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In situ generated diphenylphosphine-chelated imidazo[1,5-*a*]pyridin-3-ylidene nickel(0) catalysts for highly efficient acrylate synthesis from ethylene and CO_2

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ABSTRACT

Diphenylphosphine-chelated imidazo[1,5-*a*]pyridin-3-ylidene (PPh_2-ImPy) nickel(0) catalysts were synthesized in-situ from imidazolium salts and various commercially available nickel(0) complexes using a base. These catalysts exhibited a highly planar and rigid structure, as confirmed by X-ray crystallographic analysis. Remarkably, the in-situ generated PPh_2-ImPy-Ni(0) catalyst demonstrated a turnover number (TON) of 570 while maintaining a high yield of 82 %, overcoming the typical trade-off between TON and yield often observed in acrylate synthesis reactions, where the use of excess base to achieve high TON typically results in lower product yields. Moreover, the ligand precursors (PPh_2-ImPy•HCl salts) were stable under open-air conditions, making them easy to handle. The in-situ generation protocol using the ligand precursors and commercially available metal sources, eliminates the need for synthesizing sensitive Ni(0) catalysts. Furthermore, the sodium acrylate product was efficiently isolated from the reaction mixture through a straightforward extraction process.

Acrylic acid and its derivatives represent a class of compounds that are extensively used in the production of various polymeric materials, such as superabsorbent polymers, adhesives, coatings, and textiles. Sodium acrylate, the sodium salt of acrylic acid, is particularly important owing to its wide range of applications and versatility as a monomer in the synthesis of various polymers [1]. Direct carboxylation of ethylene with CO_2, a sustainable feedstock, has gained significant attention as an important method for producing sodium acrylate [2]. This method can offer greater economic and environmental benefits than conventional synthetic approaches [3]. In the 1980s, Hoberg et al. reported the first stoichiometric coupling of ethylene and CO_2 using zero-valent nickel and various ligands, including bipyridine, bisphosphine, and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) [4]. Several studies have attempted to develop catalytic systems for acrylate synthesis. However, such catalytic reactions are difficult to achieve due to the stable metalalactones with geometries that render β-H elimination challenging [5].

In 2014, significant progress was made in catalytic reactions through the successful implementation of two key strategies. Vogt et al [6]. employed a Lewis acid to facilitate β-H elimination by weakening the Ni-O bond in the stable metalalactone, reporting a catalytic reaction with a turnover number (TON) of 21 and a yield of 21 %. Simultaneously, Limbach et al [7]. achieved success in one-pot catalytic reactions by effectively removing the β-hydrogen using a strong base, resulting in a TON of 107 and a yield of 36 %. Subsequently, several studies have reported catalytic reactions using Ni and Pd with bidentate bisphosphine ligands (Detailed reaction conditions are summarized in Table S1) [8]. Among these, several remarkable results have been reported (Fig. 1A). Schaub et al. utilized a 1,2-bis(dicyclohexylphosphino) ethane (DCPE) ligand in combination with $Pd(PPh_3)_4$, achieving a TON of 130 with a high yield of 99 % in N,N-dibutylformamide (DBF) solvent, and a TON of 514 with a yield of 21 % in N-cyclohexylpyrrolidone (CHP) solvent under a total pressure of 50 bar [8d]. In a related study by the

Abbreviations: ImPy, imidazo[1,5-*a*]pyridin3-ylidene; NHC, *N*-Heterocyclic carbene.

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same group, using the same DCPE with $Pd(PPh_3)_4$ system, a TON of 50 with a yield of 99 % and a TON of 88 with a yield of 88 % were achieved in tetrahydrofuran (THF) solvent under a total pressure of 30 bar [8e]. Bernskoetter et al. improved upon the results previously reported by Limbach et al. by metalating the BenzP* ligand with $Ni(COD)_2$ to form (BenzP*)Ni(COD), which led to an enhanced TON of 404 and a moderate yield of 51 % with sodium iodide and Zinc additives [8g]. Recently, dicyclohexylphosphine-chelated N-heterocyclic carbene (P-NHC) ligands [9], which offer enhanced coordination stability with metals compared to bisphosphine ligands, have demonstrated a TON of 450 with a yield of 38 % using sodium acetate as an additive. Despite significant advancements, acrylate synthesis reactions still face certain limitations. While some studies have reported high yields of 88–99 %, the TON remain in the range of 50–130 (Fig. 1B). In cases where the TON is improved to 400–500 through the use of large amounts of base, the reaction yields remain limited to 21–51 %. This issue remains a significant challenge that must be addressed for further progress in acrylate synthesis. Therefore, the development of new catalysts capable of achieving both high TON and high yields is essential.

We hypothesized that the coordination of ligands used in previous studies, which form distorted bidentate structures, makes the catalyst more susceptible to decomposition [10]. Therefore, we envisioned that a catalyst with a rigid and highly planar structure would exhibit enhanced durability during the reaction. Herein, we report the development of a new class of rigid bidentate PPh_2-ImPy (ImPy = imidazo[1,5-*a*]pyridin-3-ylidene) ligands and their application in the highly efficient synthesis of acrylates from ethylene and CO_2. The ImPy framework is well-known for its structural rigidity and has been used as a bidentate ligand by coordinating through the C5 position, which is located near the metal center [11]. The ligand precursors (PPh_2-ImPy•HCl salts) are stable under open-air conditions, allowing for easy handling. The in-situ generation of these ligands facilitates the use of various commercially available metal precursors and eliminates the need to prepare air-sensitive Ni(0) complexes. Notably, the in-situ generated PPh_2-Im-Py-Ni(0) catalysts provided sodium acrylate with the highest reported turnover number (up to TON 570) and a high yield of 82 %.

1. Results and discussion

Synthesis and Structural Analysis of PPh_2-ImPy Nickel Complexes. The PPh_2-ImPy ligand precursors (**4a** and **4b**) were prepared using the procedure shown in Scheme 1. Ligand precursors **1**–**4** were obtained based on previously reported methods for the synthesis of imidazo[1,5-*a*]pyridinium salts [10c] as follows: (1) Lithiation of 2-bromo-6-(1,3-dioxolan-2-yl)pyridine and introduction of a phosphine group with chlorodiphenylphosphine; (2) deprotection of the acetal; (3) condensation of the amine and formaldehyde; and (4) cyclization with chloromethyl ethyl ether.

The Ag(I) complex (**5b**) was synthesized by reacting silver oxide with **4b**. Subsequent transmetalation of the Ag(I) complex with $(DME)NiCl_2$ yielded the Ni(II) complex (**6b**) with a high yield of 90 %. The nickelalactone complex (**7b**) was synthesized via free carbene generation and ligand exchange, with an isolated yield of 45 %. The structures of the Ag and Ni complexes were confirmed through X-ray crystallography.

