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**CHEMICAL FIXATION OF CO₂ TO ACRYLATES USING LOW-VALENT
MOLYBDENUM SOURCES**

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ABSTRACT: The kinetic, mechanistic, and reactivity experiments to assess the viability and possible reaction design of coupling of carbon dioxide and ethylene at a zerovalent molybdenum for the production of acrylates are described. A general model of the reaction mechanism has been outlined, including assessment of the rate limiting step in the reaction. Kinetic and computational data have evaluated the influence of a range of tridentate ligand platforms on the rate of coupling. An *in situ* reduction and acrylate formation activity screen protocol has also been developed to aid in the technology development of this process. Portions of descriptions of the research products presented here have also been adapted with permission from journal publications.⁶

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EXECUTIVE SUMMARY

The objective of our collaborative proposal between Brown University and the Charles Stark Draper Laboratories is to assess the viability of catalytic carbon dioxide reduction with ethylene to produce acrylic acid using low-valent molybdenum sources. This and other breakthrough technologies in the catalytic fixation of carbon dioxide represent an opportunity to harness one of the world's most under-utilized resources while aiding mitigation of harmful greenhouse gas emissions. The primary barrier to these technologies is the low energy state of CO₂ which necessitates substantial energy investments in the fixation of carbon dioxide to many attractive fuels and chemicals. A promising strategy to circumvent these economic and thermodynamic limitations is the introduction of the necessary reduction potential in the form of ethylene to produce acrylic acid, a commodity with an existing market valued at over \$1 billion annually.

The potential environmental and economic advantages of producing acrylates from carbon dioxide and ethylene have spurred substantial research into catalysts to promote this transformation. Over the past 20+ years a select number of transition metal complexes have shown the ability to couple CO₂ and ethylene, with molybdenum complexes demonstrating particular promise by forming acrylate hydrides complexes. These complexes lack only reductive formation of an O-H bond to close the hypothesized catalytic cycle for acrylic acid synthesis. Disappointingly, elimination of free acrylic acid has yet to be observed for any complex capable of uniting CO₂/ethylene. Given the time span of research in this field, the absence of even stoichiometric examples of acrylic acid extrusion raises legitimate questions about the viability of this approach, despite computational evidence suggesting the process has a slight thermodynamic favorability. Our proposal moves beyond the exhaustive approach of random catalyst preparation and reactivity study and outlines a systematic evaluation of those factors/mechanisms which may impact the kinetics of reductive O-H elimination from acrylate hydride complexes in route to providing definitive assessment of the potential for acrylic acid production in this manner.

This report details the project's experimental and computational work to) expand the range of molybdenum complexes capable of coupling CO₂ and ethylene by defining the available ligand architectures which facilitate acrylate formation, 2) leverage computational and experimental mechanistic investigations to determine the catalyst coordination environment and reaction conditions necessary to enhance the catalytic limiting step, reductive acrylate elimination 3) design and prepare enhanced molybdenum or related transition metal catalyst targets acrylate formation from CO₂, 4) develop *in situ* methods for accessing low zerovalent ligand-transition metal species which are compatible with higher throughput screen of catalyst target activity for acrylate formation and do not require laborious isolation of all zerovalent species Our efforts to realize acrylate formation have been most successfully using [bis(diphenylphosphino)ethylphenylphosphine]molybdenum bis(dinitrogen) ethylene which can form acrylate from the desired coupling reaction. The pathway was modeled by kinetic analysis and low temperature

NMR to identify a key reaction intermediate whose structure was validated by computation. The observed rate constant of the acrylate formation was measured as $3.8(3) \times 10^{-5} \text{ s}^{-1}$ once both CO_2 and ethylene are bound at the metal. This corresponds to an activation energy of 23.5(2) kcal/mol. Kinetic analysis of the conversion of **I** to **D** revealed an isotope effect of 1.2(2) for functionalization with C_2H_4 v. C_2D_4 and activation parameters of $\Delta S^\ddagger = 1(7)$ eu and $\Delta H^\ddagger = 24(3)$ kcal/mol, consistent with rate limiting oxidative C-C bond formation during acrylate formation. These findings suggested the electrophilicity and coordination geometry of the metal center may dominate the facility of acrylate formation from carbon dioxide and ethylene, though attenuations for steric factors must also be made. Screening of ligand structure-reactivity relationship has shown the ligand geometry/size was the dominate of these two influences on reaction rate. To enable these studies, a protocol using sodium triethylborohydride to promote *in situ* reduction and test CO_2 utilization was created and used to screen a small library of potential catalyst platforms. Portions of descriptions of the research products presented here have also been adapted with permission from journal publications.⁶

REPORT DETAILS

Experimental Methods. All manipulations were carried out using standard vacuum, Schlenk, cannula or glovebox techniques. Ethylene and carbon dioxide were purchased from Corp Brothers and stored over 4 Å molecular sieves in heavy walled glass vessels prior to use. All other chemicals were purchased from Aldrich, VWR, Strem or Cambridge Isotope Laboratories and used as received. Solvents were dried and deoxygenated using previously described procedures.¹

^1H , ^{13}C , ^{31}P and ^{15}N NMR spectra were recorded on Bruker DRX 400 Avance and 300 Avance MHz spectrometers. ^1H and ^{13}C chemical shifts are referenced to residual protio solvent signals; ^{31}P chemical shifts are referenced to an external standard of H_3PO_4 . ^{15}N chemical shifts are referenced to an external standard of liquid ammonia. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.² IR spectra were recorded on Jasco 4100 FTIR and Metler Toledo React IR spectrometers. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ. For kinetic analyses a J. Young NMR tube was charged with 410 mg of a benzene- d_6 solution of **1** of known concentration (*ca* 0.03 M) and a capillary of triphenylphosphite in benzene- d_6 for use as an integration standard. Then 12 equiv of carbon dioxide were added via calibrated gas bulb at -196 °C. The reaction was thawed, shaken, and inserted into a temperature controlled NMR probe. The reaction progress was by ^{31}P NMR spectroscopy over greater than 2 half-lives beginning after all observable quantities of **I** had converted to **D**. The decay of the resonances for **I** were converted to concentration and fitted to first-order plot of $\ln [\text{I}]$ versus time, which gave observed rate constants as the slope.

Results and Discussion. Preparation of Supporting Ligands and Molybdenum Complexes. The synthesis of ligands **1-8** to support the tridentate and tetradentate zerovalent molybdenum complexes in this project were prepared using either a radical induced coupling approach or nucleophilic substitution as illustrated in Scheme 1. The radical induced coupling reactions were performed either neat or with small amounts of benzene solvent using catalytic quantities (~ 5 mol%) of AIBN and photolyzed for 1-2 days. Alternative nucleophilic substitution methods were employed using alkali metal phosphide reagents with the corresponding phosphine or amine ethyl halide precursors. Both of these approaches provided the necessary ligands in sufficient quantities to permit preparation of the trivalent molybdenum precursors. Treating tetrahydrofuran solutions of the respective ligands with molybdenum trichloride³ resulted in formation of the corresponding tri- or tetradentate molybdenum trichloride complexes **1-Cl₃ – 8-Cl₃** (Scheme 2). For complexes **1-Cl₃, 4-Cl₃, 5-Cl₃, 6-Cl₃, 7-Cl₃, and 8-Cl₃**, the products precipitated directly from tetrahydrofuran as yellow powders after stirring overnight. For trichloride complexes, **2-Cl₃** and **3-Cl₃**, addition of pentane and agitation forced the product from solution, again as a yellow powder. The trichloride products **1-Cl₃ - 8-Cl₃** are all relatively insoluble paramagnetic species, and were thus either characterized solely by combustion analysis or used directly as obtained from the above procedure. The target complexes for these tasks were prepared by sodium metal reduction of the corresponding trichloride precursor under atmospheres of dinitrogen or ethylene/dinitrogen mixtures (Scheme 3). The resulting zerovalent molybdenum bis(dinitrogen) and bis(dinitrogen) ethylene complexes (**1-N₄C₂H₄ - 8-N₄C₂H₄**) were isolated by extraction from the reduction mixtures using either toluene or tetrahydrofuran to afford yellow to yellow-green products. Optimized geometries computed for a representative selection of the zerovalent molybdenum complexes are illustrated in Scheme 4.

Mechanistic Investigation of CO₂-Ethylene Coupling to Acrylate at Triphos-Molybdenum. Tetrakis(phosphine) molybdenum and tungsten complexes have afforded some of the most promising results for producing acrylates from CO₂ and ethylene, however these functionalizations occur with concomitant loss of two ancillary ligands.¹⁷ This ligand extrusion process may be required to activate the molybdenum center for CO₂ binding, limit the stability of the complex, or permit dimerization of the acrylate hydride complex. To assess the potential effects of ligand loss on CO₂-ethylene coupling and provide a thermally robust support, a commercially available chelating ligand, (Ph₂PCH₂CH₂)₂PPh (Triphos), was employed to stabilize low-valent molybdenum species for CO₂ reduction. Although, previous findings have suggested problems for chelating ligands on molybdenum in CO₂-ethylene coupling reactions,⁴ with judicious selection of the other spectator ligands, there seems little reason why suitable (Triphos)Mo complexes for acrylate formation should not be feasible. To this end, our project has performed investigations into the preparation of low oxidation state (Triphos)Mo species bearing ethylene and weakly bound spectator ligands.

