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Formation of Methyl Acrylate from CO_2 and Ethylene via Methylation of Nickelalactones

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Summary: The nickel-induced coupling of ethylene and CO_2 represents a promising pathway toward acrylates. To overcome the high bond dissociation energies of the M−O moieties, we worked out an in situ methylation of nickelalactones to realize the β-hydride elimination and the liberation of the acrylate species.

For more than 20 years metallacyclic nickel carboxylates ("nickelalactones") have been discussed with regard to potential catalytic pathways toward the synthesis of acrylic acid from ethylene and CO_2.[1−3] From a thermodynamic point of view, the formation of acrylic acid from ethylene and CO_2 is allowed under standard conditions.[4] The advantages of CO_2 as a C_1 feedstock are not only its nontoxic and nonflammable properties but also the high cost effectiveness caused by its abundant availability.[5,6]

The essential steps of such a hypothetical catalytic cycle, as has been broadly discussed in the literature, are on the one hand the oxidative coupling of these substrates to form nickelalactones and on the other hand a β-hydride elimination and a reductive elimination of the acrylate to regenerate the Ni(0) species (Scheme 1).[7]

The entire catalytic process has to date never been realized experimentally. However, at least for some parts of it, successful model reactions have been performed. The first step, the oxidative coupling of Ni(0), ethylene, and CO_2, is known in the literature for several ligand systems and was recently investigated by means of DFT calculations.[1−3,8−11] Also, for the β-hydride elimination there have been some examples.

The first indication of a β-hydride transfer in a metallalactone was the synthesis of cinnamic acid by heating up the coupling product of CO_2, styrene, and a stoichiometric amount of a Ni(0) complex, followed by hydrolysis.[8]

The first clear proof for a β-hydride-transfer in an unsubstituted nickelalactone was performed 2006 by *Walther et al.*[7] generating a fully characterized acrylate complex from a metallacyclic nickel carboxylate (eq. A, Scheme 2).

However, the liberation of acrylic acid from a nickel−hydrido−acrylate species, as shown in Scheme 1, requires a reductive elimination of the acrylate and hydride ligands. Due to the high bond dissociation energies of the M−O moieties in the acrylate intermediates, the substantial kinetic barriers to the elimination of acrylic acid have not been overcome to date.[10]

The first liberation of alkyl esters of acrylic acids in this context was performed by Aresta et al.[4] using a Pd complex with a preformed carboxylic moiety that circumvents these kinetic barriers (eq B, Scheme 2). Although this is only a model system without a potential application for a coupling of ethylene and CO_2, this work shows that liberation of methyl acrylates, at least in a Pd complex, is possible even at room temperature. In addition to that, DFT calculations on nickelalactones showed that an elongation of the Ni−O bond promotes the β-hydride transfer.[10]

On the basis of these facts, a new synthetic approach toward a catalytic coupling of ethylene and CO_2, including an in situ methylation, was considered by our group. This led to a new hypothetical catalytic cycle (Scheme 3).

The first step in this cycle is again the oxidative coupling of Ni(0), ethylene, and CO_2, as has been known from the literature going back on the work of Hoberg et al.[1−3,8,11] For the last step, the reductive elimination of HX to regenerate the Ni(0) species and thus complete the catalytic cycle, there are at least examples in the literature for hydridopalladium-containing systems.[12,13]

The most challenging step in this sequence is the liberation of the acrylate species from the complex formed by insertion of ethylene and CO_2. Therefore, we investigated the reaction behavior of the model Ni complex **1** toward in situ methylation and a subsequent β-hydride transfer (Scheme 4). Nickelacycles such as β-substituted cyclic amides and lactones were shown to undergo methylation by MeI at the α-carbon atom without any β-hydride elimination.[14,15]

In contrast, addition of 2 equiv of MeI to a solution of complex **1** in dichloromethane gave 10% of methyl acrylate, quantified directly by NMR spectroscopy and characterized indirectly by ESI mass spectrometry (Table1, entry 1). For the