The structure of the Ni(II) complex (**6b**) displayed several distinct characteristics compared to the pyridine-chelated ImPy nickel complex (**N-ImPy-$NiCl_2$**) reported in previous study [10e]. (Fig. 2). Notably, complex **6b** adopted a square planar geometry, whereas the **N-ImPy--$NiCl_2$** complex exhibited a tetrahedral geometry. The square planar configuration of **6b** is likely due to the stronger σ-donor properties of the

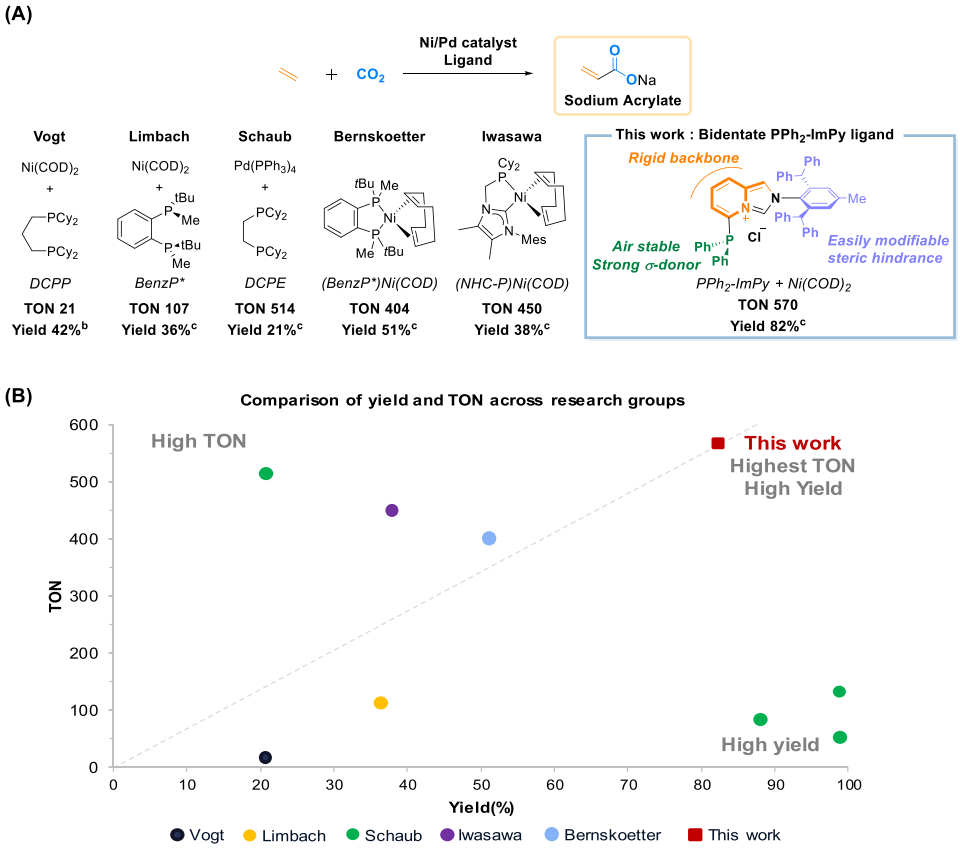
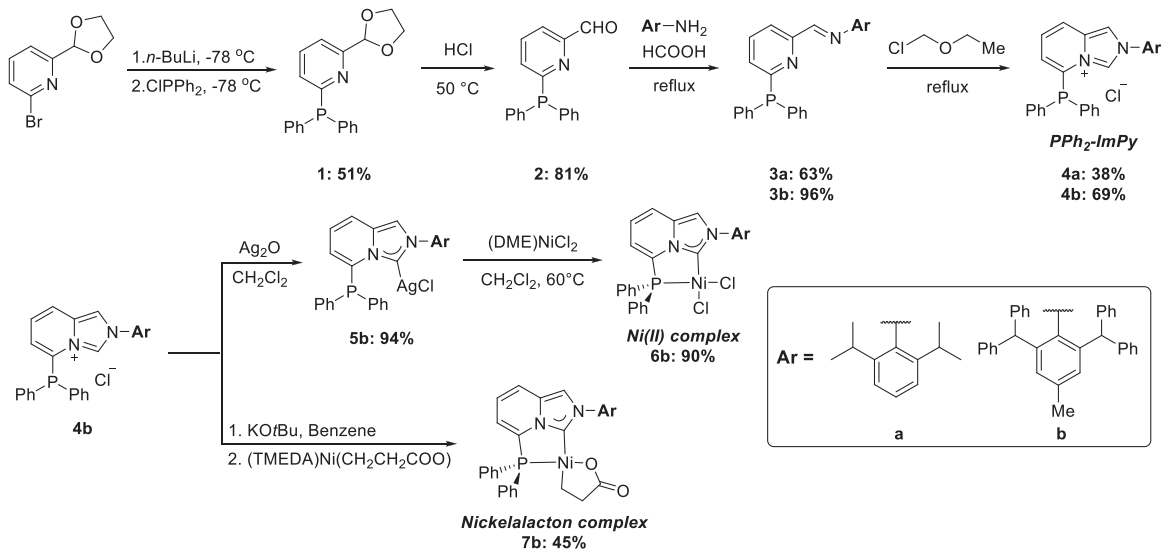


Fig. 1. (A) Previously reported bidentate ligands and complexes and this work. (B) Comparison of yield and TON across research groups. [a]TON determined by ^1H NMR spectroscopy using sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate as an internal standard. [b]Yield was calculated by 100 X (TON/LiI). [c]Yield was calculated by 100 X (TON/sodium-based base).



Scheme 1. Synthesis of PPh_2-ImPy•HCl ligand salts and Ni complexes.

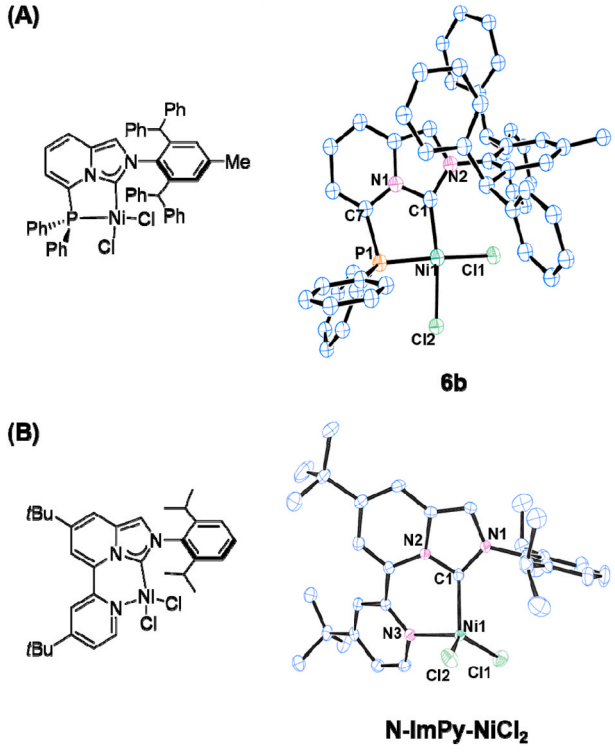
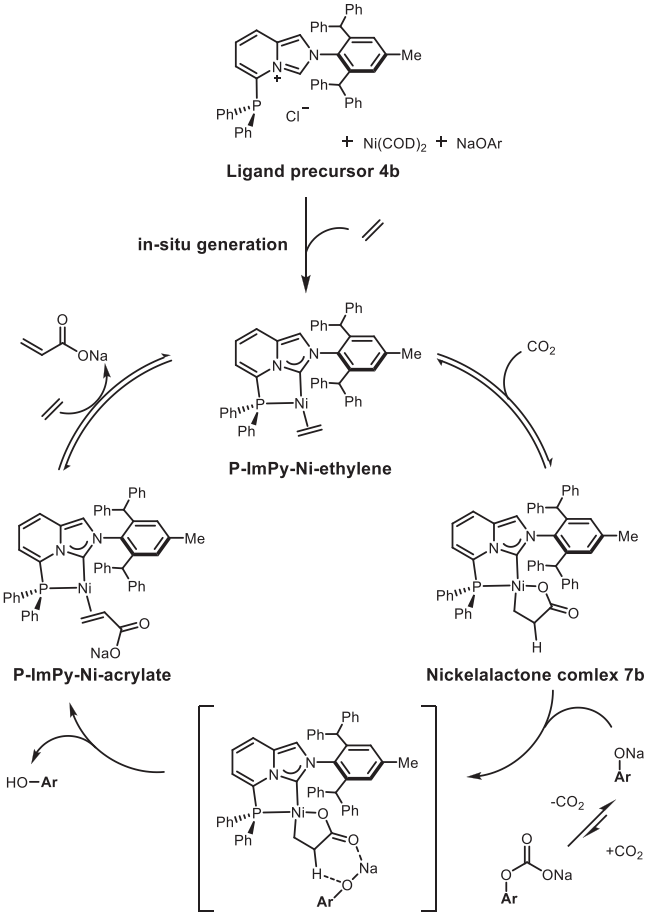