Synthetic efforts found alkali metal reduction of (Triphos)MoCl₃⁵ in the presence of excess dinitrogen and ethylene afforded a new zerovalent complex, *trans-*

(Triphos)Mo(N₂)₂(C₂H₄) (**1-N₄C₂H₄**), in good yield (Scheme 5). This bright yellow complex was characterized by infrared and multinuclear NMR spectroscopy and reactivity studies, details of which have been published.⁶

Numerous molybdenum(0) and tungsten(0) bis(dinitrogen) complexes have been prepared since Chatt's early work to utilize this motif in the reduction of N₂ to ammonia.⁷ Often these complexes are stabilized by four donating ligands such as phosphines or amines,⁸ although a few examples of related bis(dinitrogen) compounds bearing additional π -acid ligands, as in **1-N₄C₂H₄**, have been reported using olefins,⁹ CO,¹⁰ and additional N₂ ligands.¹¹ Complex **1-N₄C₂H₄** is a particularly attractive platform for studying the coupling of ethylene and carbon dioxide at zerovalent molybdenum as the chelating Triphos ligand should minimize complications arising from ancillary ligand loss and facile liberation of the dinitrogen ligands should allow ready use of carbon dioxide in the metal coordination sphere. Gratifyingly, the addition of a small excess of carbon dioxide (4 equiv) to **1-N₄C₂H₄** afforded a bridging acrylate hydride complex, [(Triphos)Mo(H)(CO₂CH=CH₂)₂] (**D**), over several hours at ambient temperature (Scheme 6). The ³¹P {¹H} NMR spectrum of **D** displays six signals, three appearing as well-resolved doublet of doublets and three as unresolved multiplets. The signals at 100.3, 92.8, and 81.0 ppm are slightly more intense (an approximate ratio of 1:1.3) than those at 96.0, 90.3, and 80.2 ppm. This data is consistent with the formation of two similar energy diastereomers, as may be expected for a dimeric complex formed from two seven coordinate metal centers.¹² Attempts to interconvert the two isomers by thermolysis at 85 °C resulted in decomposition prior to an observable change in isomer ratio. Although the ²J_{P-P} couplings were not well resolved for all ³¹P NMR signals, a maximum coupling constant of approximately 30 Hz determined from the peak widths discounts a rigorously *trans* orientation of any two phosphine ligands. The assignment of the isomers of **D** as dimolybdenum acrylate hydride complexes was further supported by the observation of two molybdenum-hydride resonances in the ¹H NMR spectrum at -6.73 and -7.15 ppm. Each metal-hydride is coupled to three inequivalent ³¹P nuclei, resulting in an eight line splitting pattern, with ²J_{P-H} constants ranging from 13.2 to 96.0 Hz.

Examination of the infrared spectrum for the isomers of complex **D** revealed a broad band at 1512 cm⁻¹, consistent with a bidentate carboxylate ligand.¹³ Employing ¹³CO₂ in the coupling reaction confirmed the origin of this IR band.¹⁴ Incorporation of ¹³CO₂ also resulted in two enhanced resonances at 189.9 and 192.3 ppm in the ¹³C {¹H} NMR spectrum. Additionally, the absence of ¹H NMR signals between 4.5 and 6.5 ppm suggests the acrylate olefins are bound to molybdenum. With the data in hand, distinction between the two coordination geometries in which the acrylate ligands bridge the two metal centers through the carboxylate fragment or through one oxygen atom and the olefin, could not be made. On the basis of computational data we believe the carboxylates are bridged in a fashion that leaves kappa-2 to a single Mo center.

The inability to obtain X-ray quality crystals of either isomer of **D** has, unfortunately, limited more detailed analysis of the coordination geometry about the molybdenum centers. Given this point of structural ambiguity, a reactivity study was used to confirm the identity of **D**

as a bridging acrylate molybdenum hydride complex. Treatment of **D** with triphenylphosphine resulted in immediate formation of the red monomeric acrylate hydride species, (Triphos)Mo(H)(PPh₃)(CO₂CH=CH₂) (**1-P**) which was unambiguously characterized by multinuclear NMR spectroscopy, X-ray diffraction and elemental analysis. Benzene-*d*₆ solutions of **1-P** exhibit ¹H NMR resonances at 4.68, 5.15, and 5.48 ppm assigned to an unbound acrylic olefin. These signals display coupling constants, splitting patterns, and chemical shift values quite similar to those observed for free acrylic acid. Additionally, a triplet of doublet of doublets is observed at -4.71 ppm establishing the presence of a molybdenum-hydride ligand. The ³¹P {¹H} NMR spectrum of **1-P** displays a doublet of doublets at 109.7 ppm for the two PPh₂ fragments and two doublet of triplets resonances at 47.7 and 99.4 ppm assigned to the PPh and PPh₃ groups, respectively. Solid state infrared analysis revealed a band at 1519 cm⁻¹, again consistent with a bidentate acrylate ligand.¹³

Complex **1-P** was also obtained by independent preparation from *trans*-(Triphos)Mo(N₂)₂(PPh₃) (**1-N₂P**) (Scheme 7).⁵ Treating benzene-*d*₆ solutions of the previously reported bis(dinitrogen) molybdenum(0) triphenylphosphine complex with equimolar excesses (6 equiv) of carbon dioxide and ethylene at ambient temperature overnight afforded ¹H and ³¹P {¹H} NMR spectra identical to those from PPh₃ addition to **D**. Most likely triphenylphosphine dissociation from *trans*-(Triphos)Mo(N₂)₂(PPh₃) provides access to a reactive (Triphos)Mo⁰ center analogous to reactive intermediates in the reduction of CO₂ with complex **1-N₄C₂H₄**. However, the qualitatively slower acrylate formation and the presence of minor amounts of free Ph₃P formed during the reaction render CO₂-ethylene coupling from *trans*-(Triphos)Mo(N₂)₂(PPh₃) somewhat less attractive for study than CO₂ addition to **1-N₄C₂H₄**. Finally, complete confirmation of the structure of **1-P** was obtained by single crystal X-ray diffraction was illustrated in Scheme 8.

The facile reductive functionalization of carbon dioxide to acrylates is a relatively rare transformation dominated by a small family of related zerovalent molybdenum and tungsten complexes.¹⁷ The pathway for the formation of acrylate from complex **1-N₄C₂H₄** likely bears a strong resemblance to the reactivity of those molybdenum mediated functionalizations reported or inspired by Carmona.¹⁷ However, no experiments to probe the mechanism or kinetics of this intriguing molybdenum promoted CO₂-ethylene coupling have been reported. Qualitatively, acrylate formation from complex **1-N₄C₂H₄** upon CO₂ addition appears slower than the previously described tetrakis(phosphine) molybdenum bis(ethylene) complexes. The reported synthetic procedures indicate modest yields of those acrylate complexes may be obtained in a matter of minutes with low pressures of CO₂ for the monodenate phosphine (or phosphate) molybdenum ethylene complexes,¹⁷ while **1-N₄C₂H₄** requires many hours under similar conditions. Understanding the origins of this slower CO₂-ethylene coupling requires elucidation of the reaction mechanism and identification of the rate influencing event. This motivation, along with an interest in designing complexes to enhance acrylate preparation lead to examination of the pathway for acrylate formation.

Monitoring the addition of approximately 12 equivalents CO₂ to a benzene-*d*₆ solution of the bis(dinitrogen) molybdenum(0) ethylene complex *in situ* by NMR spectroscopy revealed the formation of a long-lived reaction intermediate characterized as (Triphos)Mo(C₂H₄)(CO₂) (**I**) (Scheme 9). Interestingly, this species was also observed as an intermediate in the formation of the triphenylphosphine acrylate hydride complex **1-P** from CO₂ and ethylene addition to *trans*-(Triphos)Mo(N₂)₂(PPh₃). Complex **I** formed rapidly from **1-N₄C₂H₄** in the presence of excess CO₂ (~15 minutes) and converted slowly to the acrylate hydride species **D** over several hours. The molybdenum(0) carbon dioxide ethylene complex exhibited a doublet resonance at 64.7 ppm and a triplet resonance at 95.3 ppm (²J_{P-P} = 6.1 Hz) in the ³¹P {¹H} NMR spectrum which were assigned to the PPh₂ and PPh fragments, respectively. The ¹H NMR spectrum displayed a broad resonance at 0.21 ppm, attributed to the protons on the bound ethylene. This assignment was again confirmed by deuterium labeling with the preparation of (Triphos)Mo(C₂D₄)(CO₂) (**I-d₄**). The broad signal at 0.21 correlates to a single ¹³C NMR chemical shift of 41.6 ppm in the ¹H-¹³C HSQC NMR spectrum. Cooling the sample to -20 °C did not decoalesce this signal (limited solubility of complex **D** at lower temperatures prohibited further variable temperature study) suggesting that the interchange of the two ethylene CH₂ units is either a low energy process or that the ethylene binds in a symmetrically disposed position coplanar with the Triphos ligand. The ¹H and ¹³C chemical shifts for the bound ethylene ligand are similar to those reported for a range of six-coordinate molybdenum ethylene complexes,^{8, c} with the proton signal in **D** shifted slightly upfield (~0.5 ppm) relative to the coordinatively saturated analogues. This small perturbation in the chemical shift may arise from enhanced reduction of the C=C bond in the Dewar-Chatt-Duncanson model¹⁵ or the variation in metal coordination number.¹⁶

Further spectral analysis of the reaction intermediate was obtained by preparation of (Triphos)Mo(C₂H₄)(¹³CO₂) (**I-¹³C**) from addition of excess ¹³CO₂ to **1-N₄C₂H₄**. Incorporation of the ¹³C label resulted in an enhanced doublet of triplets signal at 193.6 ppm in the ¹³C NMR spectrum with coupling constants of 14.9 and 27.7 Hz (Figure 4). The magnitude of this coupling is similar to the ²J_{C-P} = 17.5 Hz coupling reported for *trans*-(PMe₃)₄Mo(¹³CO₂)₂,¹⁷ and significantly greater than the ³J_{C-P} < 6 Hz couplings reported for more commonly isolated metallalactone complexes.¹⁸ The labeling experiment also alters the ³¹P {¹H} NMR spectrum, with **I-¹³C** splitting the two signals into a doublet of triplets (PPh) and a doublet of doublets (PPh₂) indicating only one ¹³CO₂ molecule is incorporated into the intermediate (Scheme 10). Infrared spectroscopy confirms the presence of a C=O fragment with a band at 1700 cm⁻¹ for **I** in KBr, which shifts to 1654 cm⁻¹ for **I-¹³C**, though the IR bands for transition metal carbon dioxide complexes and metallalactones do not have characteristically distinguishing frequencies.¹⁷ Notably, no strong bands were observed for either isotopologue of **I** from 2200-1800 cm⁻¹, suggesting both dinitrogen ligands of **1-N₄C₂H₄** dissociate when binding carbon dioxide. The observation of a pseudo-five coordinate molybdenum(0) complex was unexpected, given that **I** may be observed in the presence of additional carbon dioxide, ethylene, dinitrogen, and triphenylphosphine. However no spectroscopy signals indicative of a bound sixth ligand were observed, and the use of relatively non-coordinating solvent (benzene) tentatively supports

assignment of the coordinatively unsaturated intermediate.¹⁶ The overall structural assignment of **I** was further supported by computational analysis which indicated this intermediate was a reasonable local minimum on the potential energy surface (Scheme 11).

