Lactones

Effect of Sodium Cation on Metallacycle β -Hydride Elimination in CO₂–Ethylene Coupling to Acrylates

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Abstract: The catalytic conversion of carbon dioxide and olefins into acrylates has been a long standing target, because society attempts to synthesize commodity chemicals in a more economical and sustainable fashion. Although nickel complexes have been known to successfully couple CO_2 and ethylene for decades, a key β -hydride elimination step has proven a major obstacle to the development of a catalytic process. Recent studies have shown that Lewis acid additives can be used to create a lower-energy pathway for β -hydride elimination and facilitate a low number of catalytic turnovers. However, the exact manner, in which the

Introduction

The functionalization of CO₂ into value-added chemicals has the potential to profoundly impact the cost and sustainability of many consumer products.^[1] Although it is unlikely that the transformation of CO₂ into chemicals will directly mitigate climate change originating from anthropogenic release, CO₂ is a nearly ideal C₁ feedstock for the production of commodity chemicals.^[2] The primary barrier to widespread utilization of CO₂ is its significant thermodynamic stability. One method to circumvent this obstacle is coupling CO₂ with higher-energy small molecules, which can provide reduction potential to help drive the CO₂ functionalization. A limited number of largescale commodity chemical processes already employ this technique, including the synthesis of urea from CO₂ and ammonia.^[3] Another attractive target, which could dramatically expand this methodology, is the functionalization of CO₂ with olefins to produce acrylates, a family of polar monomers used heavily in fibers, fabrics, and super water absorbent polymers.

Currently, acrylates are industrially synthesized by the oxidation of propylene, a non-renewable carbon source, cost of which tightly controls that of most acrylates. As a result, a potential alternative route to acrylic acid and its derivatives by

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	Supporting information for this article is available on the WWW under
()	http://dx.doi.org/10.1002/chem.201304196.

Lewis acid promotes β -hydride elimination remains to be elucidated. Herein, we describe the kinetic and thermodynamic role that commercially relevant and weakly Lewis acidic sodium salts play in promoting β -hydride elimination from nickelalactones synthesized from CO₂ and ethylene. This process is compared to a non-Lewis acid promoted pathway, and DFT calculations were used to identify differences between the two systems. The sodium-free isomerization reaction gave a rare CO₂-derived β -nickelalactone complex, which was structurally characterized.

the coupling of CO₂ and ethylene has received considerable attention.^[4] Hoberg and co-workers were among the first to report a well-defined coupling of these gases by using the bis-(dicyclohexylphosphino)ethane (dcpe) ligand with nickel-1,5,9-cyclododecatriene to produce the γ -nickelalactone, [Ni(dcpe)(κ C, κ O-CH₂CH₂COO] (1- γ lactone).^[5] Although this seminal contribution demonstrated C-C bond formation between CO₂ and ethylene, 1- γ lactone and most subsequently described nickelalactones species have been described as unable to undergo the β -hydride elimination reaction necessary to form acrylate.^[6]

In the last five years, several groups have found that excess methylating agents can induce β -hydride elimination from γ nickelalactone complexes giving limited quantities of acrylate.^[7] However, the use of methylating agents results in the formation of oxidized metal species unsuitable for further coupling of CO₂ and ethylene. More recent investigations by Limbach and co-workers have developed an exciting two-stage reaction, in which strong external bases react directly with nickelalactone complexes to produce multiple equivalents of acrylate in the presence of sodium.^[8] Unfortunately, in these systems, the direct reaction between the external base and CO₂ hinders a single-stage catalytic process, and the exact role of the sodium cation is unclear. Recently, our group has reported that the relatively strong Lewis acid tris(pentaflurophenyl)boron can promote β -hydride elimination from a 1,1'-bis(diphenylphosphino)ferrocene (dppf)-supported γ-nickelalactone species.^[9] This activation by Lewis acid suggested that catalytic acrylate formation could be achieved by use of an electron-accepting co-catalysts, though this proved improbable for the dppf-nickel system, because the CO2-ethylene coupling did not occur. Therefore, we were interested in exploring the role

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of Lewis acid activators in promoting the key β -hydride elimination reaction in γ -nickelalactone complexes generated from CO₂-ethylene coupling. Herein, we describe the role of sodium cation in promoting β -hydride elimination from a nickelalactone. We believe that this is the weakest Lewis acid, which is likely to be sufficient for this purpose. Furthermore, both theoretical and experimental studies have been used to compare the Lewis acid promoted pathway with a non-Lewis acid promoted pathway, and the role of the sodium cation has been elucidated. Studies of the non-Lewis acid promoted pathway for β -hydride elimination have led to the characterization of the first example of an unactivated β -nickelalactone synthesized directly from CO₂-ethylene coupling.