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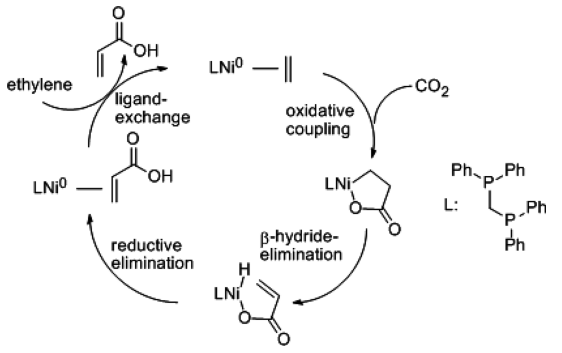
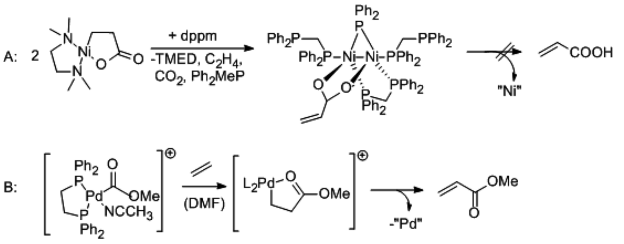
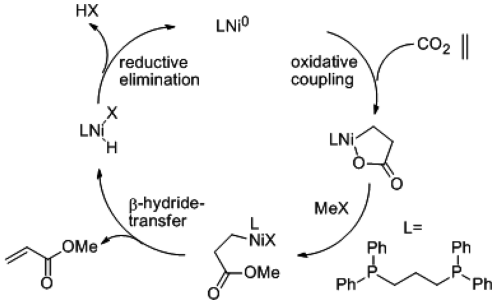
Scheme 1. Hypothetical Catalytic Cycle As Discussed by Walther et al.[8]



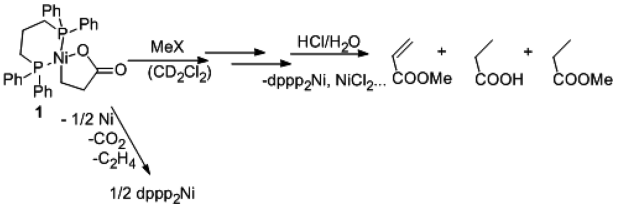
Scheme 2. Transformation of a Nickelalactone into a Nickel Acrylate Complex without Liberation of Acrylates (Eq A) and Release of Acrylates from a Model Complex (Eq B)[4,7]



Scheme 3. New Hypothetical Catalytic Cycle Leading to the Formation of Methyl Acrylate from Ethylene, CO_2, and MeI



Scheme 4. Methylation of Nickelalactone 1



spectroscopic measurements the metallic species had to be removed by hydrolysis due to technical reasons. To ensure that the formation of methyl acrylate is not caused by hydrolysis, a blank reaction was performed without addition of MeI, which gave no olefinic derivatives. Therefore, the detected olefin protons in reactions with MeI are a clear proof for the β-hydride elimination as predicted in Scheme 3. Furthermore, the assumption that this β-hydride elimination is an effect of a prior splitting of the Ni−O bond by the in situ methylation is in perfect agreement with the DFT calculations demanding an elongation of the Ni−O bond for a β-hydride transfer.[10] To prove directly that the weakening of this bond is caused by methylation of the carboxylic group after addition of MeI and does not depend on hydrolysis, we carried out an in situ IR measurement, which will be discussed later on.

Table 1. Yield of Methyl Acrylate in the Reaction of Complex 1 with Various Amounts of Methylation Agent[a]

entry	reactant	yield[b] (%)
1	MeI, 2 equiv	10
2	MeI, 10 equiv	16
3	MeI, 100 equiv	29
4	neat MeI	33

[a] Conditions: solvent CD_2Cl_2, 48 h, room temperature. [b] Detected via NMR spectroscopy ($CHCl_3$ standard).

