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Lewis Acid Induced β-Elimination from a Nickelalactone: Efforts toward Acrylate Production from CO_2 and Ethylene

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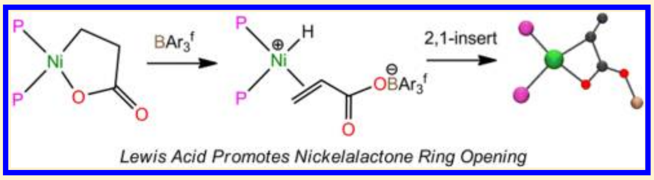
Ⓢ *Supporting Information*

ABSTRACT: The Lewis acid tris(pentafluorophenyl)borane was found to rapidly promote ring-opening β-hydride elimination in a 1,1′-bis(diphenylphosphino)ferrocene (dppf) nickelalactone complex under ambient conditions. The thermodynamic product of nickelalactone ring-opening was characterized as $(\mathrm{dppf})\mathrm{Ni}(\mathrm{CH}(\mathrm{CH_3})\mathrm{CO_2BAr^f_3})$, the result of β-hydride elimination and subsequent 2,1-insertion from a transient nickel(II) acrylate hydride intermediate. Treatment of $(\mathrm{dppf})\mathrm{Ni}(\mathrm{CH}(\mathrm{CH_3})\mathrm{CO_2BAr^f_3})$ with a nitrogen-containing base afforded a diphosphine nickel(0) η^2-acryl borate adduct. Formation of the diphosphine nickel(0) η^2-acryl borate adduct completes a net conversion of nickelalactone to acrylate species, a significant obstacle to catalytic acrylate production from CO_2 and ethylene. Displacement of the η^2-acrylate fragment from the nickel center was accomplished by addition of ethylene to yield a free acrylate salt and $(\mathrm{dppf})\mathrm{Ni}(\mathrm{CH_2{=}CH_2})$.



INTRODUCTION

The utilization of CO_2 as a feedstock for the production of commodity chemicals potentially offers a more cost-effective and renewable alternative to fossil fuel based carbon sources in the chemical industry.[1] Unfortunately, the kinetic and thermodynamic stability of CO_2 has limited its exploitation thus far to a handful of commercial chemicals.[2] One method to surmount this stability is the reduction of CO_2 via coupling to other relatively high energy small molecules, a technique that is already employed in the commercial production of urea and polycarbonates from ammonia and epoxides, respectively.[3] The functionalization of CO_2 with light olefins to produce α,β-unsaturated carboxylic acids is yet another intriguing target for this methodology, with potentially significant implications for the manufacture of acrylates used in superabsorbent polymers, elastomers, and detergents.[4]

Transition metal promoted coupling of CO_2 and ethylene toward acrylate formation has been explored as an alternative to currently used propylene oxidation technology since the seminal reports of Hoberg and Carmona in the 1980s (Figure 1).[5] These pioneering investigators independently pursued new routes for CO_2−ethylene coupling using zerovalent nickel[6] and group VI metals,[7] respectively, though catalytic activity remained elusive. Subsequent experimental and computational mechanistic studies on these reactions suggest that the early and late metal complexes likely share several common intermediates on the desired catalytic pathway, but are challenged by different steps in the proposed cycle (Figure 2).[8] In the case of group VI metals, the oxidative coupling of CO_2 and ethylene appears relatively facile, occurring at ambient temperature and pressures. The couplings at molybdenum and tungsten have consistently afforded acrylate products, implying that β-hydride elimination from computationally predicted metalalactone intermediates is swift.[5b,7,8a,9] Unfortunately, the strong oxophilicity of molybdenum and tungsten has hampered reductive acrylate removal using methods compatible with catalysis, as proven examples of acrylate liberation require either a harsh base (i.e., butyllithium) or a strong electrophile (i.e., iodomethane).[7a,9]

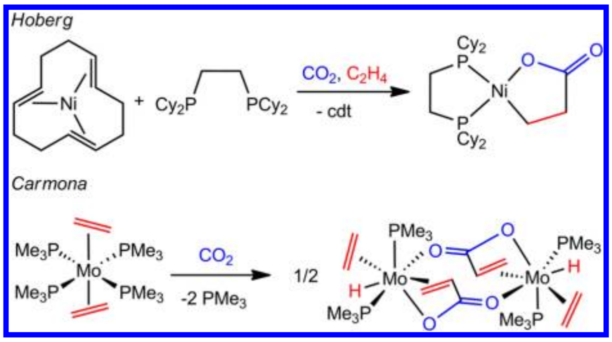


Figure 1. Pioneering reports of CO_2−ethylene coupling at transitions metal complexes.[5]

By contrast, removal of acrylate from nickel should be more facile owing to its lower oxophilicity and reduction potential as well as its greater tolerance of protic functional groups. The principal obstacles for catalytic acrylate formation at nickel seem to lie in the high pressures required for most oxidative couplings (up to 40 bar) and a strong reticence for β-hydride elimination from the nickelalactone intermediates. The

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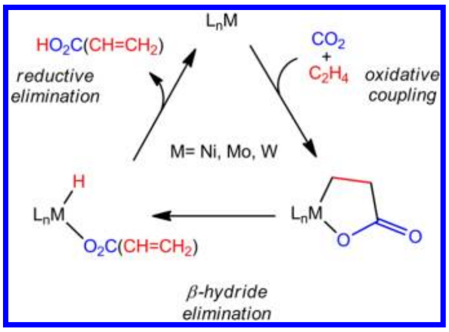