Fig. 2. X-ray structures of complex **6b** (A) and **N-ImPy-NiCl$_2$** (B). Selected bond lengths (Å) and angles (°) for 6b: Ni(1)-C(1) = 1.888(3), Ni(1)-P(1) = 2.1489(9), Ni(1)-Cl(1) = 2.1976(8), Ni(1)-Cl(2) = 2.2027(8); C(1)-Ni(1)-P(1) = 86.52(8), N(1)-C(7)-P(1) = 108.2(2); selected torsion angles (°): C(1)-N(1)-C(7)-P(1) = 6.7(3), N(1)-C(7)-P(1)-Ni(1) = -10.8(2).

-PPh_2 group, which replaces the pyridine in coordination. Additionally, **6b** featured a flat five-membered bidentate ring, in contrast to the slightly bent six-membered bidentate ring of the N-ImPy-$NiCl_2$ complex. The presence of the Ni(1)-P(1) bond caused the N(1)-C(7)-P(1) bond angle in 6b to be slightly bent at 108.23°.

Proposed Catalytic Mechanism for Ethylene-CO_2 Conversion. A plausible catalytic cycle has been proposed starting with the ligand precursor **4b**, which acts as a starting point for the in-situ generation of a nickel(0) complex using a phenoxide base and $Ni(COD)_2$ (Scheme 2).



Scheme 2. Plausible catalytic cycle.

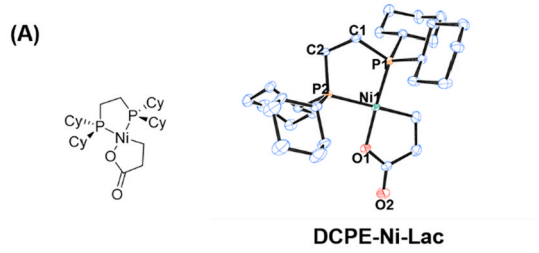
This nickel(0) complex serves as the active species in the catalytic cycle, coordinating with ethylene to form a **P-ImPy-Ni-ethylene** complex. Subsequently, oxidative coupling with CO_2 occurs to yield the key intermediate nickelalactone complex **7b**. Due to the strong electron-donating properties of the carbene ligand, the oxidative coupling proceeds rapidly even at room temperature (Scheme S2) [9]. High-pressure CO_2 is typically beneficial up to this stage of the catalytic cycle; however,

beyond this point, it may induce adverse effects [12]. While high-pressure CO_2 facilitates the formation of nickelalactone, it can also promote side reactions with phenoxide, leading to the formation of carbonates. Such carbonate formation consumes active base species and can decrease the overall reactivity of the system. Notably, bases like NaOMe form more stable carbonates, whereas carbonates formed from bulky alkoxide bases such as NaO*t*Bu or various phenoxide derivatives are relatively labile [8e]. The nickelalactone complex **7b** undergoes deprotonation facilitated by phenoxide, forming the **P-ImPy-Ni-acrylate** complex and releasing phenol. Nickelalactone complexes generally have a square planar geometry, and this structural characteristic can make β-H elimination challenging [13]. Therefore, β-H elimination requires high activation energy, but the addition of suitable bases like phenoxide can promote the cleavage of the nickelalactone. Finally, the **P-ImPy-Ni-acrylate** complex undergoes ligand exchange with ethylene, releasing sodium acrylate and regenerating the initial **P-ImPy-Ni--ethylene** complex. This allows the catalytic cycle to restart and maintain continuous turnover.

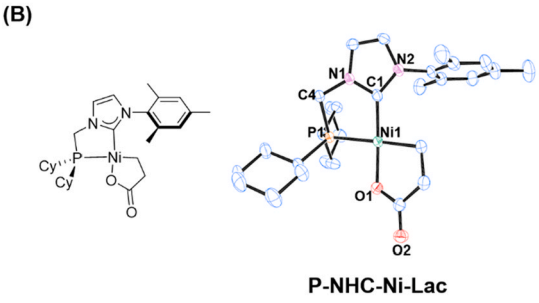
Structural Comparison of Nickelalactone Complexes. We compared the structural characteristics of **DCPE-Ni-Lac** and **P-NHC-Ni-Lac** [9] with nickelalactone complex **7b** (Fig. 3). All three complexes had a square planar geometry and formed a five-membered bidentate ring. The nickelalactone ring structures of each complexes had a square planar geometry and formed a five-membered bidentate ring. The nickelalactone ring structures of each complex had almost similar lengths and angles. The Ni(1)-C(lactone) in complex **7b** had a length of 1.955 Å, which was slightly longer than those of **DCPE-Ni-Lac** (1.944 Å) and **P-NHC-Ni-Lac** (1.947 Å). The distinct structural feature was observed in the bidentate 5-membered ring formed by the ligand and nickel center. The alkyl-tethered **DCPE-Ni-Lac** exhibited significant torsion angles (Fig. 3A). Similarly, the **P-NHC-Ni-Lac** also showed high torsion angles (Fig. 3B). In contrast, the torsion angles of complex **7b** were remarkably planar, indicating minimal distortion (Fig. 3C).

Another interesting point is that both **P-NHC-Ni-Lac** and complex **7b** had two possible isomers with respect to the geometry of the nickel center. The major isomers of the two complexes were opposite each other (Fig. 4). The complex **7b** has a nickelalactone carbon located at the *trans* position of the carbene carbon, whereas **P-NHC-Ni-Lac** has nickelalactone oxygen at the trans position of the carbene carbon. Energy calculations for each isomer revealed a significant energy difference of 2.9 kcal/mol between **7b** and **7b'**. In contrast, the major and minor isomers of **P-NHC-Ni-Lac** showed a difference of only 0.45 kcal/mol, which aligns well with the experimental synthesis outcomes.