Results and Discussion

A modest number of γ -nickelalactone complexes derived from CO₂ and ethylene have been reported since Hoberg's et al. initial discovery,^[8] but given its historical significance to the field, 1- γ lactone and a closely related analogue using bis(dicyclohexylphosphino)methane (dcpm; 2- γ lactone) were selected for investigation.^[11] In our hands, the γ -nickelalactone species were best synthesized by treatment of Ni(COD)₂ (COD = 1,5-cyclooctadiene) with diphosphine in the presence of excess CO₂ and ethylene (Figure 1). This permits use of a convenient and commercially available nickel source. The successful preparation of



Figure 1. Synthesis of γ -nickelalactone species from CO₂-ethylene coupling.

1-γlactone was confirmed by comparison to previously reported spectral data, as well as by X-ray diffraction (Figure 2). The Ni center in 1-γlactone displays a distorted square-planar geometry typical for γ -nickelalactones,^[8] with the five-membered lactone ring close to planarity. The related complex 2-γlactone was also characterized by NMR spectroscopy and combustion analysis. Interestingly, 2-γlactone proved quite stable to isolation in the absence of a CO₂ or ethylene atmosphere, contrary



Figure 2. Molecular structures of 1- γ lactone (left), 1- γ lactoneNa (middle), and 1- β lactone (right) with ellipsoids at 30% probability level. All hydrogen atoms, counteranions, and co-crystallized solvent molecules are omitted for clarity.

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to observations using the *t*Bu substituted congener, bis(di-*tert*-butylphosphino)methane.^[8]

The convenient isolation of the γ -nickelalactone complexes enabled study of the role of Lewis acids in promotion of β -hydride elimination reactions, in systems which in principle could be catalytically relevant due to their facile synthesis from CO₂ and ethylene. A particular focus was placed upon identifying a Lewis acid, which binds reversibly to metallactones creating the potential for a catalyzed elimination reaction. Inspired by Limbach and co-workers' empirical observation that exogenous sodium salts were essential to acrylate formation from γ -nickelalactone complexes in highly basic environments, the effect of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr₄^F) was investigated.^[8] Treatment of an ethereal or arene solution of 1-ylactone with NaBAr4 F immediately resulted in coordination of the sodium cation to the metallactone to produce 1-ylactoneNa (Figure 3). The influence of the Lewis acid was evident by a subtle shift of the lactone methylene resonances



Figure 3. Sodium activation and isomerization of nickelalactone species.

in the ¹H NMR spectrum to δ = 0.82 and 2.31 ppm from 0.89 and 2.60 ppm, respectively. In the solid-state structure (Figure 2), $1-\gamma$ lactoneNa is a dimer with each sodium bridging between the carboxylate oxygen atoms of one metallacycle and the exocyclic carboxylate oxygen atom of another. Notably, the Ni(1)–O(2) bond length in 1-γlactoneNa (1.937(2) Å) is slightly elongated compared to that of 1-ylactone (1.880(3) Å), suggesting a mild weakening of the nickel-oxygen bond, which may assist in ring opening and β -elimination.^[9] Interestingly, heating 1- $\gamma lactoneNa$ in THF at 55 $^\circ C$ for several hours induced partial isomerization to the sodium-activated β -nickelalactone, 1- β lactoneNa, with a K_{eq} of 0.28(2). This process is formally equivalent to β -hydride elimination, followed by subsequent 2,1-insertion from a transient nickel(II) acrylate hydride intermediate. Van't Hoff analysis of the interconversion between 1-ylactoneNa and 1-βlactoneNa gave parameters of $\Delta S^{\circ} = 15(2) \text{ Jmol}^{-1} \text{ K}$ and $\Delta H^{\circ} = 8.5(2) \text{ kJmol}^{-1}$ suggesting a small entropic preference for 1-βlactoneNa. Analogous isomerization behavior was observed for the dcpm congener, with a K_{eq} of 0.13(3) (55 $^{\circ}\text{C})$ between 2-ylactoneNa and 2-βlactoneNa. $^{[14]}$

Over the course of our investigations of 1- γ lactone, it was observed that this species undergoes reductive decoupling to expel CO₂ and ethylene at elevated temperature, as has been previously reported.^[5] Yet surprisingly, when the thermolysis of 1- γ lactone was conducted under CO₂ and ethylene at 55 °C for one day, partial conversion to an unactivated β -nickelalactone, 1- β lactone, was observed even in the absence of Lewis acid (Figure 4). This remarkable species was characterized by a com-



Figure 4. Formation of an unstabilized β -nickelalactone complex.

bination of multinuclear 1D and 2D NMR spectroscopy, as well as single-crystal X-ray diffraction. The solid-state structure of 1- β lactone is a rare example of an unactivated four-membered metallactone (i.e., no stabilizing group is present on the exocyclic carbonyl oxygen) and the first such species produced from CO₂-olefin coupling (Figure 2).^[12] The metrical parameters show a clear distinction between the carbon-oxygen bond lengths of 1.214(6) (C(1)–O(1)) and 1.322(6) Å (C(1)–O(2)) indicating strong localization of the double bond. The Ni(1)–O(2) distance of 1.900(3) Å is analogous to those observed in related activated β -nickelalactone structures.^[7] Substantial puckering of the four-membered lactone ring was also observed with a torsion angle of approximately 20°. Notably, isomerization of 2- γ lactone to its corresponding unactivated β -nickelalactone was not observed under analogous conditions.^[11]