Figure 2. Proposed catalytic cycle for production of acrylic acid from CO_2 and ethylene.

pressures typically required for nickel-promoted CO_2−ethylene coupling may be attained in autoclave reactors, but can spur undesired side reactions, such as ligand degradation and multiple CO_2 insertions.[6] The high CO_2 pressure can also interfere with later steps in catalytic acrylate production (*vide infra*).[10] Nevertheless, it appears that inducing β-hydride elimination from nickelalactone complexes is the more systematic barrier, as the few well-defined examples of nickelalactone β-hydride elimination occur only with ancillary ligand activation or the use of vast excesses of electrophile.[11]

The origin of stability to β-hydride elimination in square planar nickelalactone species is probably the result of two interrelated factors: the strain energy associated with distorting the five-membered lactone ring and the absence of an accessible low-lying orbital for a β-agostic interaction. Crystallographic evidence from multiple nickelalactone structures indicates the key C−H bonds β-to-the-metal are oriented away from the nickel and would likely require significant twisting of the five-membered ring to be brought within a covalent interaction distance.[6c,10,11a,c,12] However the observation of swift elimination from proposed metalalactones of molybdenum and tungsten suggests that additional orbital constraints may also contribute.[5b,7,8a,9] Brookhart, Green, and others have shown that β-hydride elimination in late transition metals occurs via formation of an agostic intermediate, which necessitates an empty orbital on the metal to accept electron donation from the target C−H bond.[13] As is illustrated in the classic slow associative (or associative interchange) mechanism for ligand substitution at square planar d^8-complexes,[14] the vacant $d_{x^2-y^2}$ orbital in the nickel(II) lactone is inaccessible to incoming ligands (or β-hydrogens) due to the position of the existing square planar ligands (Figure 3). Thus coordination of the β-C−H bond in nickelalactone complexes would require use of a higher energy empty orbital or significant ligand rearrangement.

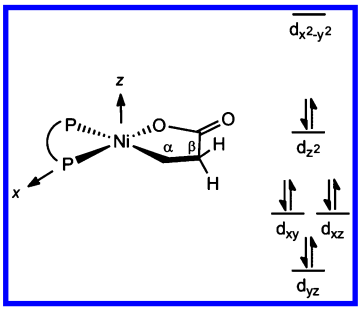


Figure 3. Qualitative d-orbital splitting diagram for square planar nickel(II) metalalactone.

Recently Limbach and co-workers have circumvented these barriers to β-hydride elimination by adding external bases such as sodium *tert*-butoxide to diphosphine nickelalactone species, which deprotonate the β-hydrogen directly without necessitating transfer of the hydride to nickel.[10] This approach affords sodium acrylate ($NaCO_2CHCH_2$) in good yield, and by repeated sequential additions of CO_2, ethylene, and base, several equivalents of sodium acrylate may be obtained in one reaction vessel. Unfortunately, the strong sodium base required for the deprotonation is not compatible with the high CO_2 pressure needed for nickelalactone formation, obviating catalytic production under a constant set of reaction conditions. An alternative method that has interested our laboratory is the facilitation of β-hydride elimination by ring-opening of the metalalactone. This approach could afford a transient three-coordinate nickel species, which alleviates the ring strain and orbital constraints. Herein we describe the synthesis, characterization, and pathway of formation for a ring-opened diphosphine nickelalactone complex using a Lewis acid as well as the implications of Lewis acid addition on base-mediated acrylate formation.

■ RESULTS AND DISCUSSION

The interconversion between a four-coordinate nickelalactone species and the corresponding η^2-acrylic acid complex is central to the catalytic production of acrylates from the coupling of CO_2 and ethylene. However, to date, there is no evidence of direct interconversion between these species. Given the significance of this transformation, our laboratory sought to leverage one of the few easily prepared ligand platforms known to support isolable examples of both isomers on nickel, 1,1′-bis(diphenylphosphino)ferrocene (dppf). Walther and co-workers have previously demonstrated that the metalalactone species $(dppf)Ni(CH_2CH_2CO_2)$ (**A**) and the η^2-acrylic acid complex $(dppf)Ni(CH_2{=}CHCO_2H)$ (**B**) may be prepared independently via ligand substitution reactions (Figure 4).[12b] In our hands, no interconversion between these two isomers was detected in DMSO, THF, or arene solution at temperatures up to 45 °C, above which decomposition of **A** occurred via reductive decoupling of CO_2 and ethylene. Similar to the observations of other diphosphine nickelalactone compounds,[10]

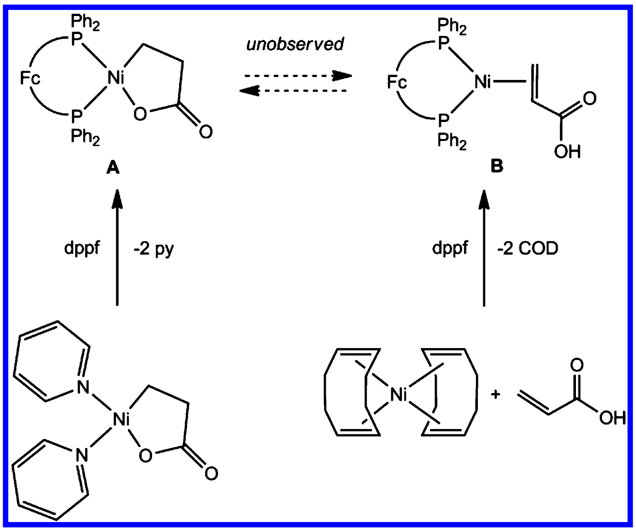
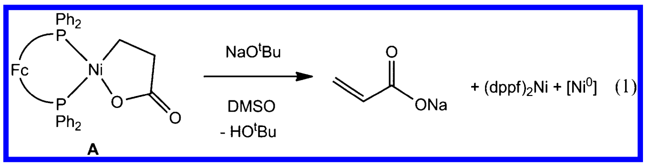


