

Kinetics and Mechanism of Molybdenum-Mediated Acrylate Formation from Carbon Dioxide and Ethylene

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A zerovalent molybdenum complex, $[(Ph_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$, was found to promote coupling of CO_2 and ethylene to afford a molybdenum(II) acrylate hydride complex. The identity of the molybdenum(II) acrylate hydride complex was established by spectroscopy and reactivity studies. The mechanism of carbon dioxide functionalization with ethylene has been investigated by a series of kinetic and isotopic labeling studies, in addition to the observation of a formally molybdenum(0) carbon dioxide-ethylene intermediate along the reaction pathway. Acrylate formation from the molybdenum(0) intermediate proceeds with a rate constant of $3.8(3) \times 10^{-5}$ s⁻¹ and an isotope effect of 1.2(2) for C₂H₄ vs C₂D₄ at 23 °C. Measuring rate constants of the CO₂ reduction over a 40 °C temperature range established activation parameters for acrylate formation of $\Delta S^{\ddagger} = 1(7)$ eu and $\Delta H^{\ddagger} = 24(3)$ kcal/mol. The mechanism of CO₂-ethylene coupling is proposed to proceed from a molybdenum(0) carbon dioxide-ethylene adduct via rate-limiting oxidative C-C bond formation followed by rapid β -hydride elimination from a metallalactone complex.

Introduction

The steady increase in demand for finite petroleum resources,¹ a primary carbon feedstock, has spurred considerable efforts to leverage renewable carbon sources as precursors for commodity chemicals.² Carbon dioxide in particular has been touted as a promising target on the basis of its incredible abundance, cheap availability, and relative ease of transport.³ Unfortunately, the thermodynamic stability of CO₂ has led to its reticence in performing synthetically useful transformations. One technique that has achieved success is coupling CO_2 with other small molecules to provide the necessary reduction energy and functionalization agent from one source.⁴ Among the leading examples of this methodology is the production of urea from CO₂/ammonia and carbonates (and polycarbonates) from CO₂/epoxides.⁵

Coupling carbon dioxide to olefins is another highly attractive target for CO₂ utilization, but one that has achieved limited success thus far.⁶ Since Hoberg and Schaefers's first report of nickelalactone formation from CO2 and ethylene in 1983 (eq 1),⁷



cdt = 1,5,9-cyclododecatriene

transition metal chemists have pursued the production of acrylic acid and other acrylates by coupling these unsaturates for uses in superabsorbing polymers, coatings, and adhesives.⁸ Unfortunately Hoberg's complex, as well as most titanium,⁹ zirconium,¹⁰ vanadium,¹¹ palladium,¹² rhodium,¹³ and other nickel¹⁴ examples that followed it, proved resistant toward β -hydride elimination reactions to form acrylate compounds.

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Figure 1. Acrylate formations from nickelalactone complexes.

More recently Walther¹⁵ and Rieger¹⁶ have independently surmounted this barrier to induce modest yields of acrylates from nickelalactones by either ancillary ligand substitution and chelate activation following CO_2 -ethylene coupling or addition of strong electrophiles (Figure 1). The most striking progress toward acrylate production from CO_2 has been reported by Carmona and co-workers,^{17a} in which *trans*-(PMe₃)₄Mo(C₂H₄)₂ reduces carbon dioxide at mild temperature and pressure to afford



 $[(PMe_3)_2(C_2H_4)MoH(CO_2CH=CH_2)]_2$ (eq 2). This remarkable transformation yields two acrylate ligands bridging between two metal centers, although eventual acrylate displacement required use of harsh bases. Following this initial report, Carmona^{17b,c} and others^{17d} have described a small family of closely related molybdenum and tungsten complexes found to exhibit similar reactivity; however the mechanism of acrylate formation was not investigated.

The potential for producing valuable commodity chemicals from carbon dioxide has sustained interest in the mechanism of CO2-ethylene coupling at transition metals since Hoberg and Carmona's early discoveries. Numerous computational studies have explored the mechanism of metallalactone formation at late transition metals¹⁸ (nickel in particular) and acrylate production at molybdenum complexes.¹⁹ While many similarities between these two reactions have been predicted, consensus on some mechanistic features has remained elusive (vide infra). Indeed, the mechanism for CO₂-ethylene coupling may well differ from early to late transition metals. However, the practical application of this mechanistic information toward improved complexes for CO₂ activation requires detailed understanding of the reaction intermediates and rate-influencing event(s). Given this, our laboratory has begun an effort to develop new platforms

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for acrylate formation from CO_2 and ethylene and experimentally examine the kinetics and mechanism of this transformation. Herein, we describe the preparation of a new tridentate phosphine molybdenum(0) complex that functionalizes carbon dioxide with ethylene to afford metal-bound acrylates. The mechanism of acrylate formation was explored by kinetic and isotopic labeling studies and is supported by the direct observation of a key reaction intermediate.