Non-equilibrium mixtures of 1- γ lactone and 1- β lactone were also generated by treating a dcpe/Ni(COD)₂ solution with acrylic acid, which first gave [Ni(dcpe)(η^2 -CH₂=CHCO₂H)] (1-AA), followed by isomerization to an approximate 2:1 initial ratio of the metallacycles favoring 1- β lactone (Figure 5^{1,[11]} Unfortunately, attempts to determine the equilibrium constant between the unactivated nickelalactones by thermolysis under CO₂ and ethylene were obviated by partial sample degradation into a mixture containing [Ni(dcpe)($\kappa O, \kappa O$ -CO₃)] and other nickel compounds.^[13] Despite the lower stability of unactivated nickelalactones compared to the respective sodium adducts, a strong qualitative thermodynamic preference for 1- γ lactone over 1- β lactone was still observed.

The faster equilibration between nickelalactones with a sodium cation present offers a significant window into the role of Lewis acid in promoting the key β -elimination step proposed for catalytic CO2-ethylene coupling routes.^[6] To gain greater insight into this process, DFT calculations were performed. In the calculations, the cyclohexyl substituents on dcpe were replaced with methyl groups (denoted by the addition of ' after the compound number, so 1 with methyl substituents on the phosphines is written as 1'). The validity of this model was confirmed by performing selected calculations with more sterically hindered substituents on the phosphine ligands.^[11] For structures including sodium ions, three THF molecules and two oxygen atoms of the metallactone molecule were used to form the coordination sphere around sodium. Consistent with the observed trend, the calculations indicated a stabilization of the β -nickelalactone by sodium. The DFT model predicted a 1.84 kcal mol⁻¹ preference for 1'- γ lactone over 1'- β lactone, whereas 1'- β lactoneNa was 9.77 kJ mol⁻¹ more stable than 1'- γ lactoneNa (Figure 6). In the optimized structures of 1'-ylactone and 1'-ylactoneNa, both five-membered metallactone rings are nearly planar, closely matching the experimental structures. In contrast, the inclusion of a sodium ion substantially alters the planarity of the four-membered metallacycle. Sodium coordination increases the 19.2° torsion angle computed for 1'- β lactone to 29.6° in 1'- β lactone-Na. Thus, the origin of the stabilization of β -nickelalactone by sodium appears to be amelioration of ring strain associated with the four-membered metallacycle.

The pathway for the gamma-to-beta isomerization and the kinetic influence of the sodium cation were also probed computationally (Figure 6). Related calculations by Limbach and co-workers have proposed that complexes featuring agostic interactions play a key role in facilitating isomerization between cationic nickelalactone species, in which the metallactone was stabilized by methylation.^[8] The key intermediate in that system was an olefin hydride complex, and a similar structure was located for the interconversion of 1'- γ lactone/1'- β lactone and $1' - \gamma$ lactoneNa/1'- β lactoneNa (Figure 6).^[11] However, due to a relatively flat potential energy surface and a sharp energetic well leading to the formation of 1'- $\!\gamma$ lactone and 1'- $\!\beta$ lactone (or 1'- γ lactoneNa and 1'- β lactoneNa), it was not possible to optimize structures for the agostic intermediates without placing a constraint on the Ni-O bond, except in the case of 1'-βagosticNa.^[14] Nevertheless, comparison of the relative energies of the nickel-olefin hydride intermediates suggests a lower-energy isomerization pathway in the presence of



Figure 5. Alternative generation of 1-γlactone/1-βlactone mixture from acrylic acid.

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Figure 6. Energies of intermediates in the isomerization of a) 1'-ylactone to 1'-βlactone and b) 1'-ylactoneNa to 1'-βlactoneNa.

sodium. Relative to the respective γ -nickelalactones, the nickel–olefin hydride intermediate was almost 40 kJ mol^-1 lower in energy when activated by sodium. Furthermore, no direct pathway for β -hydride elimination was identified.^[6b] The dramatic stabilizing effect of the sodium cation is likely from compensation for the negative charge built up on the carboxylate. This would also explain the higher temperatures necessary for isomerization of 1'- γ lactone/1'- β lactone compared to methylated nickelalactone species, in which no negatively charged carboxylate is present.^[8]

Conclusion

We have observed a gamma-to-beta isomerization between a diphosphine-supported nickelalactone with and without sodium present, which has permitted a combined experimental and theoretical elucidation of the role of this highly attractive Lewis acid in the key β -hydride elimination step required for catalytic acrylate formation. The sodium cation is important in isomerization for two reasons: 1) it provides thermodynamic stabilization of the β -nickelalactone structure through suppression of ring stain and 2) it lowers the barrier to isomerization by stabilizing the charge on high energy carboxylate anion intermediate. Our results are consistent with the hypothesis that as the Lewis acidity of the promoter increases and a stronger acid-oxygen bond is formed, the process of β -hydride elimination becomes more facile. Thus, a key for effecting catalytic CO₂-olefin coupling to acrylate is the use of Lewis acid co-catalysts, which can promote β -hydride elimination, but still bind weakly enough to allow its removal from substrate. The sodium cation, particularly desirable for the synthesis of sodium acrylate, appears to be one of the weakest Lewis acids, which may be utilized, because the non-promoted pathway occurs with only mildly greater difficulty.

