ni(η²-C₂H₃COOH)(d$t$bpe)] (**6**; 31.5 mg, 70.1 μmol) was dissolved in [D₈]THF (600 μL) and transferred to a high-pressure NMR tube. The tube was filled with ethylene (8 bar) and heated at 60 °C for 18 h. ^{31}P{^{1}H} NMR analysis revealed the product to be mainly the starting material (95.6 %; $\delta = 86.8$ (d, $^3J_{PP} = 55$ Hz), 95.2 ppm (d, $^3J_{PP} = 55$ Hz)), along with minor amounts of [Ni(η²-C₂H₄)(d$t$bpe)] (**3e**, 3.1 %; $\delta = 91.9$ ppm (s)) and free d$t$bpe (1.3 %; $\delta = 35.9$ ppm (s)).

General procedure for cleavage of nickelalactone 2e to form [Ni(η²-C₂H₃COONa)(d$t$bpe)]: The corresponding base (100 μmol) and, if indicated, NaBAr$_F$ (50.0 μmol) were added to a solution of **2e** (11.2 mg,

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25.0 μmol) in the corresponding solvent (1 mL) at RT. The suspension was stirred at the indicated temperature for the indicated time. Subsequently, the mixture was transferred into an autoclave vessel and pressurized with ethylene (30 bar) for 15 min. After the autoclave was opened, the mixture was diluted with Et_2O (1 mL) and extracted with D_2O. NMe_4I (5.0 mg, 25 μmol) was added to the aqueous phase as an internal standard. Reported yields were derived from integral ratios in ^1H NMR spectra.

NaOtBu (9.6 mg, 100 μmol) in PhCl for 15 min provided, after workup, 22.5 μmol (90% yield) of sodium acrylate.

NaHMDS (18.3 mg, 100 μmol) in PhCl for 15 min provided, after workup, 21.8 μmol (87% yield) of sodium acrylate.

NaOMe (5.4 mg, 100 μmol) in PhCl at 50°C for 24 h provided, after workup, 12.8 μmol (51% yield) of sodium acrylate.

NaOMe (5.4 mg, 100 μmol) in PhCl/MeOH (0.5 mL:0.5 mL) at 50°C for 24 h provided, after workup, 17.8 μmol (71% yield) of sodium acrylate.

NaOH (4.0 mg, 100 μmol) in PhCl at 50°C for 24 h did not provide detectable amounts of sodium acrylate.

NaOH (4.0 mg, 100 μmol) in MeOH/H_2O (0.5/0.5 mL) at 50°C for 24 h provided, after workup, 17.5 μmol (70% yield) of sodium acrylate.

NBu$_4$OMe (136.8 mg of a 20% (w/w) solution in MeOH, 100 μmol) in PhCl at 50°C for 72 h did not provide detectable amounts of sodium acrylate.

NBu$_4$OMe (136.8 mg of a 20% (w/w) solution in MeOH, 100 μmol) and NaBAr$_F$ (44.3 mg, 50.0 μmol) in PhCl at 50°C for 72 h provided, after workup, 11.8 μmol (47% yield) of sodium acrylate.

DBU (4.0 mg, 100 μmol) in PhCl at 70°C for 72 h did not provide detectable amounts of sodium acrylate.

DBU (15.2 mg, 100 μmol) and NaBAr$_F$ (44.3 mg, 50.0 μmol) in PhCl at 70°C for 72 h did not provide detectable amounts of sodium acrylate.

tert-Butyliminotri(pyrrolidino)phosphorane (P1, 31.2 mg, 100 μmol) in PhCl at 50°C for 72 h did not provide detectable amounts of sodium acrylate.

tert-Butyliminotri(pyrrolidino)phosphorane (P1, 31.2 mg, 100 μmol) and NaBAr$_F$ (44.3 mg, 50.0 μmol) in PhCl at 50°C for 72 h provided, after workup, 10 μmol (40% yield) of sodium acrylate.

Catalytic synthesis of sodium acrylate: A suspension of d$t$bpe (79.5 mg, 250 μmol) and [Ni(cod)$_2$] (69 mg, 250 μmol) in PhCl (10 mL) was stirred until a red solution was formed. The mixture was transferred into an autoclave vessel and diluted with PhCl (10 mL). The autoclave was pressurized with ethylene (20 bar) and the mixture was stirred (600 rpm) at 45°C for 30 min. In step 1, the mixture was cooled to RT, the ethylene pressure was reduced (10 bar) and CO_2 was added until a final pressure of 50 bar was reached. The reaction was stirred (600 rpm) at 60°C for 2 h. The reactor was depressurized and pressurized with ethylene (20 bar), the mixture was stirred for 1 min and then the pressure was dropped to 1 bar. This pressurization/depressurization procedure was repeated three times. In step 2, NaOtBu (48 mg, 0.5 μmol) was added to the mixture under an atmosphere of ethylene (1 bar), and the mixture was stirred for 1 h. The autoclave was pressurized with ethylene (20 bar) and stirred for 1 h at 45°C. After 18 cycles (steps 1 and 2), the pressure was released. D_2O (46 mL) and the internal standard NMe_4I (25.1 mg, 125 μmol) were added to the mixture. The ^1H NMR spectrum of the aqueous phase revealed formation of sodium acrylate (2.55 mmol, 1020% yield of sodium acrylate based on the amount of [Ni(cod)$_2$] used in the reaction). HPLC (Shodex RSpak KC-811, 300×8 mm (2 columns), 40°C, injection volume: 100 μL, flow: 1 mL min^{-1}, detection: $\lambda = 205$ nm, eluent: 0.1% phosphoric acid): $t_R = 23.4$ min (acrylic acid).

Acknowledgements

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[43] When a sample of [Ni(η^2-CH$_2$=CHCO$_2$H)(d*t*bpe)] (**6**) was heated under an ethylene atmosphere (8 bar, 60 °C, [D$_8$]THF), after 18 h approximately 3% (as shown by ^{31}P NMR spectroscopy) of [Ni(η^2-C$_2$H$_4$)(d*t*bpe)] (**3e**) was formed. Because no free acrylic acid was detectable by ^{1}H NMR spectroscopy, we assign the observed conversion, not to a ligand-exchange reaction, but to a decarboxylation reaction.

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Green chemistry

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The First Catalytic Synthesis of an Acrylate from CO₂ and an Alkene—A Rational Approach
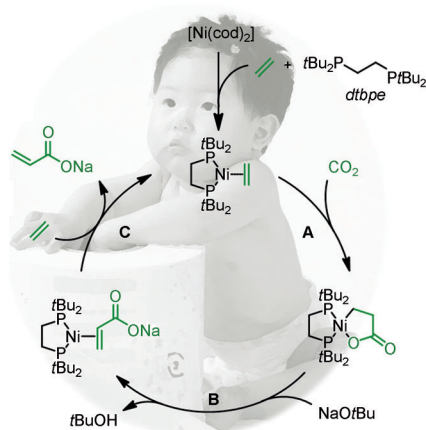
A dream come true: For over three decades the catalytic synthesis of acrylates from the cheap and abundantly available C$_1$ building block CO$_2$ and alkenes has been an unsolved problem in catalysis research. A homogeneous catalyst system based on a Ni complex has now been developed that permits the catalytic synthesis of Na acrylate from CO$_2$, ethylene, and a base (see scheme), as shown by a turnover number of greater than 10 with respect to the metal.