The mechanism of carbon dioxide substitution with **1-N₄C₂H₄** was briefly explored using a series of parallel NMR tube experiments. The coordinative saturation of complex **1-N₄C₂H₄** implies that the substitution process to form **I** is dissociative in nature,¹⁹ however, the concentration of CO₂ or N₂ may influence the reaction rate if ligand dissociation is reversible. Parallel experiments with stock solutions of **1-N₄C₂H₄** were used to investigate these possibilities as this technique reduces complications from gases mixing into solution. To assess the influence of CO₂ on the formation of **I**, two degassed samples of **1-N₄C₂H₄** in benzene-*d*₆ were treated with 4 and 12 equiv of CO₂ by calibrated gas bulb at -196 °C. After warming to ambient temperature for 10 minutes, a 36% greater conversion to **I** (average of 3 trials) was observed by ³¹P {¹H} NMR spectroscopy for the samples containing additional carbon dioxide. Likewise, parallel tube experiments with added dinitrogen in addition to carbon dioxide exhibit lower conversions to **I** in the presence of N₂.²⁰ More significantly, upon formation of complex **I**, removal of excess CO₂ and introduction of a dinitrogen atmosphere at ambient temperature did not result in reversion to **1-N₄C₂H₄** prior to formation of the acrylate hydride species **D**. These experiments are consistent with formation of intermediate **I** by reversible dinitrogen loss from **1-N₄C₂H₄** followed by slow, effectively irreversible, binding of carbon dioxide with loss of a second N₂ ligand.

The observation of **I** en route to the bridging acrylate molybdenum hydride complex experimentally verifies that simultaneous coordination of both ethylene and carbon dioxide is a prerequisite for coupling at early transition centers. The requirement of substrate pre-coordination for transition metal mediated metallalactone or acrylate formation is an area which has been investigated computationally for many years with inconsistent conclusions.^{21,22} Early calculations by Dedieu^{21a} and others^{21d,e} concluded that nickelalactone formation precedes without coordination of ethylene, instead occurring via nucleophilic attack by incoming C₂H₄ on a bound carbon dioxide ligand. Later, Sakaki^{21b,c} and coworkers supported CO₂-ethylene coupling at similar nickel(0) complexes with prerequisite coordination of both substrates. More recently, Schubert and Pápai have investigated the coupling of carbon dioxide to (PMe₃)₄Mo(C₂H₄)₂ with DFT calculations and supported the argument that the C-C bond forming event occurs with a metal centered transition structure.²² The characterization of the carbon dioxide ethylene complex **I** provides the first direct evidence that pre-coordination of the two unsaturates lies on the path to C-C bond formation between CO₂ and ethylene, and while its implications may be less strong for nickel, the requirement is likely general for early transition metals centers investigated to date.

The preparation of intermediate complex **I** also serves as an instrument to further study the kinetics and mechanism of molybdenum mediated acrylate formation from CO₂ and ethylene. Due to the acceleration in the formation of **I** with added CO₂, solutions of

(Triphos)Mo(C₂H₄)(CO₂) could be generated cleanly prior to substantial formation of the bridging acrylate hydride species by treatment of **I** with 12 equiv of CO₂.²³ Monitoring the decay of the signal for complex **I** versus an internal standard in the ¹P {¹H} NMR spectrum at 23 °C afforded an observed rate constant of 3.8(3) × 10⁻⁵ s⁻¹ for acrylate formation. This corresponds to an activation energy of 23.5(2) kcal/mol. As expected, control experiments varying the equivalents of added CO₂ did not alter the conversion rate of **I** to **D**. Previous computational studies of acrylate formation from (PMe₃)₄Mo(C₂H₄)₂,²² as well as the experimental observation of numerous metallalactones,^{24,25} suggest the formation of **2** proceeds from complex **I** by formally oxidative C-C bond formation between bound CO₂ and ethylene,²⁶ followed by β-hydride elimination from the resulting metallocycle, and finally a dimerization of the Triphos molybdenum acrylate hydride complex. Unfortunately, the DFT analysis could not distinguish the rate limiting step of acrylate formation from (PMe₃)₄Mo(C₂H₄)₂ and CO₂ as the computed barriers of several steps were quite similar in energy.²² Given the importance of determining the rate limiting step for rationally optimizing metal complexes for CO₂-ethylene coupling, we proceeded to further probe the kinetics of acrylate formation.

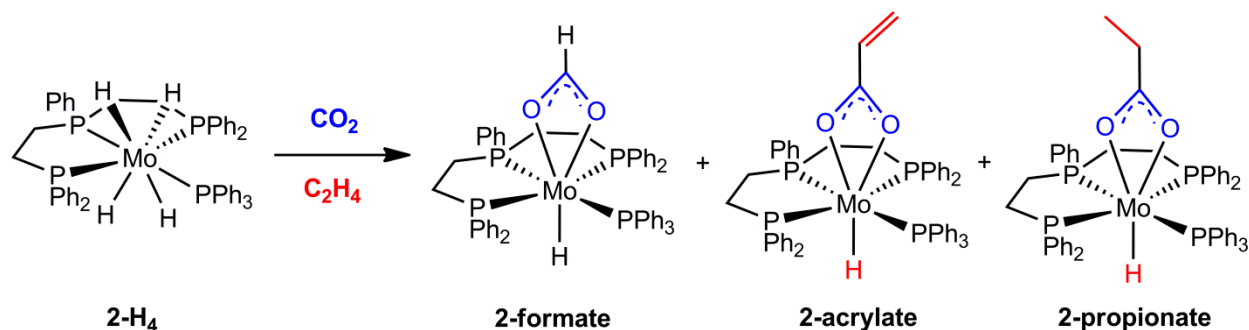
The modest stability of **I** as an intermediate during carbon dioxide reduction, along with the absence of any other detectable intermediates during formation of **D**, implicates two likely kinetic profiles for acrylate production. In one case complex **I** is favored in a rapid equilibrium with the metallalactone species followed by rate limiting β-hydride elimination and fast dimerization to afford **D**. An alternative kinetic profile is rate limiting oxidative C-C bond coupling from **I** followed by rapid β-hydride elimination and dimerization.²⁷ An isotope effect experiment was employed to differentiate between these two reaction profiles by comparing the rates of acrylate formation from **I** and **I-d₄**. Incorporation of deuterium into the bound ethylene produced only a minimal decrease in the observed rate constant, affording an isotope effect of 1.2(2) at 23 °C. This small isotope effect is inconsistent with a rate limiting β-hydride elimination from a metallacyclic complex which is expected to produce a significant primary isotope effect.²⁸

The activation parameters for acrylate formation from complex **I** were also examined by measuring the observed rate constant for the reaction over a 40 °C temperature range. The effect of temperature on the rate of molybdenum acrylate hydride formation was plotted. From the Eyring plot an activation entropy (ΔS[‡]) of 1(7) eu and an activation enthalpy (ΔH[‡]) of 24(3) kcal/mol were computed. The near zero ΔS[‡] implicates a unimolecular transition structure for the rate limiting event, which along with the small isotope effect for *k*_{C₂H₄}/*k*_{C₂D₄}, is consistent with oxidative C-C bond formation as the slow step in acrylate formation. Rate limiting C-C bond formation for CO₂-ethylene coupling was unanticipated given that related coupling reactions outside group VI transition metals are arrested at metallalactone structures with β-hydride elimination pathways often unobserved. Together these mechanistic experiments are consistent with a model for the reaction which is depicted in Scheme 12.

Our findings suggested that efforts to engender electron rich early transition metal centers may enhance the rate of acrylate formation, though possible interference from sterically large ligands needs to be considered. Clearly other features of the metal coordination environment may also impact the facility of acrylate production from CO₂ and ethylene. These include the ability to bind carbon dioxide and ethylene in a *cis* orientation, the availability of a vacant coordination site to ensure rapid β-hydride elimination from the metallacycle,²⁹ and the chelation mode of the ancillary ligand. Given these observations and the evident need to prepare complexes with more varied ligand platforms lead our team to pursue a rapid in-situ method to reduce molybdenum complexes and test them for acrylate formation activity.

Methods for In-Situ Reduction and Screening of Acrylate Reduction Activity. Most synthetic routes to low valent molybdenum- and tungsten-phosphine complexes used in CO₂ reduction reactions apply alkali metals sources (*e.g.* sodium amalgam, potassium graphite) to metal chloride precursors in the presence of modest stabilizing ligands (*e.g.* dinitrogen, phosphine).³⁰ Homogenous hydride reducing agents offer a relatively mild and convenient alternative to accessing lower valent metals, either by direct reduction of a metal halide precursor or reductive elimination from intermediate metal-hydride species.³¹ Treatment of a tetrahydrofuran suspension of (Triphos)MoCl₃ (**1-Cl₃**) with two equivalents of NaEt₃BH in the presence of triphenylphosphine rapidly afforded a molybdenum(II) species, (Triphos)Mo(H)Cl(PPh₃) as a deep green solid in excellent yield. This complex has proven a useful synthetic precursor to several new molybdenum species relevant to our studies in CO₂ functionalization, but without the sodium amalgam reductions employed previously.^{6,30b}

The molybdenum(II) hydrido chloride species provided more convenient access to **1-N₄C₂H₄** for CO₂-ethylene coupling reactions, but also proved a mere intermediate in the overall process to achieve zero-valent molybdenum for CO₂ utilization. To induce further reactivity, the remaining chloride ligand was substituted for hydride using one equivalent of NaEt₃BH (3 in total with H₂) to give (Triphos)MoH₄PPh₃ as a yellow solid. The molybdenum(IV) tetrahydride complexes isolated was treated with 1 atm of a 5:1 ethylene to carbon dioxide mixture produced what initially appeared an intractable mixture of products. However, subsequent experiments which altered the ratio and sequence of ethylene and carbon dioxide addition permitted isolation of (Triphos)Mo(H)(κ²-CHO₂)(PPh₃) (**1-formate**), (Triphos)Mo(H)(κ²-C₃H₅O₂)(PPh₃) (**1-propionate**), and **1-P**, three distinct CO₂ activation products (Scheme 13). While applying a 5:1 ethylene to carbon dioxide mixture to (Triphos)MoH₄PPh₃



produced **1-formate** as the major product of CO₂ functionalization, increasing the carbon dioxide fraction to a 1:1 mixture gave virtually quantitative formation of the molybdenum(II) formate hydride species as judged by NMR spectroscopy. On preparative scales experiments, **1-formate** was isolated in good yield by treating (Triphos)MoH₄PPh₃ with an atmosphere of pure CO₂ over 2 hours.