Experimental Section

General

NaBAr₄^F was prepared according to the previously described procedure.^[15] All air- and moisture-sensitive manipulations were carried out by using standard vacuum line, Schlenk, cannula, or glove-box

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techniques. Volatile chemicals were dried with 4 Å molecular sieves and distilled prior to use. All chemicals were purchased from Aldrich, VWR, Fisher Scientific, Strem, or Cambridge Isotope Laboratories. Solvents were dried and deoxygenated by using literature procedures.^[16]

 $^1\text{H},~^{13}\text{C},~^{19}\text{F},$ and ^{31}P NMR spectra were recorded on Bruker DRX 400, Avance 300 and 600 MHz spectrometers. ¹H and ¹³C NMR chemical shifts are referenced to residual protio solvent signals; ¹⁹F and ³¹P NMR chemical shifts are referenced to the external standards $C_6H_5CF_3$ and H_3PO_4 , respectively. In some cases, the inequivalent ³¹P nuclei have coupling constants too small to be observed due to the combination of ²J and ³J couplings, these are denoted as singlets. Probe temperatures were calibrated by using ethylene glycol, as was previously described.^[17] Unless otherwise indicated, spectra were obtained at ambient temperature. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ or Atlantic Micro Labs in Norcross, GA. X-ray crystallographic data were collected on a Bruker D8 Quest diffractometer. Samples were collected in inert oil and quickly transferred to a cold gas stream. The structures were solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all nonhydrogen atoms. Crystallographic calculations were carried out by using SHELXTL. CCDC-961246 (1-γlactone), CCDC-961247 (1-βlactone), and CCDC-961248 (1-ylactoneNa) 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.

Computational details

All geometry optimizations were performed by using Gaussian 09, Revision A.02.^[18] Initial geometries were obtained by using the coordinates from X-ray structures when possible. The M06 L functional was used in all calculations after evaluation of a variety of different functionals (see the Supporting Information). The LANL2DZ basis set was used for Ni and the 6-31G + +(d,p) basis set was used for all other atoms. The LANL2DZ pseudo-potential was used for Ni. For calculations involving systems containing sodium, QMMM calculations were performed by using ONIOM(M06 L:UFF), as implemented in Gaussian. In these calculations, three THF molecules were used to complete the coordination sphere around sodium, which also included the oxygen atoms from the lactone. These THF molecules were modeled at the MM level, with the exception of the oxygen atoms directly bound to the sodium, which were part of the QM section of the molecule. Frequency calculations were performed on all optimized structures to ensure that they were true minima. Solvent was modeled by using the integral equation polarizable continuum model (THF), as implemented in Gaussian. All energies presented are Gibbs free energies with solvent corrections.

Synthesis of [Ni(dcpe)(κC,κO-CH₂CH₂COO)] (1-γlactone)

This species was prepared by modification of procedure described by Hoberg and co-workers by using Ni(COD)₂ as the metal source.^[18] A 50 mL heavy-walled glass reaction vessel was charged with dcpe (0.178 g, 0.421 mmol), Ni(COD)₂ (0.118 g, 0.429 mmol), and THF (ca. 6 mL). On a high-vacuum line, ethylene (5 equiv, 390 Torr in 101 mL) followed by carbon dioxide (5 equiv, 390 Torr in 101 mL) was admitted to the reaction mixture at -196 °C through a calibrated gas bulb. After the mixture was stirred for one day at 50 °C, the volatiles were removed in vacuo. The residue was washed with diethyl ether (ca. 3 mL) and toluene (1 mL), and extracted with THF to remove trace nickel metal particulates. The extract was then dried to give 0.208 g (89%) of 1-γlactone with good purity. The material may be further purified by layering *n*-pentane on a concentrated THF solution and chilling at -35 °C. The spectral data presented below are in agreement with those previously reported by Hoberg and co-workers. ¹H NMR (400 MHz, [D₆]benzene): $\delta = 0.89$ (m, 2 H, (PCy₂)), 1.00 (m, 2 H, Ni- α -CH₂), 1.02–1.65 (42 H, PCy₂), 2.02 (m, 2 H, PCH₂CH₂P), 2.20 (m, 2 H, PCH₂CH₂P), 2.85 (m, 2 H, Ni- β -CH₂); ¹³C(¹H} NMR (100 MHz, [D₆]benzene): $\delta = 11.64$ (Ni- α -CH₂), 24.70, 26.42, 27.13–27.47, 29.17 (PCy₂-CH₂), 29.45 (PCH₂CH₂P), 29.70 (PCH₂CH₂P), 33.80, 35.30 (PCy₂-CH), 37.76 (Ni- β -CH₂), 188.83 (CO₂); ³¹P(¹H) NMR (162 MHz, [D₆]benzene): $\delta = 63.65$ (bs s, 1P, PCy₂), 69.79 (br s, 1P, PCy₂); elemental analysis calcd for C₂₉H₅₂NiO₂P₂ (553.36): C 62.94, H 9.47; found: C 63.21, H 9.77.