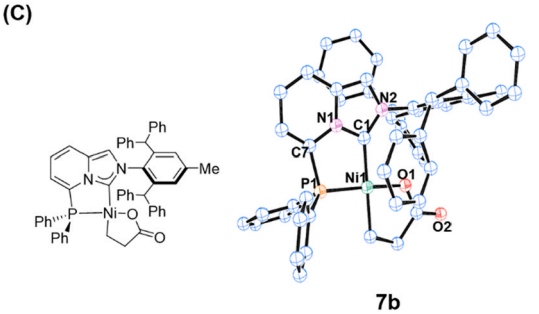
Acrylate Synthesis with Ethylene and CO_2. In most previous studies, the performance of each ligand precursors varied significantly depending on the base. Thus, identifying a base that appropriately matches the ligand precursor is a priority. We performed a comprehensive base screening (Table 1). Sodium phenoxide demonstrated a TON of 12 and 4 for both ligand precursors (Table 1, entry 1). Typically, phenoxides with lower pKa values, owing to their electron- withdrawing



Entry	DCPE-Ni-Lac	Torsion(°)
1	Ni(1)-P(1)-C(1)-C(2)	-29.1(2)
2	P(1)-C(1)-C(2)-P(2)	42.9(2)
3	C(1)-C(2)-P(2)-Ni(1)	-39.4(2)
4	C(2)-P(2)-Ni(1)-P(1)	17.8(1)
5	P(2)-Ni(1)-P(1)-C(1)	3.4(1)



Entry	P-NHC-Ni-Lac	Torsion(°)
1	Ni(1)-C(1)-N(1)-C(4)	-4.3(2)
2	C(1)-N(1)-C(4)-P(1)	-15.9(1)
3	N(1)-C(4)-P(1)-Ni(1)	23.95(9)
4	C(4)-P(1)-Ni(1)-C(1)	-21.73(6)
5	P(1)-Ni(1)-C(1)-N(1)	17.8(1)



Entry	7b	Torsion(°)
1	Ni(1)-C(1)-N(1)-C(7)	-1.8(2)
2	C(1)-N(1)-C(7)-P(1)	4.4(2)
3	N(1)-C(7)-P(1)-Ni(1)	-4.6(1)
4	C(7)-P(1)-Ni(1)-C(1)	3.13(8)
5	P(1)-Ni(1)-C(1)-N(1)	-1.5(1)

Fig. 3. X-ray structure of the nickelalactone complex with DCPE (A), P-NHC (B), and 7b (C). Selected bond lengths (Å) and angles (°) for **7b**: Ni(1)-C(1) = 1.942(2), Ni(1)-C(20) = 1.955(2), Ni(1)-O(1) = 1.882(1), Ni(1)-P(1) = 2.1176(6); C(1)-Ni(1)-P(1) = 87.12(6); selected torsion angles for **7b** (°): C(1)-N(1)-C(7)-P(1) = 4.4(2), N(1)-C(7)-P(1)-Ni(1) = -4.6(1), C(7)-P(1)-Ni(1)-C(1) = 3.13(8), P(1)-Ni(1)-C(1)-N(1) = -1.5(1).

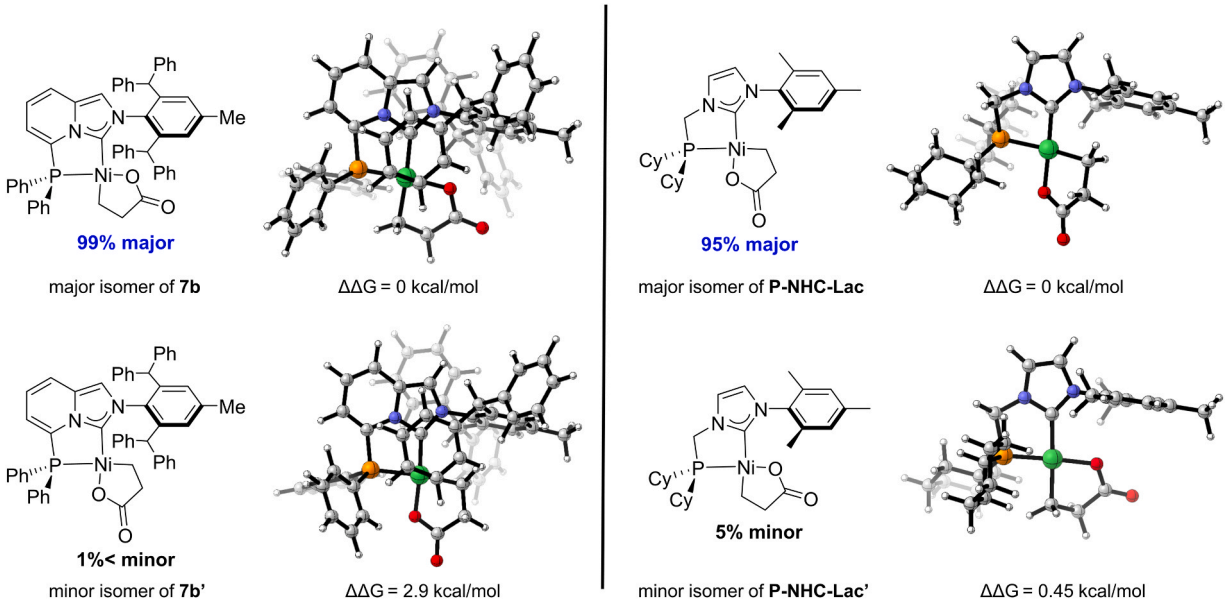
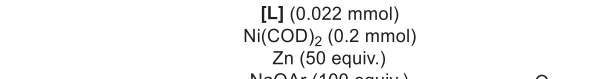
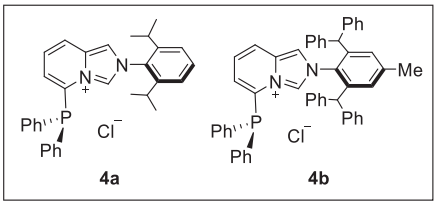


Fig. 4. Relative energies of major and minor isomer of **7b** and **P-NHC-Lac** complex.

Table 1
Comparison of base for acrylate formation.[a,b]

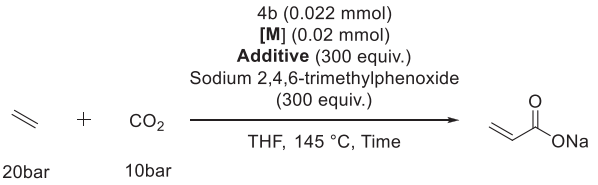




Entry	NaOAr	TON	
		4a	4b
1	PhONa	12	4
2	2,6-$F_2C_6H_3ONa$	0	1
3	2,6-$Cl_2C_6H_3ONa$	-	0
4	2,6-$^tBu_2C_6H_3ONa$	15	12
5	2,6-$Me_2C_6H_3ONa$	32	2
6	2,4,6-$Me_3C_6H_2ONa$	69	78

[a] TON determined by ^{1}H NMR spectroscopy using sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate as the internal standard.
[b] average of two runs.