Complex **1-formate** was obtained as a red powder and characterized by NMR and IR spectroscopy, isotopic labeling, and elemental analysis. The ¹H and ³¹P {¹H} NMR spectra of **1-formate** bear several similarities to those reported for **1-P** including a Mo-H signal at -4.74 ppm and three phosphorus resonances at 122.6, 103.5 and 50.1 ppm. The ¹H NMR spectrum also exhibited a signal at 7.11 ppm originating from the formate hydrogen. Its identity was confirmed by ¹³CO₂ isotopic labeling which resulted in enhanced coupling. The ¹H NMR signal and growth in a resonance at 169.13 ppm in the ¹³C {¹H} NMR spectrum. ¹³C-labeling also altered the solid state infrared spectrum, red shifting bands at 1550 and 1362 cm⁻¹ for **1-formate** down to 1511 and 1340 cm⁻¹ for the labeled isotopologue.

The insertion of carbon dioxide into transition metal-hydride bonds is a key step in the hydrogenation of CO₂ to formate and has previously been observed for other molybdenum complexes.³² Recent advances in the catalytic hydrogenation of carbon dioxide under basic conditions at late transition metals have enhanced the potential of CO₂ hydrogenation as an energy carrier for molecular hydrogen and an input for carbon fuel cells.³³ The insertion of carbon dioxide into (Triphos)MoH₄PPh₃ occurred with loss of dihydrogen (detected by ¹H NMR spectroscopy) and no evidence of organic formate products. Elegant work by Harzari and others contend that CO₂ insertion into a metal-hydride may occur without pre-coordination of the heterocumulene.³⁴ Thus it is reasonable to consider the direct insertion of CO₂ into 18-electron (Triphos)MoH₄PPh₃, followed by reductive H₂ elimination as a possible route to **1-formate**. However, monitoring the conversion of (Triphos)MoH₄PPh₃ to **1-formate** over a range of CO₂ pressures showed no influence on the observed rate constant of the reaction. The persistent 2.9(2) × 10⁻⁴ s⁻¹ (25 °C) rate constant indicates that incorporation of CO₂ occurs after the rate limiting step, suggesting that elimination of dihydrogen precedes CO₂ insertion in this case.³⁵

Completing the characterization of **1-formate** shifted our focus toward selective synthesis of the CO₂ functionalization products which incorporated ethylene, **1-propionate** and **1-P**. The formation of **1-formate**, **1-propionate**, and **1-P** in the same reaction suggested that at

least two distinct CO₂ reduction pathways from (Triphos)MoH₄PPh₃ were competitive. Divergence between the formate and acrylate/propionate production routes could be influenced by the relative rates of (Triphos)MoH₄PPh₃ (or species derived from (Triphos)MoH₄PPh₃) reacting with carbon dioxide versus ethylene. However observation that addition of a 5:1 ethylene to carbon dioxide mixture to (Triphos)MoH₄PPh₃ still afforded **1-formate** as the major product prompted sequential addition of ethylene and carbon dioxide instead of experiments which further altered the ratio of gases.

Treatment of (Triphos)MoH₄PPh₃ with 1 atm of ethylene for 5 hours followed by addition of 0.1 atm of CO₂ and stirring for a further 14 hours afforded an approximately 7:1 of **1-propionate** and **1-P** with no detectable formation of **1-formate**. The previously reported characterization data for **1-acrylate** were used to differentiate the signals corresponding to **1-propionate**.⁶ Many of the NMR signals for **1-propionate** closely resemble those of **1-P**, including ³¹P {¹H} NMR resonances at 110.9, 101.5, and 48.2 ppm and a Mo-H peak centered at -4.70 ppm in the ¹H NMR spectrum. The proton spectrum also revealed broad triplet and quartet signals at 0.47 and 1.10 ppm, respectively, assigned to the ethyl moiety of the propionate ligand. The assignments were confirmed by ¹H-¹³C HSQC NMR spectroscopy which exhibited correlations to methyl and methylene resonances at 8.85 and 30.43 in the ¹³C NMR spectrum. ¹³CO₂ isotopic labeling induced additional coupling in the propionate methyl signal in the ¹H NMR spectrum, confirming coupling of the saturated ethylene and ¹³CO₂. Observation of J_{C-H} coupling was expected for the methylene signal as well, but was not clearly resolved due to the broad peak width and overlap with residual solvent. ¹³CO₂ labeling also enhanced a peak at 182.68 ppm in the ¹³C {¹H} NMR spectrum. Additionally, bands at 1514 and 1445 cm⁻¹ in the infrared spectrum of **1-propionate** red shifted to 1486 and 1414 cm⁻¹ upon ¹³C labeling.

The origin of **1-propionate** was initially hypothesized as CO₂ insertion into a transient molybdenum ethyl complex, but subsequent observations suggested that the complex more likely derives from hydrogenation of **1-P**. Repeated syntheses of the **1-propionate** and **1-P** mixture were found to increasingly favor **1-propionate** at the expense of **1-P** over longer time courses. This is consistent with **1-P** serving as an intermediate to **1-propionate**. Additionally, previous reports of CO₂ insertion indicate that the rates of reactivity with metal-hydrides outpace those of metal-alkyls in carboxylate formation.^{34b,36} Given the near certain presence of molybdenum hydride species during this synthesis, it was deemed unlikely that CO₂ insertion into a molybdenum-ethyl would be sufficiently rapid to preclude formate formation. The origin of **1-propionate** was confirmed by addition of dihydrogen to the **1-propionate** and **1-P** mixture which completed the conversion to **1-propionate**. Identical observations were made upon addition of an atmosphere of dihydrogen to isolated samples of **1-P**. During CO₂ functionalization reactions, the dihydrogen probably originates from **2-H₄** reductive elimination. This is supported by observation that **2-propionate** formation was suppressed when the head space of the reaction vessel was evacuated between the ethylene and carbon dioxide additions.³⁷

In situ monitoring of the reaction by NMR spectroscopy was continued following addition of an atmosphere of CO₂ to the **1-N₄C₂H₄** solution. After 30 minutes the resonances of

1-N₄C₂H₄ had completely disappeared from ³¹P {¹H} NMR spectrum, and were replaced by minor amounts of **1-propionate** and **1-P** along with more significant doublet and triplet signals at 64.9 and 95.5ppm, respectively. These resonances match those previously reported for **I**, a transient intermediate observed in kinetic studies of CO₂-ethylene coupling to acrylate.⁶ Over the next 8 hours the ³¹P NMR resonances of **1-propionate** and **1-P** continued to grow at the expense of TriphosMo(CO₂)(C₂H₄). Over the first 2 hours following CO₂ addition, **1-P** was observed as the major CO₂ functionalization product. However over longer time courses, **1-propionate** became the major product while the resonances for **1-P** diminished. After 12 hours, all TriphosMo(CO₂)(C₂H₄) was consumed, leaving approximate 1:3 ratio of **1-P** to **1-propionate**. The lack of complete hydrogenation of **1-P** may originate from loss of H₂ into the reaction head space or through ethylene hydrogenation. These observations create a partial description of the reaction sequence for CO₂ functionalization with ethylene from (Triphos)MoH₄PPh₃. Our laboratory is currently engaged in studies to transfer this reaction pathway to a broader array of substrates for CO₂-olefin coupling and examine the prospect for catalytic versions of these reactions. Additionally, this proved ideal to apply the *in situ* NaEt₃BH reduction procedure in pursuing a wider survey of ligand-Mo architectures for CO₂ functionalization without the restriction of isolating suitable zerovalent metal complexes.

Screening of Ligand Platforms for Acrylate Formation Activity. Examination into the role of the ancillary Triphos ligand on CO₂ functionalization began by preparation of a family of related tridentate ligands described in Scheme 1. For synthetic convenience the aryl substituents on the terminal phosphines were selected for attenuation and the ligands prepared via radical or base catalyzed coupling of divinylphenylphosphine and the corresponding diarylphosphine, though several other ligand variations which were easily accessible we also investigated. In each case the ligand-molybdenum trichloride complexes was reduced by sodium triethylborohydride and treated sequentially with ethylene and carbon dioxide. The assessment of acrylate formation activity was performed by NMR spectroscopy. As a matter of practical ease, the screening was performed in the presence of triphenylphosphine which provided a more stable and easily characterized acrylate product. The results of the ligand screening are illustrated in Table 1. These data show that the tridentate ligands are the superior platform (among those tested) for coupling CO₂ and ethylene into acrylate. Given this, we also explored a range of the tridentate promoters to further elucidate the effect of the ancillary ligand. The results of this survey are found in Scheme 13. The most obvious trend in this data is the steric effects dominate over electronic impact with the reaction favoring smaller ligand substituents. A mild electron electron effect can be noted between the phenyl and para-fluorophenyl congeners which suggest a weak preference for more donating ligands.

Ultimately, the catalytic performance of these and related molybdenum promoters will necessitate the reductive extrusion of acrylate (Scheme 14). Our computational work and experiment estimates of the pK_a of the Mo-H bond versus the acrylic acid suggest that direct thermal reductive elimination is not a viable option under temperatures where the catalyst target will persist. Alternatively we have used basic additives with **1-P** to slant the thermodynamics of

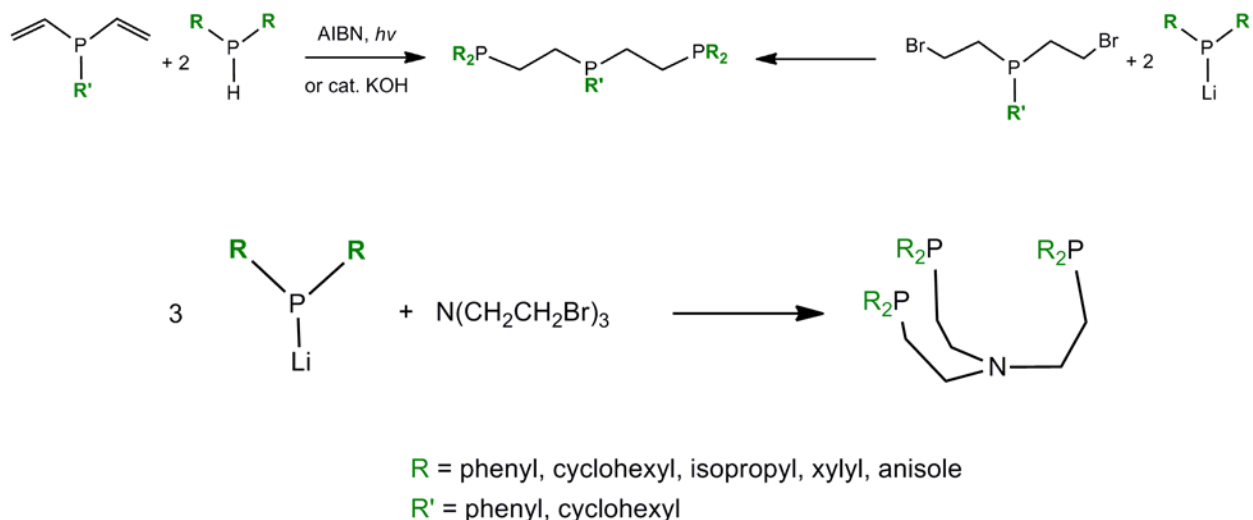
the acrylate in favor of extrusion from the metal. This approach has been highlighted by the successful reductive elimination acrylate using lithium bis(trimethylsilyl)amide, sodium t-butoxide and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene. The primary issues in making these eliminations reaction part of a batch catalytic process is that the strong ionic bases have a highly competitive side reaction with carbon dioxide to yield carbonates, and that the pendant N-H bond in 1,5,7-Triazabicyclo[4.4.0]dec-5-ene can be oxidatively added to the resulting zerovalent molybdenum, deactivating it of coupling. More recently, our work has also found that carbon monoxide can induce reductive acrylate elimination, and give a molybdenum carbonyl complex. It is quite possible that under photocatalytic conditions, this carbonyl species could be reactivated for a repeatable process for forming acrylate, though a this development is beyond the scope of this project. These methods, though imperfect for a batch reactor process, do however demonstrate that a two phase catalytic process in which the coupling and acrylate extrusion reactions are separated could be a viable way to produce acrylate from CO₂ and ethylene.