Synthesis of [Ni(dcpm)($\kappa C, \kappa O$ –CH₂CH₂COO)] (2- γ lactone)

A heavy-walled glass reaction vessel (50 mL) was charged with dcpm (0.309 g, 0.757 mmol), Ni(COD)₂ (0.207 g, 0.753 mmol), and THF (ca. 6 mL). On a high-vacuum line, ethylene (420 Torr in 101 mL) followed by carbon dioxide (700 Torr in 101 mL) were admitted to the reaction mixture at -196 °C through a calibrated gas bulb. After the mixture was stirred for one day at 50 °C, the volatiles were removed in vacuo. The residue was washed with diethyl ether and extracted with THF to remove trace nickel metal particulates. The extract was then dried to give **2**-γlactone (0.190 g, 47%) as orange powder containing minor amounts of [Ni(COD)(dcpm)]. The material may be further purified by layering *n*-pentane on a concentrated THF solution and chilling at -35 °C. Alternatively, **2**-γlactone may be obtained by charging a scintillation vial (20 mL) with dcpm (0.152 g, 0.372 mmol), Ni(COD)₂ (0.103 g, 0.374 mmol), and THF (ca. 3 mL). After the solid was dissolved, acrylic acid (29 µL, 0.423 mmol) was injected into the reaction mixture. The mixture was stirred at RT for 30 min, and the desired product was isolated as described above. ¹H NMR (400 MHz, [D₆]benzene): $\delta =$ 1.00 (m, 2 H, Ni-α-CH₂), 1.03–1.66 (40 H, PCy₂, (PCy₂)), 1.95–2.08 (6 H, PCH_2P & $PCy_2),$ 2.65 ppm (m, 2 H, Ni- β -CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_6]$ benzene): $\delta = 8.24$ (Ni- α -CH₂), 25.83, 26.25, 27.28–27.43, 28.67, 29.27, 29.56, 29.69, 30.23 (PCy2-CH2), 34.41, 34.57 (PCy2-CH), 37.37 ppm (Ni- β -CH₂), one quaternary signal was not located; $^{31}P{^{1}H} NMR$ (162 MHz, [D₆]benzene): $\delta = -7.11$ (d, $^{2}J_{P-P} = 23.3$ Hz, 1P, PCy₂), 17.73 ppm (d, ²J_{P-P} = 23.3 Hz, 1P, PCy₂); elemental analysis calcd for $C_{28}H_{50}NiO_2P_2$ (539.33): C 62.35, H 9.34; found: C 62.08, H 9.13.

Synthesis of $[Ni(dcpe)(\kappa C, \kappa O-CH_2CH_2COONa)][BAr_4^F]$ (1- γ lactoneNa)

A scintillation vial (20 mL) was charged with 1-γlactone (0.058 g, 0.105 mmol), NaBAr₄^F (0.099 g, 0.112 mmol), and THF (ca. 3 mL). After the mixture was stirred at RT for 10 min, the volatiles were removed in vacuo. The residue was washed with benzene and extracted with diethyl ether. Concentrating the solution, layering with *n*-pentane and chilling to -35 °C gave 1-γlactoneNa (0.145 g, 96%) as orange crystals. ¹H NMR (400 MHz, [D₅]bromobenzene): δ = 0.82 (m, 2H, Ni- α -CH₂), 1.1–1.72 (44 H, PCy₂), 1.94, 2.02 (m, 4H, PCH₂CH₂P), 2.31 (m, 2H, Ni- β -CH₂), 7.63 (s, 4H, BAr₄^F), 8.18 ppm (s, 8H, BAr₄^F); ¹³C{¹H} NMR (100 MHz, [D₅]bromobenzene): δ = 12.11 (Ni- α -CH₂), 25.31–25.78, 26.57–26.93, 28.60, 28.88, 29.37, 29.80 (PCy₂-CH₂), 33.49, 35.43 (PCy₂-CH), 36.67 (Ni- β -CH₂), 117.48, 123.26, 134.86, 162.11 ppm (BAr₄^F)M; one aryl and one quaternary signal was not located; ³¹P{¹H} NMR (162 MHz, [D₅]bromobenzene): δ = 60.62 (s, 1P, PCy₂), 70.93 ppm (s, 1P, PCy₂); ¹⁹F NMR (C₆D₅Br): δ =

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 $-62.95 \quad (s); \ elemental \ analysis \ calcd \ for \ C_{61}H_{64}BF_{24}NaNiO_2P_2 \\ (1439.56): C \ 50.89, \ H \ 4.48; \ found: C \ 50.94, \ H \ 4.71.$

Synthesis of [Ni(dcpm)($\kappa C, \kappa O$ -CH₂CH₂COONa)][BAr₄^F] (2- γ lactoneNa)