It has to be mentioned that all signals in the NMR spectrum could be assigned, and methyl acrylate (10% yield with 2 equiv of MeI), propionic acid (3% yield), and methyl propionate (11% yield) were the only products found in the NMR spectrum.[16] Consequently, the main part of complex **1** is converted into Ni(0), ethylene, and CO_2, as reported previously by Walther et al. (Scheme 3).[7] Indeed, evolution of CO_2 from a solution of **1** in CH_2Cl_2 was confirmed by formation of white $BaCO_3$ on passing an argon stream over the solution into aqueous $Ba(OH)_2$.

In spite of this decomposition reaction, we chose this complex with the dppp (bis(diphenylphosphino)propane) ligand as a model for its good solubility in organic solvents, its easy synthesis in high yield, and because of prior investigations that ruled out the formation of acrylic acid via β-hydride elimination from this complex by thermal reaction in the absence of further reactants.[7]

When the amount of methyl iodide is increased, the yield reaches 16% (10 equiv, entry 2) and 29% (100 equiv, entry 3), respectively. Performing the reaction in neat MeI gave a yield of 33% (entry 4), though the solubility problems of nickelalactone **1** in pure methyl iodide should be noted. The impact of methyl iodide concentration on the overall yield, despite the expected first-order reaction in methylating agent, is not that pronounced. The high concentration of MeI would even be counterproductive for realization of the full cycle shown in Scheme 3 due to the reversible reaction of MeI with Ni(0), which would reduce the amount of active centers (Scheme 5).[17]

As an alternative reagent that does not react with Ni(0) in this way, LiI was tested instead of MeI. In the analogous reactions this also led to a liberation of the acrylate, although the yields were lower due to the insolubility of LiI in dichloromethane and, perhaps, due to its insufficient destabilizing influence on nickelalactone toward β-hydride elimination (6% methyl acrylate, 3 equiv of LiI, room temperature, 5 days, CD_2Cl_2).

Increasing the reaction temperature to 40 °C (reflux) using 10 equiv of MeI resulted in 21% of methyl acrylate (Table 2). The small impact of the temperature on the yield of methyl acrylate can be ascribed to the fact that an increase of temperature accelerates not only the methylation but also the decomposition of the complex **1** with formation of CO_2 and ethylene.

The reaction of **1** with MeI was also monitored using in situ IR techniques (Figure 1). This method facilitated a direct characterization of the reaction mixture without prior removal of the metallic species by hydrolysis. The reference spectrum of the nickelalactone **1** dissolved in dichloromethane shows the characteristic C=O vibrations at 1627 cm^{-1} and at 1322 cm^{-1}.

(16) Propionic acid results from the hydrolysis of unreacted complex **1**, as confirmed by a blank reaction. The methyl propionate results mainly from the hydrolysis of the residual methylated intermediate.

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Scheme 5. Oxidative Addition of MeI to Ni(0)

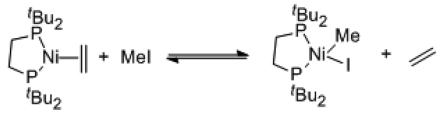


Table 2. Yield of Methyl Acrylate in the Reaction of Complex 1 with Various Methylation Agents[a]

entry	reactant	yield[b] (%)
5	MeI, 10 equiv	21
6	$(CH_3)_3O^+BF_4^-$, 3 equiv	1
7	CH_3OTf, 10 equiv	0

[a] Conditions: solvent CD_2Cl_2, 48 h, reflux. [b] Detected via NMR spectroscopy ($CHCl_3$ standard).