Figure 4. Synthetic routes for $(dppf)Ni(CH_2CH_2CO_2)$ (**A**) and $(dppf)Ni(CH_2{=}CHCO_2H)$ (**B**).

elimination from **A** may be induced by addition of a strong external base, such as sodium *tert*-butoxide, in DMSO to afford sodium acrylate (detected by NMR spectroscopy) and (dppf)$_2$Ni along with a quantity of nickel(0) particulates (eq 1).[15] However slightly weaker neutral bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or even *tert*-butyliminotri(pyrrolidino)phosphorane (BTPP) were ineffective at promoting elimination from **A**. Given the inherent compatibility challenges of using strong anionic bases in conjunction with CO_2 in coupling reactions, we directed our attention toward Lewis acid promoted methods of inducing *β*-hydride elimination from nickelactone species.



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Lewis Acid Induced Ring-Opening. Inspiration for this approach was derived from observations by Rieger and Kuhn that limited quantities of methyl acrylate may be obtained from nickelalactone complexes by treatment with a large excess of methyl iodide (Figure 5).[11] In such systems it was proposed that electrophilic attack by methyl cation on the Ni−O bond cleaves the five-membered ring to assist *β*-hydride elimination, though the role of the iodide counteranion was also deemed significant. In order to gain insight into the *β*-hydride elimination reactivity of such transient three-coordinate nickel species, nickelalactone complex **A** was treated with the potent neutral Lewis acid tris(pentafluorophenyl)borane (BAr$^f_3$) at ambient temperature. When this reaction was monitored by NMR spectroscopy, immediate formation of a new nickel species was indicated by the appearance of two doublet resonances at 15.7 and 34.3 ppm in the ^{31}P NMR spectrum. The corresponding ^{1}H NMR spectrum revealed multiplet signals at 0.84 and 2.21 ppm in a 1:1 integration ratio. These resonances were identified as CH_2 units on the basis of ^{1}H−^{13}C HSQC NMR data and are consistent with formation of the Lewis acid activated metalalactone, complex **1** (Figure 6). The orange-colored solution containing complex **1** persisted for only 2−3 h at ambient temperature, after which complete conversion to a subsequent nickel species was observed. The final product, (dppf)Ni(CH(CH$_3$)CO$_2$BAr$^f_3$) (**2**), also exhibits two doublet resonances in the ^{31}P NMR spectrum, now at 22.4 and 36.2 ppm. The ^{1}H NMR spectrum again displays two intriguing resonances, an apparent doublet of doublets at 0.23 ppm and a complex multiplet at 2.03 ppm, in a 3:1 integration ratio. Upon ^{31}P decoupling of the ^{1}H NMR spectrum the resonance at 0.23 ppm collapsed to a doublet, indicating coupling constants of $J_{H,H}$ = 7.0 Hz and $J_{P,H}$ = 7.8 Hz. Likewise the multiplet at 2.03 ppm simplified to a quartet upon ^{31}P decoupling. The corresponding ^{1}H−^{13}C HSQC NMR spectrum indicates correlations between these ^{1}H NMR peaks at 0.23 and 2.03 ppm and respective ^{13}C NMR peaks at 12.36 and 34.58 ppm. The phase of the ^{1}H−^{13}C HSQC NMR correlations are the same as those attributed to methine positions of the dppf ligand.

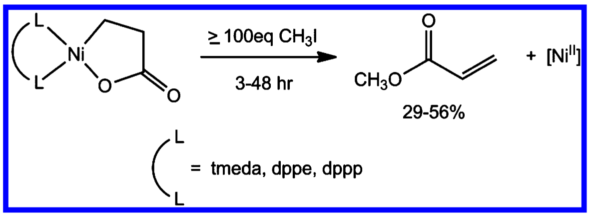


Figure 5. Methyl iodide induced elimination from nickelalactone complexes.

The NMR spectroscopic data are consistent with the presence of Ni-*α*-CH and Ni-*β*-CH$_3$ moieties in **2**. This assignment was confirmed by single-crystal X-ray diffraction experiments (Figure 7). The molecular structure of **2** exhibits a mildly distorted square planar geometry about the nickel, composed of two Ni−P bonds from the dppf ligand, a Ni−C linkage, and a close Ni−O interaction to the carbonyl. The data were of sufficient quality such that all hydrogens were located and refined from the Fourier map, establishing the C(2) unit as a methine and C(3) as a methyl. The Ni(1)−C(2) distance of 1.978(9) Å is comparable to numerous other reports of nickel−carbon bonds in metallacyclic carboxylates.[10,12] The Ni(1)−O(1) and C(1)−O(1) bond lengths of 1.905(4) and 1.27(1) Å, respectively, indicate a strong interaction between the carbonyl oxygen and nickel as well as a modest reduction of the C−O *π*-bond. Additionally, the Ni(1)−P(1) bond (2.237(2) Å) *trans* to the carbon ligand is slightly elongated compared to the Ni(1)−P(2) distance (2.135(2) Å) opposite the carbonyl oxygen ligand, consistent with the expected *trans* influence trend.