A scintillation vial (20 mL) was charged with 2-ylactone (0.040 g, 0.074 mmol), NaBAr₄^F (0.073 g, 0.082 mmol), and THF (ca. 3 mL). After the mixture was stirred at RT for 10 min, the volatiles were removed in vacuo. The residue was washed with benzene and extracted with diethyl ether. Layering the concentrated diethyl ether solution with *n*-pentane and chilling at -35 °C gave 2- γ lactoneNa (0.103 g, 97%) as orange crystals. ¹H NMR (400 MHz, $[D_5]$ bromobenzene): $\delta = 0.71$ (m, 2H, Ni- α -CH₂), 1.04–1.94 (m, 44H, $PCy_2),\ 2.01$ (m, 2H, $Ni{-}\beta{-}CH_2),\ 2.13$ (m, 2H, $PCH_2P)$ 7.63 (s, 4H, BAr₄^F), 8.18 ppm (s, 8H, BAr₄^F); ¹³C{¹H} NMR (100 MHz, $[D_5]$ bromobenzene): $\delta = 7.42$ (Ni- α -CH₂), 25.13, 25.63, 26.31, 26.66– 26.93, 28.28, 29.26, 29.34 (PCy2-CH2), 29.09 (PCH2P), 34.28, 34.52 (PCy₂-CH), 36.17 (Ni-β-CH₂), 117.48, 123.26, 134.86, 162.11 ppm (BAr_4^{F}) , one aryl and one quaternary signal not located; $^{31}P{^{1}H} NMR$ (162 MHz, [D₅]bromobenzene): $\delta = -8.70$ (d, $^{2}J_{P-P} =$ 35.5 Hz, 1P, PCy₂), 19.24 ppm (d, ²J_{P-P}=35.5 Hz, 1P, PCy₂); ¹⁹F NMR ([D₅]bromobenzene): $\delta = -62.95$ ppm (s).

Synthesis of [Ni(dcpe)(η²-C,C-CH₂=CHCO₂H)] (1-AA)

A scintillation vial (20 mL) was charged with dcpe (0.129 g, 0.305 mmol), Ni(COD)₂ (0.084 g, 0.305 mmol), and THF (ca. 4 mL). After the solid dissolved, acrylic acid (25 µL, 0.364 mmol) was injected into the reaction mixture. The mixture was stirred at RT for one hour, resulting in precipitation of a yellow solid. The solid was filtered and washed with THF (ca. 3 mL) to give [Ni(dcpe)(η^2 -CH₂CHCOOH)] (0.130 g, 82%) as a yellow powder. ¹H NMR (400 MHz, [D₅]bromobenzene): δ = 1.02–2.02 (48 H, PCy₂ & PCH₂CH₂P), 2.08 (br m, 1H, η^2 -CH₂CH), 2.40 (br m, 1H, η^2 -CH₂CH), 3.31 (br m, 1H, η^2 -CH₂CH), 12.33 ppm (br s, 1H, COOH); ¹³C{¹H} NMR (100 MHz, [D₅]bromobenzene): δ = 20.11–27.21 (PCy₂-CH₂& PCH₂CH₂P) 25.81 (η^2 -CH₂CH), 29.61, 32.11 (PCy₂-CH), 37.51 ppm (η^2 -CH₂CH), one quaternary COOH signal was not located; ³¹P{¹H} NMR (162 MHz, [D₅]bromobenzene): δ = 61.30 (d, ²J_{P-P} = 48.1 Hz, 1P, PCy₂).

Synthesis of [Ni(dcpe)($\kappa C, \kappa O$ -CH(CH₃)COO)] (1- β lactone)]

This species may be generated by either thermolysis of 1-ylactone or 1-AA. Because the isomerization from 1-AA provides a higher kinetic yield of 1- β lactone, it was used in isolation of small quantities of the pure compound. A scintillation vial (20 mL) was charged with dcpe (0.092 g, 0.218 mmol), Ni(COD)₂ (0.060 g, 0.218 mmol), and benzene (ca. 15 mL). Acrylic acid (16 µL, 0.233 mmol) was injected into the reaction mixture. After the mixture was stirred at RT for one day, the volatiles were removed in vacuo. The residue was washed with *n*-pentane and extracted with toluene to give mixture of 1-βlactone and 1-γlactone (0.050 g). The mixture was redissolved in THF and layered with pentane to give pure 1- β lactone (0.015 g, 12%) as orange crystals. ¹H NMR (400 MHz, [D₆]benzene): $\delta = 0.98 - 1.85$ (44 H, PCy₂), 1.47 (m, 3 H, Ni- β -CH₃), 2.05–2.16 (m, 4 H, PCH_2CH_2P), 2.30 ppm (br m, 1 H, Ni- α -CH); ¹³C{¹H} NMR (100 MHz, $[D_6]$ benzene): $\delta = 16.62$ (Ni- β -CH₃), 26.17–26.57, 27.06–27.57, 29.14– 29.85, 30.33, 31.26 (PCy2-CH2), 28.11 (Ni-α-CH), 33.87, 36.60 (PCy2-CH) 180.21 ppm (CO₂); ${}^{31}P{}^{1}H{}$ NMR (162 MHz, [D₆]benzene): $\delta =$ 64.36 (d, ²J_{P-P}=8.7 Hz, 1P, PCy₂), 71.09 (d, ²J_{P-P}=8.7 Hz, 1P, PCy₂); elemental analysis calcd for C₂₉H₅₂NiO₂P₂ (553.36): C 62.94, H 9.47; found: C 63.21, H 9.21.