Table 2
Optimization conditions for acrylate formation.[a,c]



ntry	[M]	Additive	Time (h)	TON	Yield (%)
1	$Ni(COD)_2$	-	12	122[b]	41
2	$Ni(PPh_3)_4$	-	12	126[b]	42
3	$Ni(PPh_3)_2Cl_2$	-	12	42	14
4	$Pd(PPh_3)_4$	-	12	88[b]	29
5	$Ni(COD)_2$	AcONa	12	204[b]	68
6[d]	$Ni(COD)_2$	AcONa	12	0[b]	0
7	$Ni(COD)_2$	AcONa	24	312[b]	99
8	$Ni(PPh_3)_4$	AcONa	24	275[b]	92
9[e]	$Ni(COD)_2$	AcONa	48	505[b]	84
10[f]	$Ni(COD)_2$	AcONa	48	570[b]	82

[a] TON determined by ^{1}H NMR spectroscopy using sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate as the internal standard.
[b] Average of two runs.
[c] The yield was calculated by 100 X (TON/sodium-based base).
[d] Absence of Sodium 2,4,6-trimethylphenoxide.
[e] Sodium acetate (600 equiv), Sodium 2,4,6-trimethylphenoxide (600 equiv).
[f] Sodium acetate (700 equiv), Sodium 2,4,6-trimethylphenoxide (700 equiv).

groups, exhibit lower TON (Table 1, entries 2 and 3). Conversely, phenoxides substituted with alkyl groups tended to yield higher TON (Table 1, entries 4–6). After several base screenings, we successfully achieved the highest TON of 69 and 78 with sodium 2,4,6-trimethylphenoxide (2,4,6-$Me_3C_6H_2ONa$) (Table 1, entry 6), thus determining the most suitable base for our ligand precursor.

The optimal conditions for the acrylate synthesis reaction were explored using ligand precursor **4b** and sodium 2,4,6-trimethylphenoxide (Table 2). More detailed screening data can be found in the Supporting Information. 4b demonstrated favorable reactivity even under in-situ conditions, prompting us to investigate its reactivity with other commercially available metals. $Ni(COD)_2$ and $Ni(PPh_3)_4$, both Ni(0) sources, showed TONs of 122 and 126, respectively (Table 2, entries 1–2). The Ni(II) species $Ni(PPh_3)_2Cl_2$ gave a TON of 42 (Table 2, entry 3). $Pd(PPh_3)_4$ also gave good results with a TON of 88, indicating its potential for palladium-based reactivity (Table 2, entry 4). Based on these results, it is clear that there is a significant difference in reactivity between the metal sources.

Sodium acetate significantly increased the TON to 204 (Table 2, entry 5). Under the same conditions, removing the phenoxide base from the reaction resulted in no observed reactivity (Table 2, entry 6), indicating that sodium acetate cannot act as the base and that the phenoxide base is necessary for the reaction.

Extending the reaction time to 24 hours resulted in a TON of 312 and a yield of 99 % using $Ni(COD)_2$ (Table 2, entry 7), and a TON of 275 with

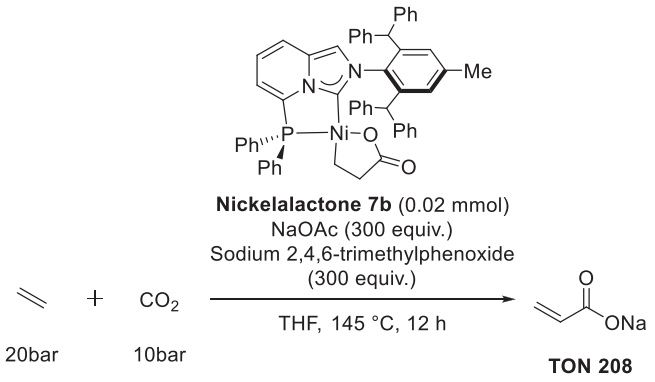
a yield of 92 % using $Ni(PPh_3)_4$ (Table 2, entry 8). Such high yields had previously only been observed with TONs in the 50–130 range, and no cases have reported achieving a yield of 99 % with a TON over 300. Subsequently, by increasing both the equivalents of base and the reaction time, a TON of 505 was obtained with 600 equivalents of base over 48 hours (Table 2, entry 9). Finally, using 700 equivalents of base, an outstanding TON of 570 was achieved, marking the highest TON ever reported for the carboxylation of ethylene with CO_2, even under in-situ conditions (Table 2, entry 10). This results demonstrated an exceptionally high yield of 82 %, achieved simultaneously with the highest TON of 570, marking a significant accomplishment in maximizing both yield and reactivity.

Control Experiments. We attempted to apply other bidentate ligand precursors containing NHCs, which had previously been used in acrylate synthesis reactions but not through in-situ generation method (Table 3). While **4b** successfully exhibited reactivity with a TON of 204 (Table 3, entry 1), **N-ImPy** and **P-NHC** showed lower reactivity, with TONs of 4 and 19, respectively (Table 3, entries 2–3). The method involving in-situ generation likely requires more detailed optimized conditions.

We used the nickelalactone complex **7b**, the intermediate in the catalytic cycle, as a pre-catalyst for the acrylate synthesis reaction. As a result, no significant difference in reactivity was observed between ligand precursor **4b** with $Ni(COD)_2$ (TON 204) and the nickelalactone complex **7b** (TON 208) (Scheme 3). The nickelalactone complex **7b** formed rapidly at room temperature and within 15 minutes in the presence of high-pressure ethylene and CO_2 (Scheme S2). This rapid formation is likely the main reason for the similar reactivity observed under the two different reaction conditions.

The changes in the yields of **4b** and **DCPE** were compared over time using 600 equivalents of sodium 2,4,6-trimethylphenoxide and sodium acetate (Fig. 5). DCPE achieved a yield of approximately 40 % after 24 h and no significant increase until 48 h. In contrast, **4b** afforded a yield of almost 40 % in 12 h and maintained catalytic activity for 48 h, resulting in a high yield of 84 %. This shows that **4b** had a higher turnover frequency (TOF) than DCPE within 12 h and retained its catalytic activity for a longer period, even after 24 h. The reaction rate appeared to decrease after 36 h owing to reagent consumption, ultimately reaching a TON of 505 and a yield of 84 % at 48 hours.

Isolation of Sodium Acrylate Product. In the synthesis of acrylate using ethylene and CO_2, isolation of the acrylate product remains a

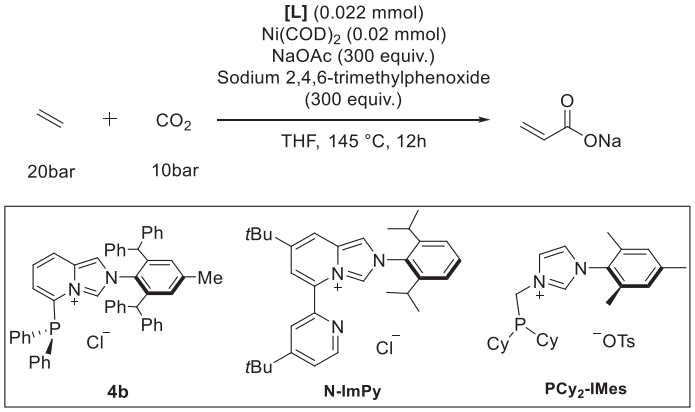


Scheme 3. Use of nickelalactone complex 7b as a precatalyst.

critical issue. Under our reaction conditions, a H_2O (or D_2O) extraction allowed for clean isolation of the product (Scheme 4). After reacting with 300 equivalents of base for 24 h, the aqueous layer was obtained via diethyl ether (Et_2O) and H_2O extraction. Concentrating H_2O layer under vacuum yielded 384 mg of sodium acrylate. Similarly, under conditions using 600 equivalents and 48 h of reaction time, 701 mg of sodium acrylate was obtained following the same procedures. Both residual phenol and phenoxide dissolved well into the Et_2O layer. However, when sodium acetate was used as an additive to enhance reactivity, the separation of sodium acetate became difficult. Further research is required to elucidate the precise role of sodium acetate and to explore alternative additives.