Conclusion. Overall this study made remarkable progress in accessing the viability of CO₂-ethylene coupling as an alternative process for acrylate synthesis. It is clear that molybdenum complexes are great promoters of the ethylene-CO₂ coupling process, with a strong preference for ligand platforms with smaller substituents and more electron donating groups. The mechanism for the coupling appears to be limited in rate by the C-C bond forming step of the reaction. In the current family of catalyst targets elucidated in this study, the kinetics are insufficient to produce acrylate on a production scale; however, the development of a higher throughput screening system enabled by this project will dramatically speed identification and optimization of new catalyst targets. The exploration of this ligand landscape for improving the acrylate formation reaction at molybdenum should now be reasonably straightforward using the *in situ* reduction and CO₂ activation process developed here.

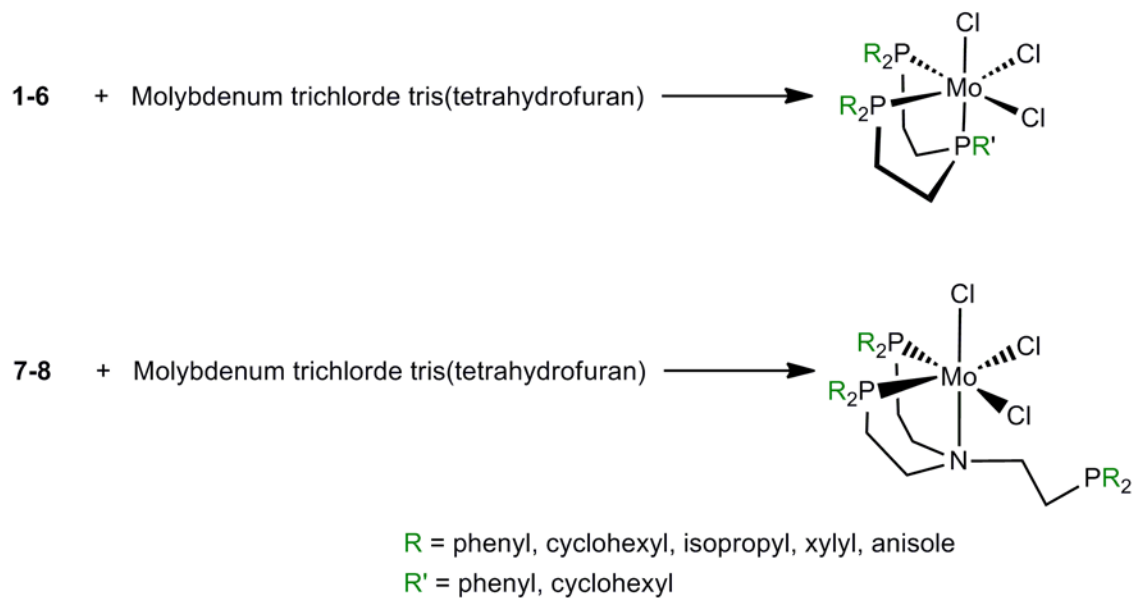
Despite the immense progress in promoting the acrylate formation reaction, the major limitation of the catalytic application of these systems appears to be poisoning by the production. Simply put, the formed acrylate sticks to the molybdenum tightly enough that it is no longer active for further CO₂ utilization. We have found several methods around this point, most notably the use of bases to remove the acrylate as high value sodium salt. The deterrent of this process is that bases and CO₂ are non-compatible rendering a single batch reaction untenable. This issue may be circumvented in a two-stage catalytic process or by immobilizing the molybdenum catalyst in a flow bed reactor with alternating stream. Operation testing of such a method was outside the scope of this work, but could well realize one of the first functional CO₂ + ethylene to acrylate process. Given the persistently lower cost of ethylene to propylene, this area of research appears a fertile domain.

GRAPHICAL MATERIALS

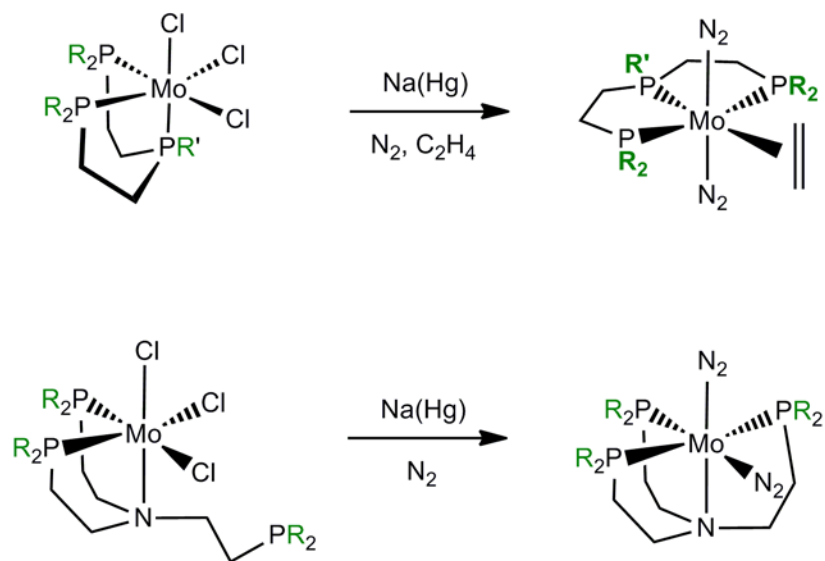
Scheme 1. Synthetic methods for tridentate and tetradentate ligand preparation.



Scheme 2. Preparation routes for tridentate and tetradentate molybdenum trichloride precursors.



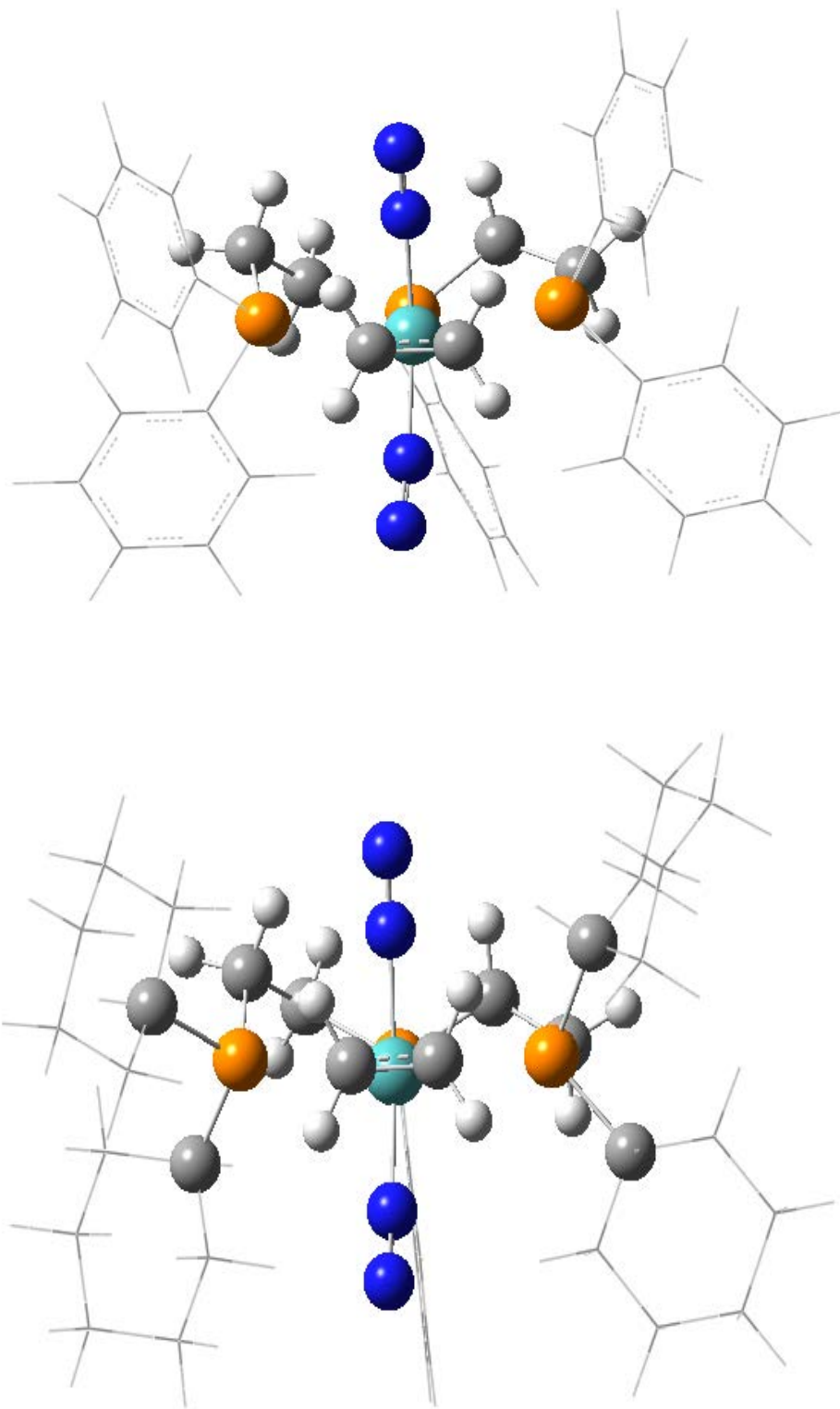
Scheme 3. Methodology for the synthesis of tridentate and tetradentate zerovalent molybdenum catalyst candidates for acrylate formation from carbon dioxide and ethylene.