Observation of [Ni(dcpm)($\kappa C, \kappa O$ –CH(CH₃)COO)] (2- β lactone)

A scintillation vial (20 mL) was charged with dcpm (0.052 g, 0.127 mmol) and Ni(COD)₂ (0.035 g, 0.127 mmol). After acrylic acid (10 µL, 0.146 mmol) was injected into the vial, THF (ca. 3 mL) was added in as the solvent. The mixture was stirred at RT for 30 min, and the volatiles were removed in vacuo. The residue was washed with diethyl ether (ca. 8 mL) and dried to give **2**-βlactone and **2**-γlactone mixture (0.057 g, 83%) highly favoring the γ-nickelalactone. Spectral data for **2**-βlactone: ¹H NMR (400 MHz, [D₆]benzene): δ =1.29 (m, 3H, Ni-β-CH₃), 1.03–2.15 (48H, PCy₂& PCH₂CH₂P), 2.18 ppm (m, 1H, Ni-α-CH); ³¹P{¹H} NMR (162 MHz, [D₆]benzene): δ =-1.89 (d, ²J_{P-P}=2.9 Hz, 1P, PCy₂), 21.92 ppm (d, ²J_{P-P}=2.9 Hz, 1P, PCy₂); partial ¹³C NMR taken from ¹H-¹³C HSQC (400 MHz, [D₆]benzene): δ =18.4 (Ni-β-CH₃), 26.7 ppm (Ni-α-CH).

Observation of [Ni(dcpe)($\kappa C, \kappa O$ -CH(CH₃)COO)Na)] [BAr₄^F] (1- β lactoneNa)

A scintillation vial (20 mL) was charged with 1-AA (0.126 g, 0.228 mmol), NaBAr₄^F (0.206 g, 0.233 mmol), and THF (ca. 5 mL). After the mixture was stirred at RT for two days, the volatiles were removed in vacuo. The residue was washed with benzene and extracted with diethyl ether to give 1- β lactoneNa and 1- γ lactoneNa mixture (0.320 g, 98%). Compound 1-βlactoneNa may also be generated by heating solutions of isolated 1-γlactoneNa at 55 °C for 5-10 h. The mixture was characterized by ¹H, ³¹P{¹H}, ¹H–¹³C HSQC, and ¹H–¹H COSY NMR spectroscopy without isolation. Spectral data for 1- β lactoneNa: ¹H NMR (400 MHz, [D₅]bromobenzene): $\delta = 0.82$ (m, 3 H, Ni-\beta-CH_3), 1.10–2.23 (48 H, PCy_2 PCH_2CH_2P), 2.23 (m, 1 H, Ni- α -CH), 7.63 (s, 4H, BAr₄^F), 8.18 ppm (s, 8H, BAr₄^F); ³¹P{¹H} NMR (162 MHz, $[D_5]$ bromobenzene): $\delta = 67.38$ (s, 1P, PCy₂), 74.03 ppm (s, 1P, PCy₂); ¹⁹F NMR (376 MHz, C₆D₅Br): $\delta = -62.95$ ppm (s); partial ¹³C NMR taken from ¹H–¹³C HSQC (400 MHz, [D₅]bromobenzene): $\delta = 15.9$ (Ni- β -CH₃), 30.0 ppm (Ni- α -CH).

Observation of $[Ni(dcpm)(\kappa C, \kappa O-CH(CH_3)COO)Na)][BAr_4^F]$ (2- β lactoneNa)

A.J. Young NMR tube was charged with **2**- γ lactone (0.020 g, 0.037 mmol), NaBAr₄^F (0.035 g, 0.040 mmol), and [D₆]acetone (ca. 0.5 mL). The mixture was heated at 55 °C for one day, showing an approximately 1:8 mixture of **2**- β lactoneNa and **2**- γ lactoneNa. The mixture was characterized by ¹H, ³¹P{¹H}, ¹H-¹³C HSQC, and ¹H-¹H COSY NMR spectroscopy without isolation. Spectral data for **2**- β lactoneNa: ¹H NMR (400 MHz, [D₆]acetone): $\delta = 0.86$ (dd, ³J_{H-H} 6.9 Hz, J_{P-H} 6.9 Hz, 3H, Ni- β -CH₃), 1.89 (m, 1H, Ni- α -CH), 1.28–2.34 (PCy₂& PCH₂P), 7.68 (s, 4H, BAr₄^F), 7.80 ppm (s, 8H, BAr₄^F); ³¹P{¹H} NMR (162 MHz, [D₆]acetone): $\delta = -4.15$ (d, ²J_{P-P} 26.9 Hz, 1P, PCy₂), 19.85 ppm (d, ²J_{P-P} 26.9 Hz, 1P, PCy₂); partial ¹³C NMR spectrum taken from ¹H-¹³C HSQC (400 MHz, [D₆]acetone): $\delta = 16.2$ (Ni- β -CH₃), 26.3 ppm (Ni- α -CH).