Potential Role of Sodium Acetate. Based on the assumption that Lewis acids may facilitate the cleavage of the nickelalactone intermediate in the catalytic cycle [5e], several alkali metal salts have been employed as additives in previous studies [6,8g]. However, the exact roles of these additives remain unclear and require further investigation. In our study, sodium acetate emerged as the only additive that improved reactivity. One possibility is that sodium acetate might act as a Lewis acid, activating the nickelalactone ring and enhancing catalytic efficiency. However, screening experiments with other additives consistently showed reduced TON values (Table 4), consistent with findings from the Iwasawa group, where only sodium acetate improved reactivity in their carbene-phosphine ligand system [9]. These results suggest that

Table 3
Ligand precursor screening under in-situ conditions.[a,b]



Entry	[L]	TON	Yield (%)
1	4b	204	68
2	N-ImPy	4	1
3	PCy_2-IMes	19	6

[a] TON determined by ^1H NMR spectroscopy using sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate as the internal standard.
[b] average of two runs.

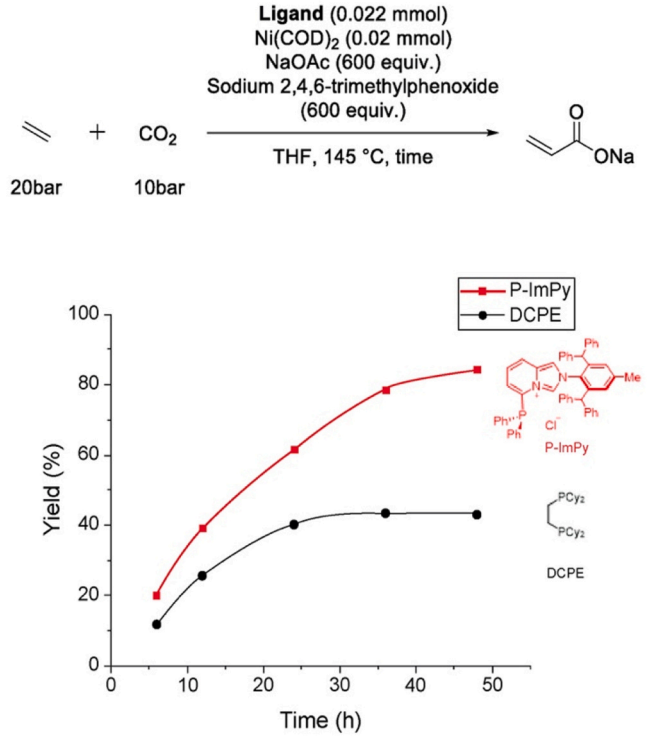
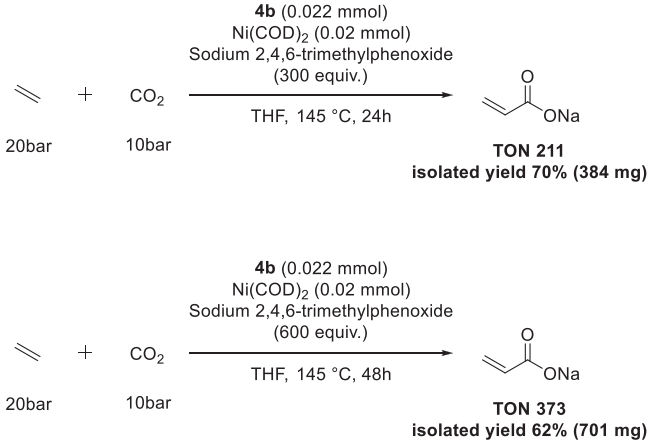


Fig. 5. Curve showing the comparison of yields from P-ImPy•HCl (4b) and DCPE. [a]TON determined by ^{1}H NMR spectroscopy using sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate as the internal standard. [b]average of two runs.

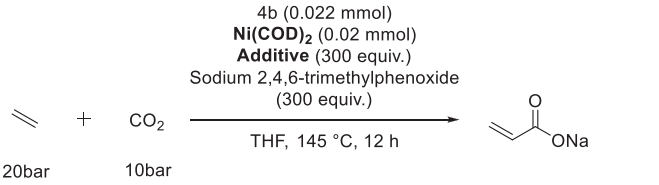


Scheme 4. Isolated yield of 4b[a].

the effect of sodium acetate cannot be working as Lewis acid. Current findings suggest that sodium acetate, as an additive, may operate through a different mechanism than previously proposed.

An alternative hypothesis considers sodium acetate's possible role in stabilizing or indirectly supporting the regeneration of the active catalyst. A study by Bertrand and Jazzar showed that potassium acetate could induce metalation of NHCs without a strong base [14], suggesting that sodium acetate might act through a similar mechanism. In this study, it was observed that sodium acetate could lead to the formation of complex **6b**, detected as a mixture of two species, **6b** and **6b-OAc** (Scheme 5). NMR and HRMS analyses support the presence of these complexes (Scheme S3). Although these complexes do not seem to directly enter the catalytic cycle, they might contribute indirectly to stabilizing the ligand-metal complex or regenerating the active catalyst. However, further work is needed to clarify exactly how sodium acetate enhances catalytic performance.

Table 4
Additive screening for acrylate formation.[a,c]



Entry	Additive	TON	Yield (%)
1	-	122[b]	41
2	AcONa	204[b]	68
3	PhCOONa	31	10
4	CF_3COONa	31	10
5	HCOONa	< 1	< 1
6	*t*BuCOONa	17	6
7	BF_4Na	0	0
8	PF_6Na	0	0

[a] TON determined by ^{1}H NMR spectroscopy using sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate as the internal standard.
[b] Average of two runs.
[c] The yield was calculated by 100 X (TON/sodium-based base).

2. Conclusion

In this study, novel diphenylphosphine-chelated ImPy ligand precursors were successfully developed for the efficient synthesis of acrylate from ethylene and CO_2. X-ray crystallographic analysis of the nickelalactone complex **7b** revealed a highly planar and rigid bidentate structure, distinguishing it from other complexes such as **DCPE-Ni-Lac** or **P-NHC-Ni-Lac**. Under optimal conditions, the in-situ generated catalyst achieved the highest TON of 570, with a high yield of 82 %, using only 700 equivalents of base. These results are particularly significant, as they overcome the typical trade-off between TON and yield, where excess base often reduces product yield in acrylate synthesis. Furthermore, the sodium acrylate product was efficiently isolated from the reaction mixture through a straightforward extraction process.

Notably, the acrylate synthesis reaction proceeds under in-situ conditions, eliminating the need for synthesizing sensitive Ni(0) complexes and allowing the use of various commercially available metal sources such as $Ni(COD)_2$ or $Ni(PPh_3)_4$, and $Pd(PPh_3)_4$. Additionally, it was confirmed that the isolated nickelalactone complex **7b** exhibited reactivity similar to those under in-situ conditions with **4b**, suggesting that the nickelalactone **7b** is a true catalytically active species.