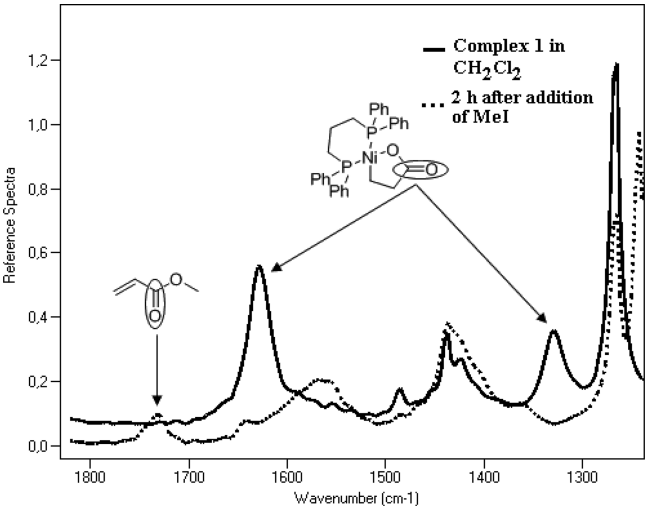


Figure 1. In situ IR measurements in the reaction of complex **1** with MeI (solvent CH_2Cl_2, 10 equiv of MeI, 40 °C, 2 h).

Addition of MeI (10 equiv) reduces the intensity of these signals, and a new band can be found at 1732 cm^{-1} which can be assigned to the C═O vibration of methyl acrylate with the help of a reference spectrum. The important point here is that the complete measurement was performed under an argon atmosphere with dry chemicals and in dry solvent. While for the mass spectrometry and the NMR measurements the metallic species had to be removed by hydrolysis, this in situ IR measurement shows clearly that the splitting of the Ni−O bond is directly induced by methyl iodide and is not a consequence of hydrolysis.

Time-dependent quantification of the reaction products was also performed by NMR measurements. Therefore, the parallel reactions (40 °C, 10 equiv of MeI) were stopped by hydrolysis after 15 min, 1.5 h, 20 h, and 48 h to give the results presented in Figure 2. Within 1.5 h 80% of the maximum yield had been reached. After 20 h there was no further increase of the yield.

On comparing the various methylation agents shown in Table 2, the best yields were reached with MeI (entry 5). $(CH_3)_3O^+BF_4^-$ was limited in its solubility, and for that reason only 3 equiv was added, yielding only 1% of acrylate (entry 6). Methyl triflate as methylation agent gave no detectable amount of acrylic ester at all (entry 7). This could result both from lower methylation activity of the latter reagents under the applied conditions and from the coordination features of leaving groups in these reagents, as well as from steric effects. In addition, the rate of β-hydride elimination is expected to strongly depend on the donating

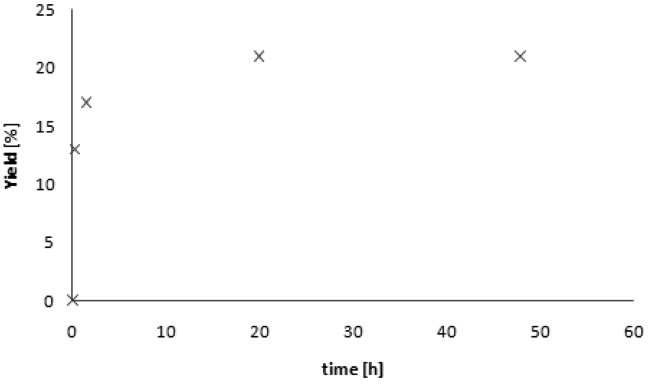
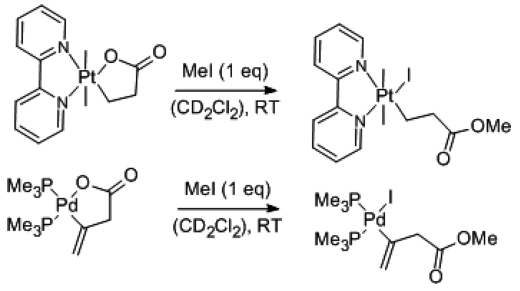


Figure 2. Kinetic study of the reaction of complex **1** with MeI (solvent CD_2Cl_2, 10 equiv of MeI, reflux).