Acknowledgements

We gratefully acknowledge support by the National Science Foundation under the Centre for Chemical Innovation " CO_2 as a Sustainable Feedstock for Chemical Commodities" (Grant No. CHE-1240020).

Keywords: density functional calculations \cdot fixation of carbon dioxide \cdot metallacycles \cdot nickel

Chem. Eur. J. **2014**, 20, 3205 – 3211

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- a) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, Angew. Chem. 2011, 123, 8662; Angew. Chem. Int. Ed. 2011, 50, 8510;
 b) Renewable Raw Materials: New Feedstocks for the Chemical Industry (Eds.: R. Ulber, D. Sell, T. Hirth), Wiley-VCH, Weinheim, 2011.
- [2] Developments and Innovations in Carbon Dioxide Capture and Storage Technology, Vol 2: Carbon Dioxide Storage and Utilisation (Ed.: M. M.Maroto-Valer), Woodhead, Cambridge, 2010.
- [3] M. Aresta, A. Dibenedetto, in *Industrial Utilization of Carbon Dioxide; Developments and Innovation in Carbon Dioxide Capture and Storage Technology* (Ed.: M. M. Maroto-Valer), Woodhead, Cambridge, **2010**, pp. 377–410.
- [4] a) R. Alvarez, E. Carmona, D. J. Cole-Hamilton, A. Galindo, E. Gutierrez-Puebla, A. Monge, M. L. Poveda, C. Ruiz, J. Am. Chem. Soc. 1985, 107, 5529; b) A. Galindo, A. Pastor, P. Perez, E. Carmona, Organometallics 1993, 12, 4443; c) C. Collazo, M. del Mar Conejo, A. Pastor, A. Galindo, Inorg. Chim. Acta 1998, 272, 125; d) R. Fischer, J. Langer, G. Malassa, D. Walther, H. Gorls, G. Vaughan, Chem. Commun. 2006, 2510; e) W. H. Bernskoetter, B. T. Tyler, Organometallics 2011, 30, 520.
- [5] H. Hoberg, D. Schaefer, J. Organomet. Chem. 1983, 251, C51.
- [6] For related computational assessments, see: a) I. Papai, G. Schubert, I. Mayer, G. Besenyei, M. Aresta, *Organometallics* 2004, 23, 5252; b) D. C. Graham, C. Mitchell, M. I. Bruce, G. F. Metha, J. H. Bowie, M. A. Buntine, *Organometallics* 2007, 26, 6784.
- [7] a) C. Bruckmeier, M. W. Lehenmeier, R. Reichardt, S. Vagin, B. Rieger, Organometallics 2010, 29, 2199; b) S. Y. T. Lee, M. Cokoja, M. Drees, Y. Li, J. Mink, W. A. Herrmann, F. E. Kuhn, ChemSusChem 2011, 4, 1275; c) P. N. Plessow, L. Weigel, R. Lindner, A. Schafer, F. Rominger, M. Limbach, P. Hofmann, Organometallics 2013, 32, 3327.
- [8] M. L. Lejkowski, R. Lindner, T. Kageyama, G. E. Bodizs, P. N. Plessow, I. B. Muller, A. Schafer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk, M. Limbach, *Chem. Eur. J.* 2012, *18*, 14017.
- [9] D. Jin, T. J. Schmeier, P. G. Williard, N. Hazari, W. H. Bernskoetter, Organometallics 2013, 32, 2152.
- [10] a) H. Hoberg, Y. Peres, C. Kruger, Y. H. Tsay, Angew. Chem. Int. Ed. Engl. 1987, 26, 771; b) H. Hoberg, A. Ballesteros, A. Sigan, C. Jegat, D. Barhausen, A. Milchereit, J. Organomet. Chem. 1991, 407, C23.

- [11] See the Experimental Section for further details.
- [12] a) S. Baba, T. Ogura, S. Kawaguchi, H. Tokunan, Y. Kai, N. Kasai, *Chem. Commun.* **1972**, 910; b) L. Pandolfo, G. Paiaro, G. Valle, P. Ganis, *Gazz. Chim. Ital.* **1985**, *115*, 65; c) W. A. Herrmann, U. Kusthardt, A. Schafer, E. Herdtweck, *Angew. Chem.* **1986**, *98*, 818; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 817; d) M. Gómez, M. Paneque, M. L. Poveda, E. Alvarez, *J. Am. Chem. Soc.* **2007**, *129*, 6092.
- [13] P. Mastrorilli, G. Moro, C. C. F. Nobile, M. Latronico, *Inorg. Chim. Acta* **1992**, *192*, 189.
- [14] See the Supporting Information for further details.
- [15] N. A. Yakelis, R. G. Bergman, Organometallics 2005, 24, 3579.
- [16] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, Organometallics 1996, 15, 1518.
- [17] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, **1982**.
- [18] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Krnox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

Received: October 28, 2014 Published online on February 12, 2014