Significantly, the formation of **2** likely proceeds via *β*-hydride elimination from complex **1** to afford an unobserved nickel

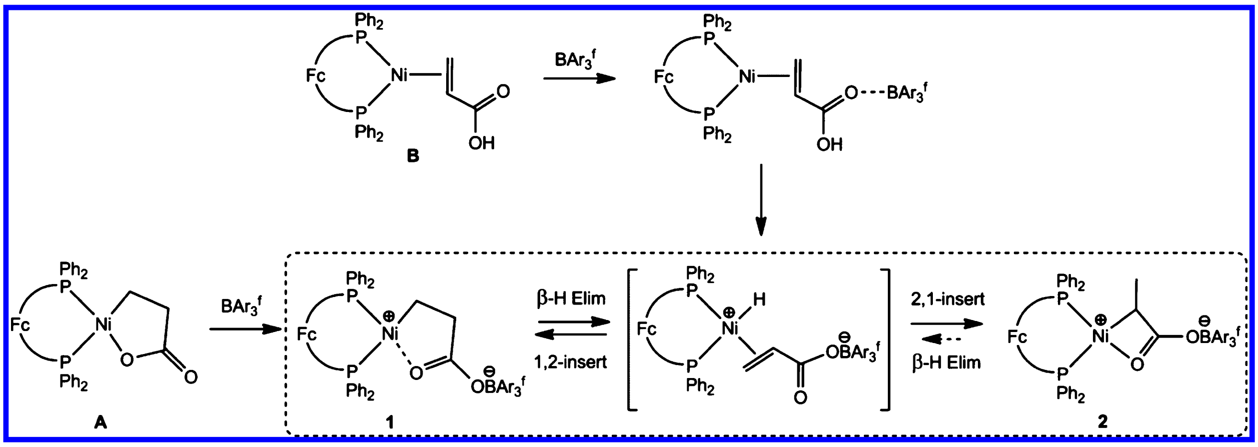


Figure 6. Pathways for formation of complex **2** and reversible *β*-hydride elimination.

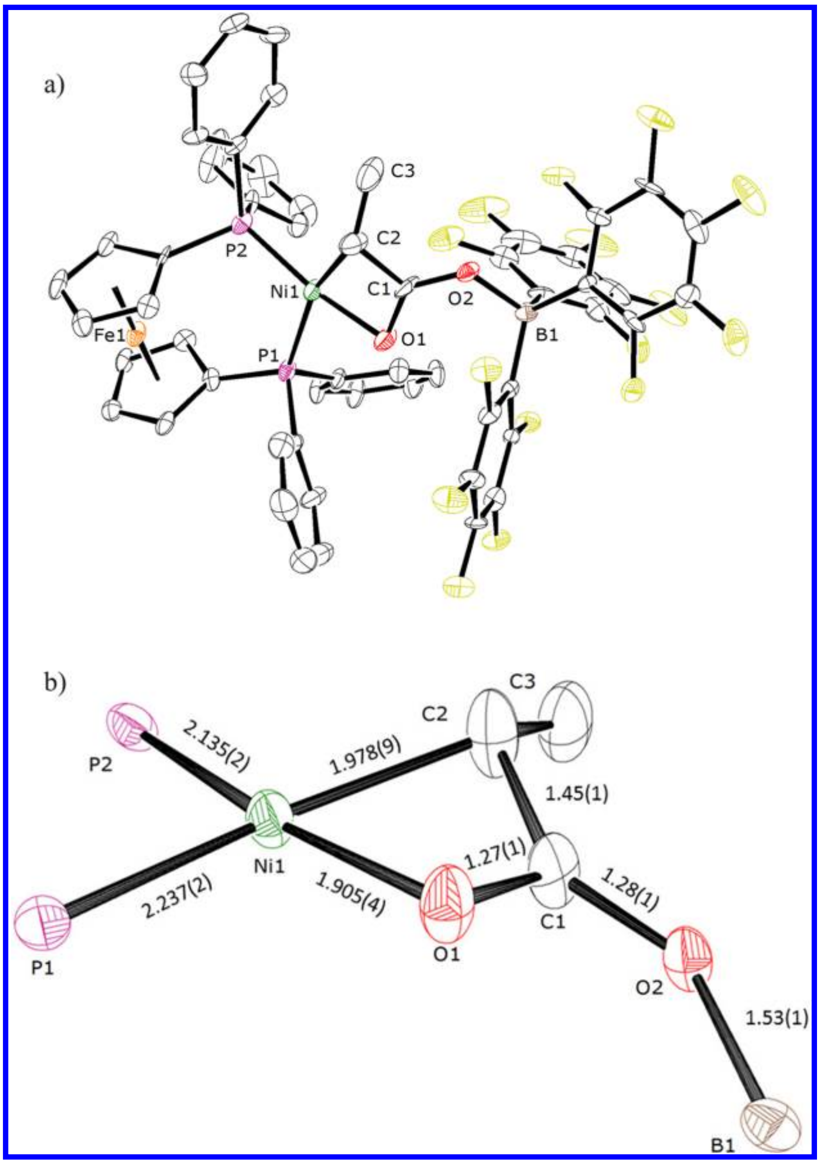
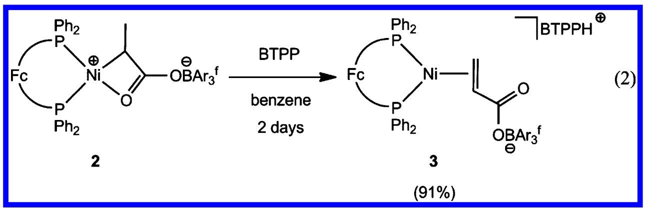