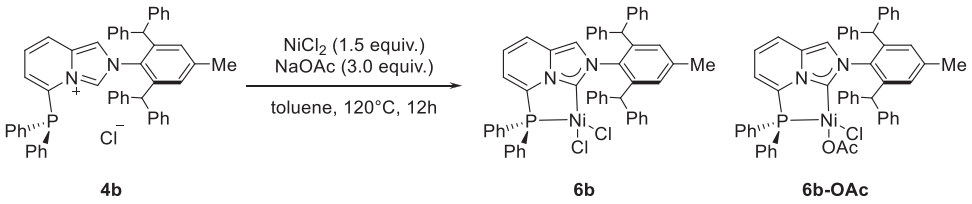
The findings from this study present a highly efficient and stable catalytic system for the direct carboxylation of ethylene with CO_2. By achieving both high TON and yield simultaneously, this research lays a strong foundation for future advancements, with the potential to further enhance catalytic performance.

The Supporting Information is available free of charge at

Detailed experimental procedures, compound characterization data, additional figures, and tables, X-ray crystallographic data, NMR spectra of complexes.

CRediT authorship contribution statement

Changmuk Kang: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Seyong Kim:** Writing – original draft, Methodology, Investigation. **Woosong Han:** Writing – review & editing, Visualization, Methodology. **Huijeong Ryu:** Visualization, Software, Methodology, Formal analysis. **Wooyong Seong:** Methodology, Investigation. **Jiyun**



Scheme 5. Generation of 6b complex with sodium acetate.

Kim: Methodology, Investigation, Conceptualization. **Da-Ae Park:** Methodology. **Seongwook Park:** Methodology. **Kyungho Park:** Methodology. **Hyun Min Park:** Methodology. **Hyun Tae Kim:** Methodology. **Chang Hee Lee:** Methodology. **Sukwon Hong:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

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Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sukwon Hong reports financial support was provided by LG Chem Ltd. Sukwon Hong reports financial support was provided by the National Research Foundation of Koea (NRF) grant funded by the Korea government (MSIT) (NRF-2021M3H4A1A02055684). Sukwon Hong has patent #CATALYST COMPOUND AND METHOD FOR SYNTHESIZING ACRYLATE USING THE SAME (10–2024–0117582) pending to Gwangju Institute of Science and Technology. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2024.103004.

Data availability

Data will be made available on request.

References

[1] (a) B. Yu, Z.-F. Diao, C.-X. Guo, L.-N. He, Carboxylation of olefins/alkynes with CO_2 to industrially relevant acrylic acid derivatives, J. CO_2 Util. 1 (2013) 60–68;
(b) S. Dabral, T. Schaub, The use of carbon dioxide (CO_2) as a building block in organic synthesis from an industrial perspective, Adv. Synth. Catal. 361 (2019) 223–246;
(c) M.V. Solmi, M. Schmitz, W. Leitner, CO_2 as a building block for the catalytic synthesis of carboxylic acids, Stud. Surf. Sci. Catal. 178 (2019) 105–124.

[2] (a) M. Limbach, Acrylates from alkenes and CO_2, the stuff that dreams are made of, Adv. Organomet. Chem. 63 (2015) 175–202;
(b) S. Kraus, B. Rieger, Ni-catalyzed synthesis of acrylic acid derivatives from CO_2 and ethylene, Top. Organomet. Chem. 53 (2015) 199–223;
(c) M. Hollering, B. Dutta, F.E. Kühn, Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates, Coord. Chem. Rev. 309 (2016) 51–67;
(d) X. Wang, H. Wang, Y. Sun, Synthesis of acrylic acid derivatives from CO_2 and ethylene, Chem 3 (2017) 211–228;
(e) T. Schaub, Sodium acrylate from ethylene and CO_2: the path from basic research to a system appropriate for a continuous process, Organometall. Proc. Chem. 65 (2019) 253–270;
(f) N. Maity, N. Garcia, E.A. Jaseer, S. Barman, A.M. Aitani, M.M. Tijani, N. Al-Yassir, Advancement of catalyst systems towards the formation of acrylates from CO_2 and ethylene, Renew. Sustain. Energy Rev. 200 (2024) 114483.

[3] (a) K. Weissermel, H. Arpe, Propene conversion products, Ind. Org. Chem. 4 (2008) 267–312;
(b) M. Aresta, A. Dibenedetto, A. Angelini, Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. technological use of CO_2, Chem. Rev. 114 (2014) 1709–1742.

[4] (a) H. Hoberg, D. Schaefer, Nickel(0)-Induzierte C–C-verknüpfung zwischen kohlendioxid und ethylen sowie mono-oder Di-substituierten alkenen, J. Organomet. Chem. 251 (3) (1983) c51–c53;
(b) H. Hoberg, D. Schaefer, G. Burkhart, C. Krüger, M.J. Romao, Nickel(0)-Induzierte C–C-Verknüpfung Zwischen Kohlendioxid und Alkinen sowie Alkenen, J. Organomet. Chem. 266 (2) (1984) 203–224;
(c) H. Hoberg, Y. Peres, A. Milchereit, C–C-Verknüpfung von Alkenen mit CO_2 an Nickel(0); n-Pentensäuren aus Ethen, J. Organomet. Chem. 307 (2) (1986) C41–C43;
(d) H. Hoberg, Y. Peres, C. Krüger, Y.H. Tsay, A 1-Oxa-2-nickela-5-cyclopentanone from ethene and carbon dioxide: preparation, structure, and reactivity, Angew. Chem., Int. Ed. Engl. 26 (8) (1987) 771–773;
(e) H. Hoberg, A. Ballesteros, A. Sigan, C. Jégat, D. Bärhausen, A. Milchereit, Ligandgesteuerte Ringkontraktion von Nickela-fünf-in Vierringkomplexe—neuartige Startsysteme für die Präparative Chemie, J. Organomet. Chem. 407 (3) (1991) C23–C29.

[5] (a) I. Pápai, G. Schubert, I. Mayer, G. Besenyei, M. Aresta, Mechanistic details of nickel(0)-assisted oxidative coupling of CO_2 with C_2H_4, Organometallics 23 (22) (2004) 5252–5259;
(b) R. Fischer, J. Langer, A. Malassa, D. Walther, H. Görls, G. Vaughan, A key step in the formation of acrylic acid from CO_2 and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex, Chem. Commun. 23 (2006) 2510–2512;
(c) D.C. Graham, C. Mitchell, M.I. Bruce, G.F. Metha, J.H. Bowie, M.A. Buntine, Production of acrylic acid through nickel-mediated coupling of ethylene and carbon dioxide—a DFT study, Organometallics 26 (27) (2007) 6784–6792;
(d) D. Jin, T.J. Schmeier, P.G. Williard, N. Hazari, W.H. Bernskoetter, Lewis acid induced β-elimination from a nickelalactone: efforts toward acrylate production from CO_2 and ethylene, Organometallics 32 (7) (2013) 2152–2159;
(e) D. Jin, P.G. Williard, N. Hazari, W.H. Bernskoetter, Effect of sodium cation on metallacycle β-hydride elimination in CO_2–ethylene coupling to acrylates, Chem. Eur. J. 20 (11) (2014) 3205–3211;
(f) Y. Zhu, Y. Mu, L. Sun, Z. Zeng, Z. Liu, Mechanistic study on the formation of the alkyl acrylates from CO_2, ethylene and alkyl iodides over nickel-based catalyst, Phys. Chem. Chem. Phys. 25 (36) (2023) 24733–24744.