Scheme 6. Characterized Methylated Metallalactones



counterion. The splitting of the Ni−O bond consequently goes hand in hand with the weakening of the Ni−O bond by methylation of the carboxylic group on the one hand and with the compensation of the so caused electron deficit at the Ni center by the induced new ligand (e.g., iodo ligand).

Additional experiments had to be carried out in order to clarify some mechanistic details on the methylation of nickelalactones by MeI with subsequent β-hydride elimination. Due to the formation of Ni(0) species after β-hydride elimination of the intermediate formed by methylation of **1**, the in situ monitoring of this reaction by NMR spectroscopy could not be realized. However, products of similar reactions on platina- and palladalactones were characterized by Aye et al. and Yamamoto et al. (Scheme 6).[18,19]

These published structures are related to that of an intermediate postulated in Scheme 3. For an NMR spectroscopic characterization of such an intermediate, any formation of Ni(0) species (i.e., β-hydride elimination, decomposition into CO_2, Ni, and olefin) has to be suppressed. This was reached by using nickelalactone **2**, where such processes are expected to be thermodynamically disfavored (Scheme 7).

Due to solubility limitations, only a low concentration of the nickelalactone **2** was used for the NMR spectroscopic studies, in which addition of 20 equiv of MeI caused a very slow intermolecular reaction. However, we were able to detect the formation of the methyl ester functionality in a good kinetic resolution. Figure 3 shows the growth of the ^1H signal assigned to the methylated caboxylato group at 4.0 ppm. Within 3 days the complex was completely methylated, although a buildup of traces of paramagnetic impurities could be noticed from the deteriorating resolution in the spectra.

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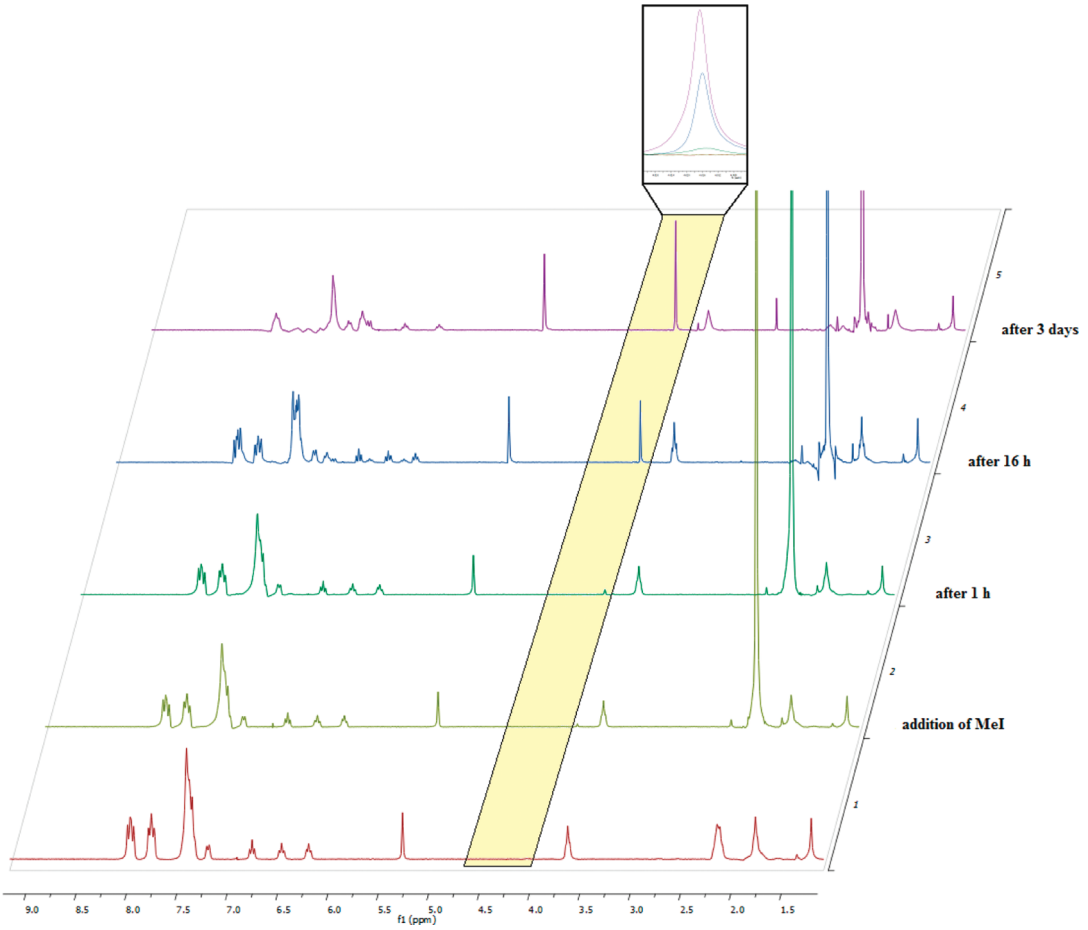
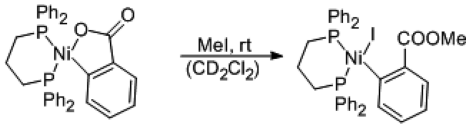