Figure 7. Molecular structure of (dppf)Ni(CH(CH$_3$)CO$_2$BAr$^f_3$) (**2**) with ellipsoids at 30% probability. All hydrogen atoms and a cocrystallized diethyl ether molecule are omitted for clarity. Full view (a) and nickel coordination core (b).

acrylate hydride intermediate (Figure 6). Subsequent 2,1-insertion of the acryl borate ligand would then produce the isolated compound **2**. Similar 2,1-insertions of acrylates into late transition metal hydrides have been observed by Brookhart and others.[16] This conversion of **A** to **2** provides a rare well-defined example of β-hydride elimination from a nickelalactone species and establishes the role of Lewis acids in promoting the transformation. Intriguingly, the ring-opened species **2** may alternatively be prepared by addition of BAr$^f_3$ to the η^2-acrylic acid complex, **B** (Figure 6). Treatment of a benzene-d_6 solution of **B** with 1 equiv of Lewis acid results in quick consumption of the starting material and formation of complexes **1** and **2** via a short-lived intermediate ($t_{1/2} \approx 15$ min). The intermediate was characterized only by NMR spectroscopy and features a pair of doublet peaks in the ^{31}P NMR spectrum at 23.42 and 33.42 ppm. The ^{19}F NMR resonances at −165.7, −160.2, and −134.8 ppm are significantly shifted from those of free BAr$^f_3$ and are comparable to those observed in **2**, suggesting the complex contains a coordinated BAr$^f_3$ unit. In addition, the observation of a broad peak at 8.45 ppm in the ^{1}H NMR spectrum, similar to the chemical shift of the −OH proton in **B**, suggests that this unstable intermediate is simply a borane adduct of the η^2-acrylic acid complex **B** (Figure 6). More significantly, Lewis acid addition to **B** produces complexes **1** and **2** *simultaneously*, with the mixture gradually shifting to solely **2** over 8 h. This contrasts the sequential formation of **1** then **2** observed in BAr$^f_3$ addition to **A**, indicating that these two synthetic reactions enter the equilibrium process at different intermediates (Figure 6). Our observations are most consistent with the reaction of **B** and BAr$^f_3$ affording the unobserved nickel(II) acrylate hydride species, which can then diverge to form complexes **1** and **2** with competitive rates of 1,2- and 2,1-insertion, respectively. Over time the reversible reaction equilibrates to the thermodynamically more stable 2,1-insertion product.[17]

Deprotonation of Complex 2. Having successfully induced β-hydride elimination from a stable nickelalactone species using a Lewis acid, experimental efforts were turned toward expelling acrylate from complex **2**. Unlike the nickelalactone species **A**, deprotonation of **2** by neutral organic bases proved an effective method of accessing acrylate. Use of the sterically hindered phosphazene base, BTPP, resulted in the formation of the η^2-acrylate complex **3** (eq 2),over two days at ambient temperature. Complex **3** exhibited limited solubility in hydrocarbon solvents, but proved modestly soluble in ethereal and halogenated solvents. The ^{1}H NMR spectrum of a chlorobenzene-d_5 solution of **3** displays resonances at 2.06, 3.16, and 3.49 ppm assigned as the vinylic protons of the bound olefin. The assignments were confirmed by ^{1}H−^{13}C HSQC NMR experiments, which indicate correlations to ^{13}C chemical shifts at 46.30 (CH_2) and 52.45 (CH) ppm. These resonances are analogous to those reported for the η^2-acrylic acid complex **B**.[12b] The ^{1}H NMR spectrum of **3** also exhibits the expected peaks for the conjugate acid of BTPP, including a broad N−H resonance at 4.75 ppm. The ^{31}P NMR spectrum completed the characterization with two doublets at 19.8 and 29.6 ppm assigned to the dppf ligand, as well as a singlet at 23.1 ppm from $[BTPPH]^+$. Addition of slightly weaker bases including DBU to complex **2** also promoted some acrylate formation, although in the case of this bicyclic amine, the η^2-acrylate complex was not formed as selectively. Addition of 1 equiv of DBU to complex **2** over two days produced a mixture of the free $[H_2C{=}CHCO_2BAr^f_3]^-[DBUH]^+$ salt,[18] a complex analogous to **3**, and some free dppf ligand.



The mechanism for deprotonation of complex **2** by nitrogen base has not been examined experimentally, but could well occur via β-hydride elimination to yield the unobserved nickel(II) acrylate hydride species, then proton abstraction by base. DuBois and co-workers have previously reported a pK_a value of 22.2 (acetonitrile) for a related nickel(II) hydride complex, suggesting a transient nickel(II) acrylate hydride species would be sufficiently acidic for deprotonation by amines.[19] Direct deprotonation of complex **2** cannot be eliminated completely, but seems less likely, as abstraction of the acidic α-C−H bond adjacent to the carbonyl would afford a nickel carbene species, which must then rearrange to produce the observed complex **3**. Alternatively, deprotonation of the less acidic β-C−H bond could directly yield complex **3**, but this proton would probably only be sufficiently acidic for amine deprotonation if activated by nickel via a β-agostic interaction. No such interaction is evident in the solid-state structure of **2** (Figure 7), making deprotonation of the unobserved nickel(II) acrylate hydride species the leading hypothesis.