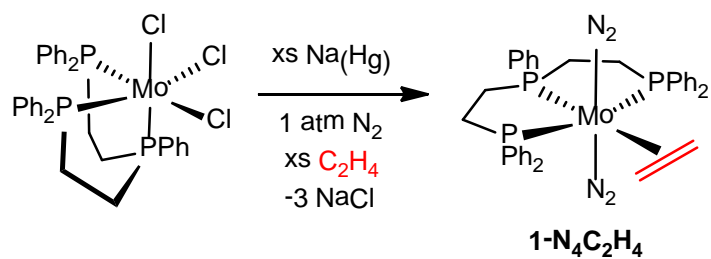
R = phenyl, cyclohexyl, isopropyl, xylyl, anisole

R' = phenyl, cyclohexyl

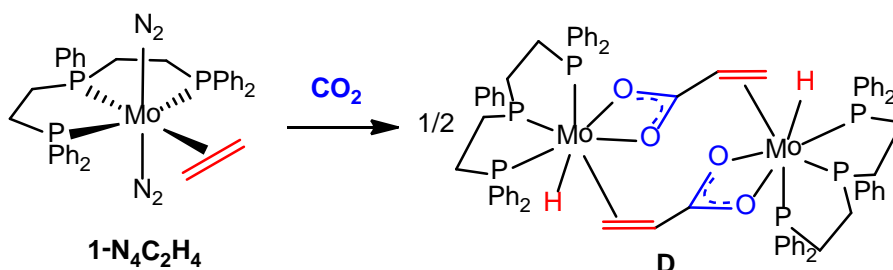
Scheme 4. Optimized Geometries for **1-N₄C₂H₄** (top) and **2-N₄C₂H₄** (bottom).



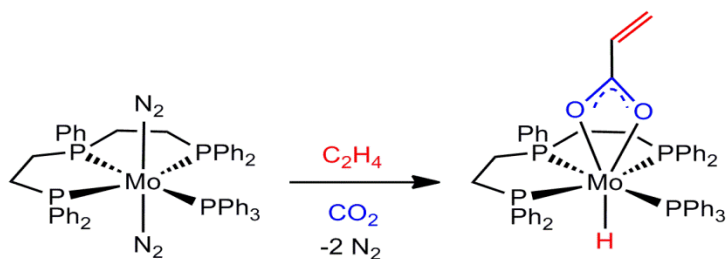
Scheme 5. Synthetic method for tridentate zerovalent molybdenum complex.



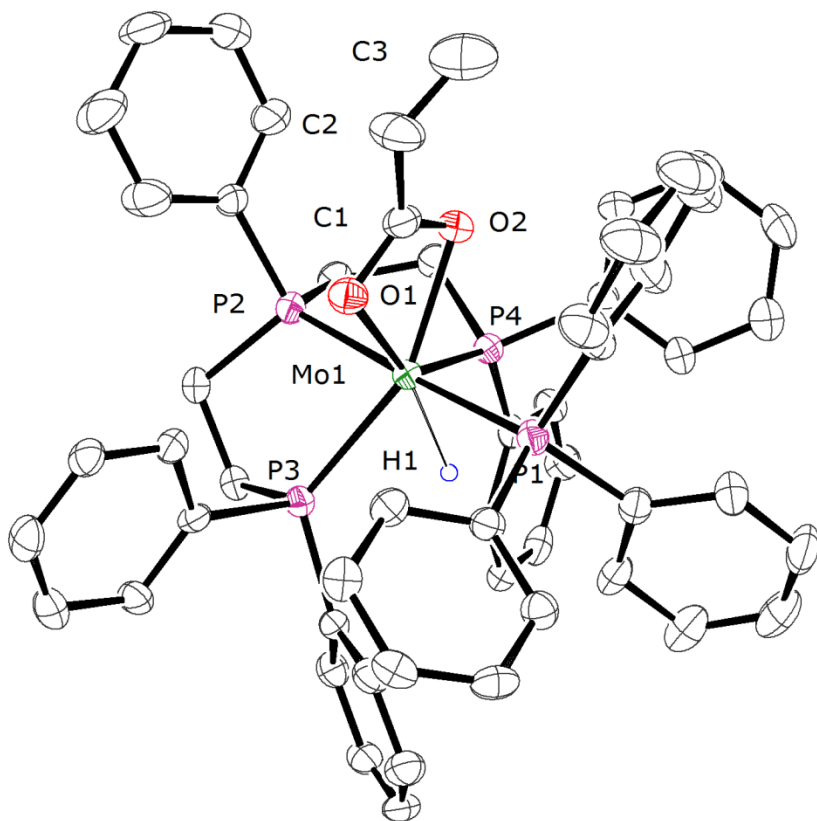
Scheme 6. Coupling of CO_2 and ethylene to afford acrylate complex **D**.



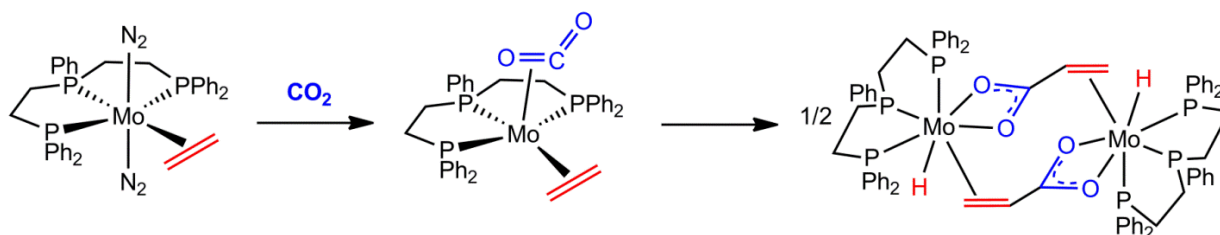
Scheme 7. Formation of **1-P** from CO_2 -ethylene coupling at **1-N₂P**.



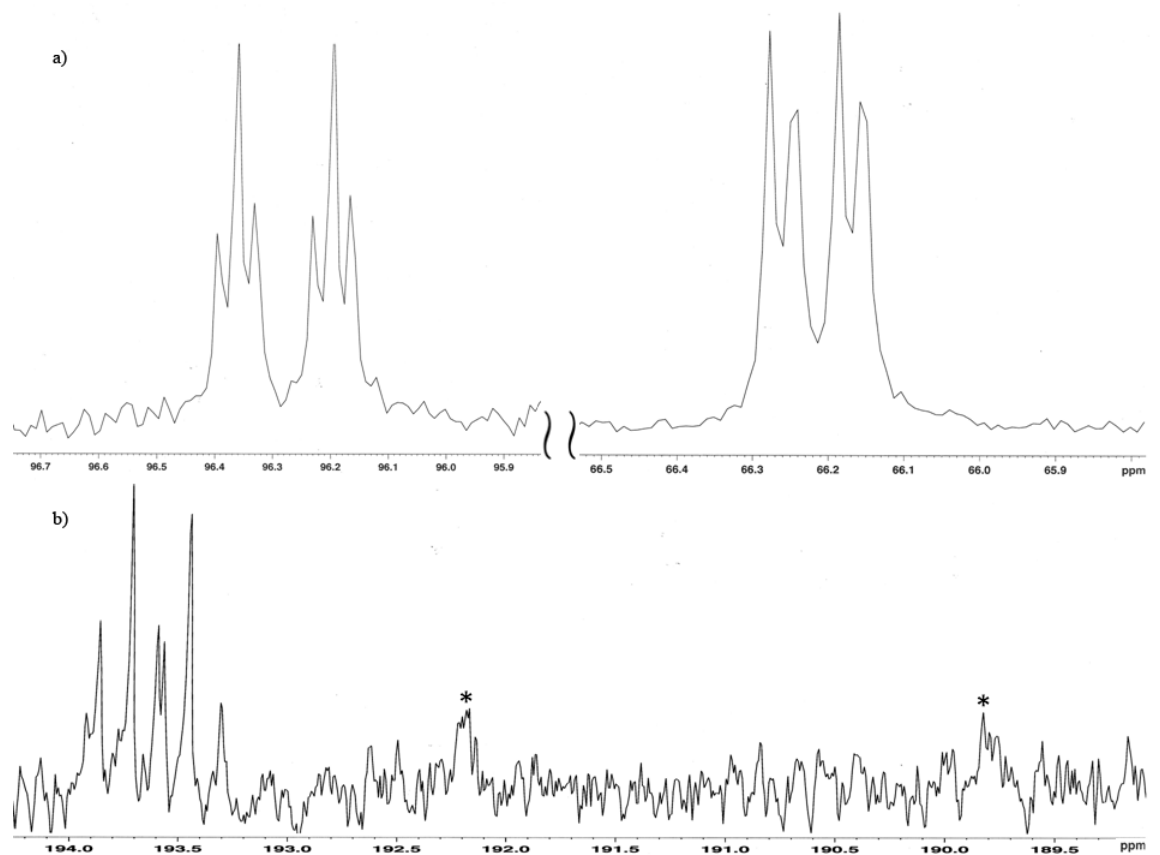
Scheme 8. Molecule structure of complex **1-P** obtained from X-ray diffraction analysis.



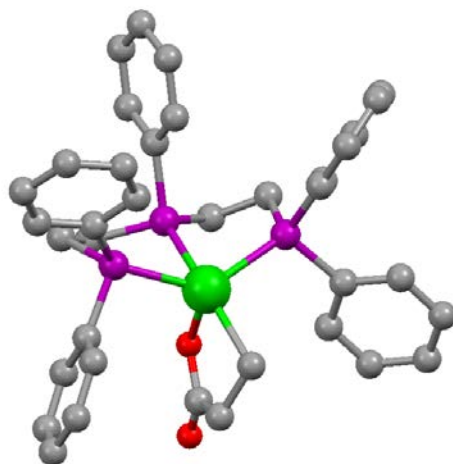
Scheme 9. Formation of intermediate **I** along the pathway for acrylate formation.



Scheme 10. Partial a) ^{31}P $\{^1\text{H}\}$ NMR and b) ^{13}C $\{^1\text{H}\}$ NMR spectra of **I**- ^{13}C . Asterisk denotes minor formation of labeled **D**. Adapted from reference 6.



Scheme 11. Optimized geometry of **I** from DFT calculations.