Figure 3. ^{1}H NMR spectroscopic study of the methylation of nickelalactone **2**.

Scheme 7. Methylation of Nickelalactone 2



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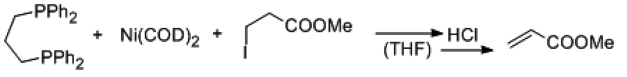
^{31}P NMR measurements (Supporting Information) show the same trend. Only the starting complex and the product of its methylation give ^{31}P signals. Esterification causes a shift of the resonance of the P atom trans to the oxygen atom toward a higher field. The P atom trans to the α-carbon atom is only slightly shifted, which indicates no splitting of the Ni−C bond. After 3 days no starting material was found in the ^{31}P NMR spectrum.

On the basis of these experiments, we therefore believe that the ester-functionalized structure suggested in Scheme 3 is a very likely intermediate before the elimination of methyl acrylate.

This is also in good agreement with the observations from oxidative addition of methyl 3-iodopropanoate to the Ni(0) complex (Scheme 8), which is expected to give the same species as postulated for the methylation of the nickelalactone **1** in Scheme 3. Instead, due to the spontaneous β-hydride elimination the reaction gave methyl acrylate, as detected by NMR spectroscopy and indirectly by ESI-MS, again confirming our mechanistic considerations.

According to the hypothetical catalytic cycle in Scheme 3, HI is expected to eliminate in the last step to give the Ni(0) species. The question arises whether HI could initiate the liberation of acrylates as well. Nickelalactone **1** stirred in

Scheme 8. Oxidative Addition of Methyl 3-Iodopropanoate on Ni(0)



dichloromethane for 6 days under an atmosphere of anhydrous HI indeed gave traces of acrylic acid, as detected by NMR spectroscopy and MS spectrometry. However, this reaction is too slow to compete with the addition of MeI followed by β-elimination with formation of methyl acrylate.

In conclusion, this work shows the first successful elimination of acrylates from nickelalactones. Although this is not yet a complete catalytic cycle and the yields obtained are far from quantitative, the in situ methylation investigated here is the first reported strategy that enables both β-hydride elimination and the liberation of acrylates. This represents the most challenging step toward a catalytic coupling of ethylene and CO_2. Further investigations will be necessary to find an appropriate ligand system and reaction conditions (CO_2 pressure, ethylene pressure, solvent, etc.) to realize satisfactory turnover numbers.

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Supporting Information Available: Text, tables, and figures giving experimental procedures, characterization data, and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.