The observed deprotonation of **2** with BTPP and DBU stands in contrast to the reactivity of nickelalactone **A**, which, similar to other diphosphine nickelacycles,[10] requires stronger bases to induce elimination. The role of Lewis acid in facilitating nickelalactone deprotonation by more mild bases is quite significant to the larger challenge of catalytic acrylate production from CO_2 and ethylene. As discussed above, several nickel compounds capable of coupling CO_2−ethylene into nickelalatone species at elevated pressures have been reported.[6,10] However, inducing elimination to produce acrylate in a fashion compatible with the presence of excess CO_2 has remained a persistent barrier. The ability to use more mild bases for acrylate liberation may enhance the viability of deprotonation techniques to overcome this barrier under high CO_2 pressure. Ideally, the use of CO_2-compatible bases such as carbonates in conjunction with mild Lewis acids or frustrated Lewis pairs could allow for a practical catalytic production of acrylate. Investigations toward this goal are still in progress in our laboratories, with some limited stoichiometric success in deprotonating complex **2** with cesium carbonate in tetrahydrofuran. However, these reactions produce low yields of free acryl borates salts (15−25% by NMR spectroscopy) over seven days at 50 °C.

Reactivity toward Ethylene and Carbon Dioxide. Having successfully induced acrylate formation from complex **2** by deprotonation using several bases, our focus shifted toward closing a hypothetical catalytic cycle (Figure 8) by coupling CO_2 and ethylene to re-form the nickelalactone species **A**. Though **A** is analogous to other nickelalactone complexes prepared directly by CO_2−ethylene coupling at zerovalent nickel, the dppf-substituted congener has not been prepared in this manner.[12b] Our initial studies into the regeneration of **A** treated complex **3** with 2 atm each of ethylene and CO_2, which resulted in immediate formation of the η^2-ethylene complex (dppf)Ni($CH_2{=}CH_2$) (**4**). After a further four days at ambient temperature, no evidence of formation of the nickelalactone **A** or other activation of CO_2 was observed by NMR spectroscopy. Heating the mixture at temperatures up to 100 °C resulted only in degradation of **4**. The ethylene complex **4** was characterized by multinuclear NMR spectroscopy and combustion analysis, as well as independent preparation by addition of ethylene to a mixture of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) and the dppf ligand (Figure 9).

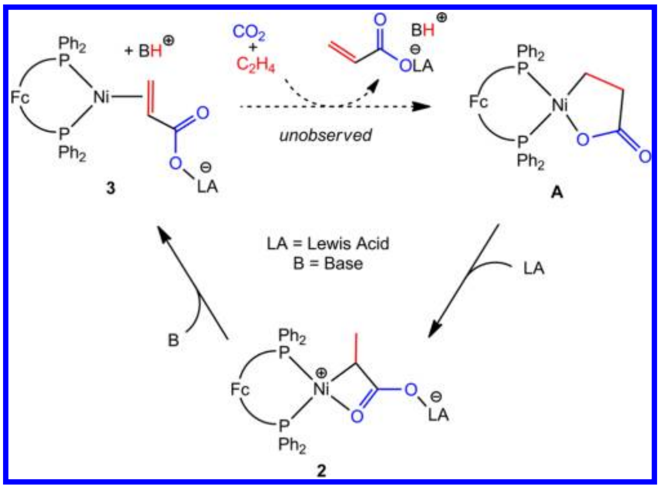


Figure 8. Hypothetical cycle for Lewis acid/base promoted coupling of CO_2 and ethylene to form acrylate.

Solutions of complex **4** are moderately stable (3−4 days) in arene solvent under N_2 or Ar atmospheres. The ^{31}P NMR spectrum of **4** in benzene-d_6 displays a singlet at 24.9 ppm, indicating a higher symmetry about the metal center than complex **3**. Along with other peaks from the dppf ligand, the ^{1}H NMR spectrum exhibits a slightly broadened resonance at 2.77 ppm, which correlates to a methylene ^{13}C chemical shift of 46.24 ppm in the ^{1}H−^{13}C HSQC NMR spectrum. These data and the ^{1}H NMR integration are consistent with a single bound

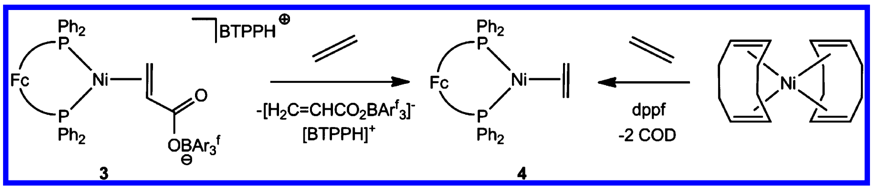


Figure 9. Synthetic pathways for the formation of complex **4**.

ethylene molecule, analogous to reports of several other diphosphine nickel(0) ethylene complexes.[10,12b,20]

The inability to produce the nickelalactone **A** from **3** in NMR tube experiments prompted further investigations at higher pressure, as multiple reports of CO_2−ethylene coupling at zerovalent nickel utilize pressures in excess of 20 bar.[6,10] For these larger scale experiments, isolated (dppf)Ni(COD) was used as the source of zerovalent nickel to better approximate procedures applied in previous nickelalactone syntheses.[5a,6,10] Unfortunately, a range of reaction conditions with pressures up to $p(CO_2)/p(C_2H_4)$ = 50 bar/13 bar at 57 °C for four days in tetrahydrofuran failed to produce any detectable quantities of **A** by NMR spectroscopy. Under these conditions, an approximate 2:1 ratio of complex **4** and $(dppf)_2Ni$ was observed for the organometallic nickel products following pressure release and extraction with dichloromethane. Although these high-pressure tests portend little promise for the dppf platform in nickel-catalyzed coupling of CO_2 and ethylene for acrylates, the technique of Lewis acid induced elimination from nickelalactones described here could well be applied to other ligand platforms better optimized for CO_2−ethylene coupling. Investigations into this application as well as the scope of viable Lewis acids for ring-opening and CO_2-compatible bases for acrylate extrusion are ongoing in our laboratories.