[6] C. Hendriksen, E.A. Pidko, G. Yang, B. Schäffner, D. Vogt, Catalytic formation of acrylate from carbon dioxide and ethene, Chem. Eur. J. 20 (38) (2014) 12037–12040.

[7] N. Huguet, I. Jevtovikj, A. Gordillo, M.L. Lejkowski, R. Lindner, M. Bru, M. Limbach, Nickel-catalyzed direct carboxylation of olefins with CO_2: one-pot synthesis of α,β-unsaturated carboxylic acid salts, Chem. Eur. J. 20 (51) (2014) 16858–16862.

[8] (a) S.C.E. Stieber, N. Huguet, T. Kageyama, I. Jevtovikj, P. Ariyananda, A. Gordillo, M. Limbach, Acrylate formation from CO_2 and ethylene: catalysis with palladium and mechanistic insight, Chem. Commun. 51 (54) (2015) 10907–10909;
(b) S. Manzini, N. Huguet, O. Trapp, T. Schaub, Palladium- and nickel-catalyzed synthesis of sodium acrylate from ethylene, CO_2, and phenolate bases: optimization of the catalytic system for a potential process, Eur. J. Org. Chem. 2015 (32) (2015) 7122–7130;
(c) I. Knopf, D. Tofan, D. Beetstra, A. Al-Nezari, K. Al-Bahily, C.C. Cummins, A family of cis-macrocyclic diphosphines: modular, stereoselective synthesis and application in catalytic CO_2/ethylene coupling, Chem. Sci. 8 (2) (2017) 1463–1468;
(d) S. Manzini, A. Cadu, A.C. Schmidt, N. Huguet, O. Trapp, R. Paciello, T. Schaub, Enhanced activity and recyclability of palladium complexes in the catalytic

synthesis of sodium acrylate from carbon dioxide and ethylene, ChemCatChem 9 (12) (2017) 2269–2274;
(e) S. Manzini, N. Huguet, O. Trapp, R.A. Paciello, T. Schaub, Synthesis of acrylates from olefins and CO_2 using sodium alkoxides as bases, Catal. Today 281 (2017) 379–386;
(f) A. Vavasori, L. Calgaro, L. Pietrobon, L. Ronchin, The coupling of carbon dioxide with ethene to produce acrylic acid sodium salt in one pot by using Ni(II) and Pd(II)-phosphine complexes as precatalysts, Pure Appl. Chem. 90 (2) (2018) 315–326;
(g) M.N. Hopkins, K. Shimmei, K.B. Uttley, W.H. Bernskoetter, Synthesis and reactivity of 1,2-Bis(di-iso-propylphosphino)benzene nickel complexes: a study of catalytic CO_2–ethylene coupling, Organometallics 37 (20) (2018) 3573–3580;
(h) K.B. Uttley, K. Shimmei, W.H. Bernskoetter, Ancillary ligand and base influences on nickel-catalyzed coupling of CO_2 and ethylene to acrylate, Organometallics 39 (9) (2020) 1573–1579;
(i) K.Y. Kunihiro, A. Marty, L. Chahen, L. Magna, J.M. Asensio, Sodium acrylate synthesis through CO_2 and ethylene coupling catalyzed by Pd: solvent effects and $PdBr_2$ as a surprisingly suitable precursor, ChemCatChem (2024) e202401074.

[9] K. Takahashi, K. Cho, A. Iwai, T. Ito, N. Iwasawa, Development of N-phosphinomethyl-substituted NHC-Nickel(0) complexes as robust catalysts for acrylate salt synthesis from ethylene and CO_2, Chem. Eur. J. 25 (59) (2019) 13504–13508.

[10] (a) R. Nakano, K. Nozaki, Copolymerization of propylene and polar monomers using Pd/IzQO catalysts, J. Am. Chem. Soc. 137 (34) (2015) 10934–10937;
(b) W.J. Tao, R. Nakano, S. Ito, K. Nozaki, Copolymerization of Ethylene and Polar Monomers by Using Ni/IzQO Catalyst, Angew. Chem. Int. Ed. 55 (8) (2016) 2835–2839;
(c) W. Tao, S. Akita, R. Nakano, S. Ito, Y. Hoshimoto, S. Ogoshi, K. Nozaki, Copolymerisation of ethylene with polar monomers by using palladium catalysts bearing an N-heterocyclic carbene–phosphine oxide bidentate ligand, Chem. Commun. 53 (17) (2017) 2630–2633;
(d) D.A. Park, S. Byun, J.Y. Ryu, J. Lee, J. Lee, S. Hong, Abnormal N-heterocyclic carbene–palladium complexes for the copolymerization of ethylene and polar monomers, ACS Catal. 10 (10) (2020) 5443–5453;
(e) J. Kim, H. Hahm, J.Y. Ryu, S. Byun, D.A. Park, S.H. Lee, S. Hong, Pyridine-chelated imidazo[1,5-a]Pyridine N-heterocyclic carbene nickel(II) complexes for acrylate synthesis from ethylene and CO_2, Catalysts 10 (7) (2020) 758.

[11] (a) C. Grohmann, T. Hashimoto, R. Fröhlich, Y. Ohki, K. Tatsumi, F. Glorius, An iron(II) complex of a diamine-bridged Bis-N-heterocyclic carbene, Organometallics 31 (23) (2012) 8047–8050;
(b) J. Dong, M. Li, B. Wang, Synthesis, structures, and norbornene polymerization behavior of imidazo[1,5-a]pyridine-sulfonate-ligated palladacycles, Organometallics 38 (19) (2019) 3786–3795;
(c) A. Varenikov, G. de Ruiter, Chiral Imidazo[1,5-a]Pyridine–oxazolines: a versatile family of NHC ligands for the highly enantioselective hydrosilylation of ketones, Organometallics 39 (2) (2020) 247–257;
(d) P. Gao, J. Xu, T. Zhou, Y. Liu, E. Bisz, B. Dziuk, M. Szostak, L-shaped heterobidentate imidazo[1,5-a]Pyridin-3-ylidene (N,C)-ligands for oxidant-free Au^{I}/Au^{III} catalysis, Angew. Chem. Int. Ed. 62 (12) (2023) e202218427.

[12] M.L. Lejkowski, R. Lindner, T. Kageyama, G.É. Bódizs, P.N. Plessow, I.B. Müller, M. Limbach, The first catalytic synthesis of an acrylate from CO_2 and an alkene—a rational approach, Chem. Eur. J. 18 (44) (2012) 14017–14025.

[13] S.T. Lee, M. Cokoja, M. Drees, Y. Li, J. Mink, W.A. Herrmann, F.E. Kühn, Transformation of nickelalactones to methyl acrylate: on the way to a catalytic conversion of carbon dioxide, ChemSusChem 4 (9) (2011).

[14] (a) J. Lorkowski, M.R. Serrato, M. Gembicki, M. Mauduit, G. Bertrand, R. Jazzar, A straightforward access to cyclic (Alkyl)(amino) carbene copper(I) complexes, Eur. J. Inorg. Chem. 26 (15) (2023) e202300074;
(b) J. Lorkowski, P. Yorkgitis, M.R. Serrato, M. Gembicky, C. Pietraszuk, G. Bertrand, R. Jazzar, Genuine carbene versus carbene-like reactivity, Angew. Chem. (2024) e202401020.