Scheme 12. Overall mechanistic model for acrylate formation at zerovalent molybdenum catalyst targets.

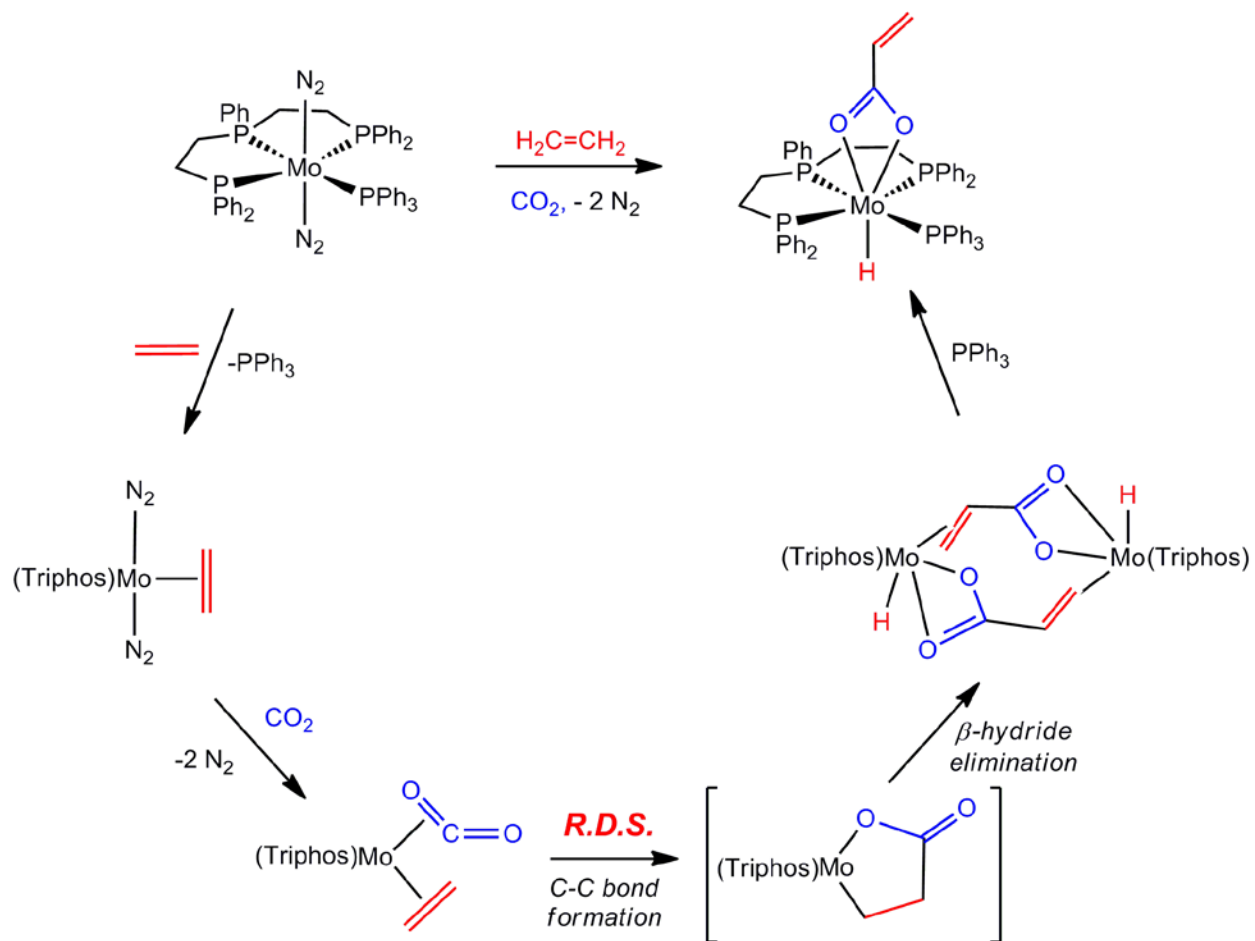
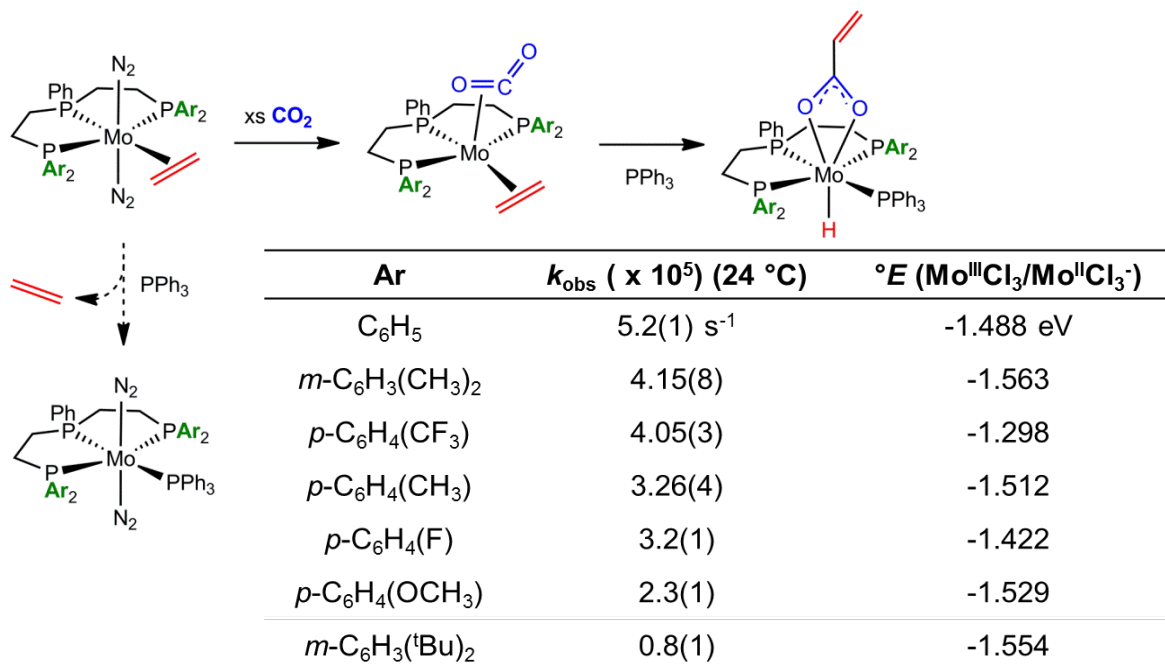


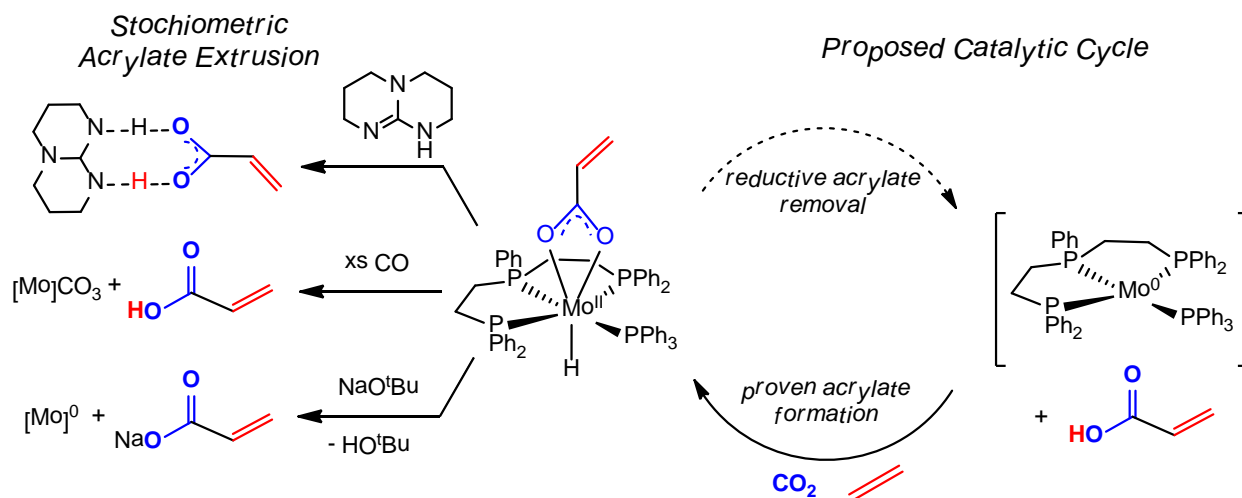
Table 1. Results of Ligand Screen for Acrylate Formation.

Ligand	Observation
[bis(diphenylphosphino)ethyl-phenylphosphine]	Clear acrylate production detected
[bis(dianisolephosphino)ethyl-phenylphosphine]	Clear acrylate production detected
[bis(di- <i>m</i> -xylyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected
[bis(di- <i>p</i> -fluorophenyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected
[bis(di- <i>p</i> -trifluoroemethyl-phenyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected
[bis(dipyrrolephosphino)ethyl-phenylphosphine]	No acrylate formation detected
1,1,1-Tris(diphenylphosphinomethyl)ethane	No acrylate formation detected
Methyl substituted 1,4,7-Triazacyclononane	No acrylate formation detected
[bis(di- <i>tert</i> butyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected
[bis(dicyclohexylphosphino)ethyl-phenylphosphine]	No acrylate formation detected
N,N'-(2,4,6-Trimethyl)-imidazolium	No acrylate formation detected
N,N'-(2,6-Diisopropylphenyl)-imidazolium	No acrylate formation detected
N-Methyl-triazacyclononane	No acrylate formation detected
1,3-Bis(di- <i>tert</i> -butylphosphinomethyl)benzene	No acrylate formation detected
N,N'-Dimethyl-imidazolium	No acrylate formation detected

Scheme 13. Ancillary ligand effect on Triphos-like molybdenum complexes for CO₂-ethylene coupling to acrylate and the reduction potential of the corresponding trichloride.



Scheme 14. Methods for the reductive extrusion of acrylates from the **1-P**.