■ CONCLUDING REMARKS

The potential economic and sustainability advantages of producing acrylates by coupling CO_2 with ethylene at nickel have resulted in many independent investigations over the last three decades. However the vast majority of these studies have been frustrated by the inability of nickelalactone complexes to undergo β-hydride elimination. In this work, a Lewis acid, tris(pentafluorophenyl)borane, has been found to promote rapid β-hydride elimination from an isolable nickelalactone species, $(dppf)Ni(CH_2CH_2CO_2)$ (**A**), under ambient conditions. The reversible β-hydride elimination ultimately results in the formation of the thermodynamically stable 2,1-acryl borate insertion product $(dppf)Ni(CH(CH_3)CO_2BAr^f_3)$ (**2**). Interestingly, the Lewis acid activation renders **2** more facile toward deprotonation by external base than the starting nickelalactone species. Treatment of **2** with nitrogen-containing bases formed either a free acrylate salt or an η^2-acrylate coordination complex with the nickel. The coordinated borate-substituted acrylate may easily be substituted by ethylene, but the (dppf)Ni platform proved resistant to CO_2−ethylene coupling. Nevertheless, the ability to both ring-open the nickelalactone with a discrete Lewis acid and promote acrylate liberation with more mild bases provides a key step toward establishing a viable catalytic process that can withstand the high CO_2 pressure conditions typical of nickel-promoted couplings. In addition, demonstration of a sequential Lewis acid, base addition to enable acrylate liberation from a nickelalactone fosters consideration of cocatalysts, such as frustrated Lewis pairs, for promoting a functional catalytic system for CO_2−ethylene to acrylate at nickel and related metals.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques. Ethylene was purchased from Corp Brothers and stored over 4 Å molecular sieves in heavy-walled glass vessels prior to use. Argon and nitrogen were purchased from Corp Brothers and used as received. $(dppf)Ni(CH_2CH_2CO_2)$ (**A**) and $(dppf)Ni(CH_2{=}CHCO_2H)$ (**B**) were prepared according to literature procedures.[12b] All other chemicals were purchased from Aldrich, VWR, Strem, Fisher Scientific, or Cambridge Isotope Laboratories. Volatile, liquid chemicals were dried over 4 Å molecular sieves and distilled prior to use. Solvents were dried and deoxygenated using literature procedures.[21]

^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker DRX 400 Avance and 300 Avance MHz spectrometers. ^1H and ^{13}C chemical shifts are referenced to residual solvent signals; ^{19}F and ^{31}P chemical shifts are referenced to the external standards $C_6H_5CF_3$ and H_3PO_4, respectively. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.[22] Unless otherwise noted, all NMR spectra were recorded at 23 °C. IR spectra were recorded on a Jasco 4100 FTIR spectrometer. 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 non-hydrogen atoms. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ, or Atlantic Microlab, Inc., in Norcross, GA.

*Observation of $(dppf)Ni(CH_2CH_2CO_2B(C_6F_5)_3)$ (**1**).* A 20 mL scintillation vial was charged with 0.013 g (0.019 μmol) of $(dppf)Ni(CH_2CH_2CO_2)$ (**A**), 0.010 g (0.019 μmol) of $B(C_6F_5)_3$, and approximately 2 mL of CH_2Cl_2. The deep orange solution was stirred for 5 min, and the volatiles were removed under vacuum. The resulting solid was then dissolved in C_6D_6 for NMR study. Identical NMR spectra may be taken at 10 °C to slow the conversion of **1** to **2** for longer time scale experiments. ^1H NMR (C_6D_6): δ 0.84 (m, 2H, Ni-α-CH_2), 2.21 (m, 2H, Ni-β-CH_2), 3.36 (s, 2H, CpH), 3.62 (s, 2H, CpH), 3.72 (s, 2H, CpH), 4.12 (s, 2H, CpH), 6.98−7.67 (Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 15.7 (d, $^2J_{P,P}$ 15.8 Hz, 1P, PPh_2), 34.3 (d, $^2J_{P,P}$ 15.8 Hz, 1P, PPh_2). ^{19}F NMR (C_6D_6): δ −166.60 (t), −161.47 (t), −135.77 (d).

*$(dppf)Ni(CH(CH_3)(CO_2B(C_6F_5)_3)$ (**2**).* A 20 mL scintillation vial was charged with 0.096 g (0.142 μmol) of $(dppf)Ni(CH_2{=}CHCO_2H)$ (**B**), 0.073 g (0.143 μmol) of $B(C_6F_5)_3$, and approximately 5 mL of toluene. The orange solution was stirred for one day, and the volatiles were removed under vacuum. The resulting solid was washed with 2 mL of pentane, extracted with diethyl ether, and chilled at −35 °C to afford 128 mg (76%) of **2** as orange crystals. Anal. Calcd for $C_{55}H_{32}BF_{15}FeNiO_2P_2$: C, 55.18; H, 2.69. Found: C, 55.50; H, 2.67. ^1H NMR (C_6D_6): δ 0.23 (dd, $J_{H,H}$ 7.0 Hz, $J_{P,H}$ 7.8 Hz, 3H, Ni-β-CH_3), 2.03 (m, 1H, Ni-α-CH), 3.59 (s, 1H, CpH), 3.67 (s, 1H, CpH), 3.71 (s, 1H, CpH), 3.73 (s, 2H, CpH), 3.81 (s, 1H, CpH), 4.05 (s, 1H, CpH), 4.35 (s, 1H, CpH), 6.91−7.11 (m, 12H, Ph), 7.34−7.39 (m, 2H, Ph), 7.51−7.59 (m, 4H, Ph), 7.67−7.70 (m, 2H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 22.4 (d, $^2J_{P,P}$ 20.0 Hz, 1P, PPh_2), 36.2 (d, $^2J_{P,P}$ 20.0 Hz, 1P, PPh_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.36 (Ni-β-CH_3), 34.58 (Ni-α-CH), 73.36, 74.81, 75.04, 75.40, 76.18 (Cp), 128.66−129.15, 131.36, 133.03, 133.15, 133.85, 133.98, 133.12, 134.12, 134.24, 134.74,

134.86 (aryl) 181.20 (CO_2). ^{19}F NMR (C_6D_6): δ −166.60 (t), −161.02 (t), −135.37 (d). IR (KBr): $\nu_{C=O}$ = 1644 cm^{-1}.

[(dppf)Ni(η^2-CH_2=CH−$CO_2B(C_6F_5)_3$)][HBTPP] **(3)**. A 20 mL scintillation vial was charged with 0.035 g (0.029 μmol) of (dppf)Ni(CH(CH_3)($CO_2B(C_6F_5)_3$) (**2**), 9 μL (0.029 μmol) of BTPP, and approximately 1 mL of benzene. The solution was stirred for two days, resulting in precipitation of a yellow solid. The solid was collected by filtration to afford 40 mg (91%) of **3** as a yellow powder. The material may be extracted with THF if necessary to remove trace nickel metal particulates. Anal. Calcd for $C_{71}H_{65}BF_{15}FeNiN_4O_2P_3$: C, 56.49; H, 4.34; N, 3.71. Found: C, 55.96; H, 4.48; N, 3.51. ^1H NMR (C_6D_5Cl): δ 0.97 (s, 9H, N-C(CH_3)$_3$), 1.39 (s, 12H, N-β-CH_2), 2.06 (m, 1H, η^2-CH_2=CH), 2.70 (s, 12H, N-α-CH_2), 3.16 (m, 1H, η^2-CH_2=CH), 3.49 (m, 1H, η^2-CH_2=CH), 3.79 (s, 1H, CpH), 3.89 (s, 1H, CpH), 3.96 (m, 1H, CpH), 3.99 (s, 1H, CpH), 4.02 (s, 2H, CpH), 4.47 (s, 1H, CpH), 4.62 (s, 1H, CpH), 4.75 (br, 1H, NH) 6.92−7.24 (m, 12H, Ph), 7.56−7.99 (m, 8H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_5Cl): δ 19.8 (d, $^2J_{P,P}$ 22.8 Hz, 1P, PPh_2), 23.1 (s, 1P, [HBTPP]$^+$), 29.6 (d, $^2J_{P,P}$ 22.8 Hz, 1P, PPh_2). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 26.01 (N-β-CH_2), 30.93 (N-C(CH_3)$_3$), 46.30 (η^2-CH_2=CH), 47.40 (N-α-CH_2), 52.45 (η^2-CH_2=CH), 70.09, 70.44, 72.62, 73.03, 73.46, 74.78, 74.90 (Cp), 127.55, 131.50, 131.94, 133.47, 135.05, 136.03, 136.38, 147.80, 149.37 (aryl) three aryl signals not located, 178.33 (CO_2). ^{19}F NMR (C_6D_5Cl): δ −168.24(t), −164.42 (t), −134.00 (d). IR (KBr): $\nu_{C=O}$ = 1642 cm^{-1}.

(dppf)Ni(CH_2=CH_2) **(4)**. A 50 mL flask was charged with 0.095 g (0.345 μmol) of Ni(COD)$_2$, 0.180 g (0.325 μmol) of dppf, and approximately 7 mL of THF. The reaction mixture was stirred for 5 min and attached to a swivel filter frit, and the volatiles were removed under vacuum. On a vacuum line, approximately 7 mL of Et_2O was transferred into the flask, and 7 equiv of ethylene (1470 Torr in 28.9 mL) was added to the apparatus via a calibrated gas bulb at −196 °C. The resulting suspension was stirred at ambient temperature for 2 h. The reaction mixture was filtered through the swivel filter frit at −78 °C to yield 0.146 g (70%) of **4** as a yellow powder. Anal. Calcd for $C_{36}H_{32}FeNiP_2$: C, 67.44; H, 5.03. Found: C, 66.87; H, 5.26. ^1H NMR (C_6D_6): δ 2.77 (s, 4H, C_2H_4), 3.93 (s, 4H, CpH), 4.30 (s, 4H, CpH), 7.03−7.40 (m, 12H, Ph), 7.78−7.81 (m, 8H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): 24.9 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.24 (η^2-C_2H_4), 71.64, 74.87 (Cp), one Cp signal not located, 129.33, 134.61 (aryl), two aryl signals not located.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected NMR spectral data; crystallographic information file for complex **2**. These data are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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