REFERENCES

- ¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- ² Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, **1982**.
- ³ Roh, S. Y. Bruno, J. W. *Inorg. Chem.* **1986**, *25*, 3105-3106.
- ⁴ Incorporation of a bidentate phosphine into Carmona's molybdenum complexes did not produce clean acrylate formation, although coupling was successful with bidentate tungsten species
- ⁵ George, A. T.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285.
- ⁶ a) Bernskoetter, W.H.; Tyler, B.T. *Organometallics*, **2011**, *30*, 520-527. b) Zhang, Y.; Hanna, B. S.; Dineen, A.; Williard, P. G.; Bernskoetter, W. H. *Organometallics*, **2013**, *32*, 3969-3979.
- ⁷ Chatt, J.; Pearman, A. J.; Richards, R. L. *Dalton. Trans.* **1977**, 1852.
- ⁸ a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. b) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014. c) Dadkhah, H.; Dilworth, J. R.; Faiman, K.; Kan, C. T.; Richards, R. L.; Hughes, D. L.; *Dalton Trans.* **1986**, 245. d) George, T. A.; De Bord, J. R. D.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295. e) Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Hughes, D. L. *Dalton Trans.* **1994**, 2431. f) George, T. A.; Rose, D.J.; Chang, Y.; Chen, Q.; Zubietta, J. *Inorg. Chem.* **1995**, *34*, 1295. g) Hidai, M. *Coord. Chem. Rev.* **1999**, *185*, 99.
- ⁹ Jackson, S. A.; Hodges, P. M.; Poliakoff, M.; Turner, J. J.; Greveld, F. W. *J. Am. Chem. Soc.* **1990**, *112*, 1221.
- ¹⁰ Goff, S. E. J.; Nolan, T. F.; George, M. W.; Poliakoff, M. *Organometallics*, **1998**, *17*, 2730.
- ¹¹ Anderson, S. N.; Richards, R. L.; Hughes, D. L. *Chem. Commun.* **1982**, 1291.
- ¹² For a representative paper addressing the stereochemistry of seven-coordinate metals see: Fay, R. C. *Coord. Chem. Rev.* **1996**, *154*, 99.
- ¹³ Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986, pp. 231-233.
- ¹⁴ The red shifted band for ¹³CO₂ labeled **2** was obscured by bands from the Triphos ligand near 1480 and 1430 cm⁻¹.
- ¹⁵ a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. b) Chatt, J.; Duncaneon, L. A. *J. Chem. Soc.* **1963**, 2339.
- ¹⁶ For examples of other formally five-coordinate molybdenum(0) complexes see: ref 24f and Niikura, F.; Seino, H.; Mizobe, Y.; *Organometallics* **2009**, *28*, 1112.
- ¹⁷ Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286.
- ¹⁸ a) Sano, K.; Yamamoto, T.; Yamamoto, A. *Chem. Let.* **1983**, 115.
- ¹⁹ Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Ligand Substitution Processes. Principles and Applications of Organotransition Metal Chemistry*. University Science Books, Sausalito; **1987**, pp. 235-278.
- ²⁰ The reduced partial pressure of CO₂ produced by N₂ addition may also influence the rate of conversion to **4**, obscuring firm conclusions regarding inhibition by dinitrogen.

- ²¹ a) Dedieu, A.; Ingold, F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1694. b) Sakaki, S.; Mine, K.; Taguchi, D.; Arai, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3289. c) Sakaki, S.; Mine, K.; Hamada, T.; Arai, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1873. d) Papai, I.; Schubert, G.; Mayer, I.; Besenyei, G.; Aresta, M. *Organometallic* **2004**, *23*, 5252. e) Graham, D. C.; Mitchell, C.; Bruce, M. I.; Metha, G. F.; Bowie, J. H.; Buntine, M. A. *Organometallics* **2007**, *26*, 6784.
- ²² Schubert, G.; Papai, I. *J. Am. Chem. Soc.* **2003**, *125*, 14847.
- ²³ Less than 15% formation of **2** was observed prior to complete conversion of **1** to **4**.
- ²⁴ a) Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1983**, *251*, C51 b) ²⁴ Cohen, S. A.; Bercaw, J. E. *Organometallics*, **1985**, *4*, 1006 c) Alt, H. G.; Denner, C. E. *J. Organomet. Chem.* **1990**, *390*, 53. d) Hessen, B.; Meetsma, A.; Bolhuis, F.; Teuben, J.; Helgesson, G.; Janger, S. *Organometallics*, **1990**, *9*, 1925. e) Langer, J.; Fischer, R.; Goerls, H.; Walther, D. *Eur. J. Inorg. Chem.* **2007**, 2257. f) Aresta, M.; Quaranta, E. *J. Organomet. Chem.* **1993**, *463*, 215.
- ²⁵ a) Hoberg, H.; Peres, Y.; Kruger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 771 and references therein. b) Hoberg, H.; Ballesteros, A. *J. Organomet. Chem.* **1991**, *411*, C11. c) Hoberg, H.; Ballesteros, A.; Sigán, A.; Jegat, C.; Barhausen, D.; Milchereit, A. *J. Organomet. Chem.* **1991**, *407*, C23.
- ²⁶ The C-C bond forming event may also be viewed as a nucleophilic attack by ethylene on the electrophilic carbon dioxide.
- ²⁷ A third possibility, rate limiting dimerization, is deemed unlikely given that the absence of observable acrylate hydride monomer necessitates two rapid equilibria between **4**- metallalactone and metallalactone-acrylate hydride monomer, both of which must favor the reactants. This possibility is also excluded based on the measured KIE and activation entropy.
- ²⁸ a) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304. b) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, *129*, 14281.
- ²⁹ Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Decomposition of Metal Alkyls by β -Hydride Elimination. Principles and Applications of Organotransition Metal Chemistry.* University Science Books, Sausalito; **1987**, pp. 386-388.
- ³⁰ For selected examples see: a) Hammud, H. H.; George, T. A.; Kurk, D. N.; Shoemaker, R. K. *Inorg. Chim. Acta* **1998**, *281*, 153. b) George, T. A.; Hammud, H. H. *J. Organomet. Chem.* **1995**, *503*, C1. c) George, T. A.; Debord, J. R. D.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295. d) Bossard, G. E.; George, T. A.; Lester, R. K.; Tisdale, R. C.; Turcotte, R. L. *Inorg. Chem.* **1985**, *24*, 1129.
- ³¹ Angelici, R. J. *Reagents for Transition Metal Complex and Organometallic Syntheses.* Wiley-VCH: Weinheim, **1990**.
- ³² a) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. b) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223. c) Ellis, R.; Henderson, R. A.; Hills, A.; Hughes, D. L. *J. Organomet. Chem.* **1987**, *333*, C6. d) Ito, T.; Matsubara, T. *Dalton Trans.* **1988**, 2241.
- ³³ a) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9777. b) Wesselbaum, S.; Hintermair, U.; Leitner, W. *Angew. Chem. Int. Ed.* **2012**, *51*, 8585.
- ³⁴ a) Suh, H-W.; Schmeier, T. J.; Hazari, N.; Kemp, R. A.; Takase, M. K. *Organometallics* **2012**, *31*, 8225. b) Fan, T.; Chen, X.; Lin, Z. *Chem. Commun.* **2012**, *48*, 10808. c) Li, J.; Yoshizawa, K. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1039. d) Urakawa, A.; Jutz, F.; Laurenczy, G.; Baiker, A. *Chem. Eur. J.* **2007**, *13*, 3886. e) Matsubara, T.; Hirao, K. *Organometallics* **2001**, *20*, 5759.

³⁵ Attempts to measure the inhibition of **1-formate** formation by H₂ were obviated by the observation that **1-formate** degrades with in the presence of 1 atm of H₂.

³⁶ a) Schmeier, T. J.; Hazari, N. ; Incarvito, C. D.; Raskatov, J. A. *Chem. Commun.* **2011**, 47, 1824. b) Sakaki, S.; Musashi, Y. *Inorg. Chem.* **1995**, 34, 1914. c) Sakaki, S.; Ohkubo, K. *Organometallics* **1989**, 8, 2970.

³⁷ Addition of trace water to **1-P** also affords **1-propionate** along with significant amounts of insoluble metal products.

LIST OF ACRONYMS AND ABBREVIATIONS

1= Triphos= bis(diphenylphosphino)ethyl-phenylphosphine

2 bis(dicyclohexylphosphino)ethyl-phenylphosphine

3 bis(diisopropylphosphino)ethyl-phenylphosphine

4 bis(dianisolephosphino)ethyl-phenylphosphine

5 bis(dixylylphosphino)ethyl-phenylphosphine

6 bis(diphenylphosphino)ethyl-cyclohexylphosphine

7 tris(diphenylphosphinoethyl)amine

8 tris(diisopropylphosphinoethyl)amine

1-Cl₃: [bis(diphenylphosphino)ethyl-phenylphosphine]molybdenum trichloride

1-N₄C₂H₄: [bis(diphenylphosphino)ethyl-phenylphosphine]molybdenumbis(dinitrogen) ethylene

2-Cl₃: [bis(dicyclohexylphosphino)ethyl-phenylphosphine]molybdenum trichloride

2-N₄C₂H₄: [bis(dicyclohexylphosphino)ethyl-phenylphosphine]molybdenumbis(dinitrogen) ethylene

3-Cl₃: [bis(diisopropylphosphino)ethyl-phenylphosphine]molybdenum trichloride

3-N₄C₂H₄: [bis(diisopropylphosphino)ethyl-phenylphosphine]molybdenumbis(dinitrogen) ethylene

4-Cl₃: [bis(dianisolephosphino)ethyl-phenylphosphine]molybdenum trichloride

4-N₄C₂H₄: [bis(dianisolephosphino)ethyl-phenylphosphine]molybdenumbis(dinitrogen) ethylene

5-Cl₃: [bis(dixylylphosphino)ethyl-phenylphosphine]molybdenum trichloride

5-N₄C₂H₄: [bis(dixylylphosphino)ethyl-phenylphosphine]molybdenumbis(dinitrogen) ethylene

6-Cl₃: [bis(diphenylphosphino)ethyl-cyclohexylphosphine]molybdenum trichloride

6-N₄C₂H₄: [bis(diphenylphosphino)ethyl-cyclohexylphosphine]molybdenumbis(dinitrogen) ethylene

7-Cl₃: [tris(diphenylphosphinoethyl)amine]molybdenum trichloride

D: dimeric [bis(diphenylphosphino)ethyl-phenylphosphine]molybdenum acrylate hydride

1-P: monomeric [bis(diphenylphosphino)ethyl-phenylphosphine]molybdenum acrylate hydride triphenyl phosphine

I: [bis(diphenylphosphino)ethyl-phenylphosphine]molybdenum carbon dioxide ethylene

1-N₂P: [bis(diphenylphosphino)ethyl-phenylphosphine]molybdenumbis(dinitrogen) triphenylphosphine

1-formate: [bis(diphenylphosphino)ethyl-phenylphosphine]Mo(H)(κ^2 -CHO₂)(PPh₃)

1-propionate: bis(diphenylphosphino)ethyl-phenylphosphine] Mo(H)(κ^2 -C₃H₅O₂)(PPh₃)