Results and Discussion

CO₂-Ethylene Coupling. 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 not augured well for the incorporation of chelating ligands on molybdenum in CO₂-ethylene coupling reactions,²⁰ 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 laboratory began 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 $(Triphos)MoCl_3^{21}$ in the presence of excess dinitrogen and ethylene afforded a new zerovalent complex, *trans*-(Triphos)Mo- $(N_2)_2(C_2H_4)$ (1), in good yield (eq 3). This bright yellow complex was



characterized by infrared and multinuclear NMR spectroscopy and reactivity studies. The ³¹P{¹H} NMR spectrum of the molybdenum(0) species in benzene- d_6 exhibits doublet and triplet resonances (² $J_{P-P} = 16.8$ Hz) at 75.0 and 92.7 ppm, respectively. ¹H NMR spectroscopy reveals a broad signal

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for the bound olefin at 1.44 ppm, and the assignment was confirmed by preparation of the *trans*-(Triphos)Mo(N₂)₂-(C₂D₄) (**1-d**₄) isotopologue. ¹H-¹³C HSQC NMR experiments indicate a correlation between this peak and a resonance at 38.76 ppm in the ¹³C NMR spectrum. Solid-state infrared analysis of **1** confirmed the presence of the two dinitrogen ligands with bands at 2051 and 1981 cm⁻¹. Addition of triphenylphosphine to **1** produced free ethylene and *trans*-(Triphos)Mo(N₂)₂PPh₃,²² further supporting the characterization of the bis(dinitrogen) molybdenum ethylene complex.

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 N_2 to ammonia.²³ Typically these complexes are stabilized by four σ -donating ligands such as phosphines or amines,²⁴ although a few examples of related bis(dinitrogen) compounds bearing additional π -acid ligands, as in 1, have been reported using olefins,²⁵ CO,²⁶ and additional N₂ ligands.²⁷ Complex 1 presented a particularly attractive platform for studying the coupling of ethylene and carbon dioxide at zerovalent molybdenum, as the chelating Triphos ligand would minimize complications arising from ancillary ligand loss and facile liberation of the dinitrogen ligands should allow ready introduction of carbon dioxide into the metal coordination sphere. Gratifyingly, the addition of a small excess of carbon dioxide (4 equiv) to 1 afforded a bridging acrylate hydride complex, [(Triphos)Mo-(H)(CO₂CH=CH₂)]₂ (2), over several hours at ambient temperature (eq 4). The ³¹P{¹H} NMR spectrum of 2 displays six signals, three



appearing as a 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.²⁸ These data are consistent with the formation of two similar energy diastereomers, as may be expected for a dimeric complex formed from two seven-coordinate metal centers.²⁹ Attempts to interconvert the two isomers by thermolysis at 85 °C resulted in

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decomposition prior to an observable change in isomer ratio. Although the ${}^{2}J_{P-P}$ couplings were not well resolved for all ${}^{31}P$ 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 **2** 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 ${}^{31}P$ nuclei, resulting in an eight-line splitting pattern, with ${}^{2}J_{P-H}$ constants ranging from 13.2 to 96.0 Hz.²⁸

Examination of the infrared spectrum for the isomers of complex **2** revealed a broad band at 1512 cm^{-1} , consistent with a bidentate carboxylate ligand.³⁰ Employing ¹³CO₂ in the coupling reaction confirmed the origin of this IR band.³¹ 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. Complex **2** is therefore depicted in the bridging carboxylate geometry on the basis of Carmona's crystal-lographically characterized complex.^{17b}

The inability to obtain X-ray quality crystals of either isomer of 2 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 2 as a bridging acrylate molybdenum hydride complex. Treatment of 2 with triphenylphosphine resulted in immediate formation of the red monomeric acrylate hydride species (Triphos)Mo(H)-(PPh₃)(CO₂CH=CH₂) (3) (Figure 2), which was unambiguously characterized by multinuclear NMR spectroscopy and elemental analysis. Benzene- d_6 solutions of **3** exhibit ¹H NMR resonances at 4.68, 5.15, and 5.48 ppm assigned to an unbound acrylic olefin.²⁸ These signals display coupling constants, splitting patterns, and chemical shift values quite similar to those observed for free acrylic acid. Additionally, a triplet of doublets of doublets is observed at -4.71 ppm, establishing the presence of a molybdenum-hydride ligand.²⁸ The ${}^{31}P{}^{1}H$ NMR spectrum of **3** displays a doublet of doublets at 109.7 ppm for the two PPh₂ fragments and two doublet of triplet 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.³⁰

Further confirmation of the identity of complex **3** was obtained by independent preparation from *trans*-(Triphos)- $Mo(N_2)_2(PPh_3)$ (Figure 2).²² 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 **2**. Most likely triphenylphosphine dissociation from *trans*-(Triphos)Mo(N₂)₂(PPh₃) provides access to

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Figure 2. Formation of 3 from CO_2 -ethylene coupling and PPh₃ addition to 2.



Figure 3. Observation of intermediate 4 prior to formation of 2.

a reactive (Triphos) Mo^0 center analogous to reactive intermediates in the reduction of CO₂ with complex 1 (*vide infra*). 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.

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 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 molybdenumpromoted CO₂-ethylene coupling have been reported. Qualitatively, acrylate formation from complex 1 upon CO_2 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 requires many hours under similar conditions. Understanding the origins of this slower CO_2 -ethylene coupling requires elucidation of the reaction mechanism and identification of the rate-influencing event(s). This motivation, along with an interest in designing complexes to enhance acrylate preparation from CO₂ and ethylene, prompted a series of experiments to investigate the reaction coordinate for CO₂-ethylene coupling.

Observation of Reaction Intermediate. Monitoring the addition of approximately 12 equiv of 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) (**4**) (Figure 3). Interestingly, this species was also observed as an intermediate in the formation of the triphenyl-phosphine acrylate hydride complex **3** from CO₂ and ethylene addition to *trans*-(Triphos)Mo(N₂)₂(PPh₃). Complex **4** formed rapidly from **1** in the presence of excess CO₂ (~15 min) and

converted slowly to the acrylate hydride species 2 over several hours (vide infra). The molybdenum(0) carbon dioxide ethylene complex exhibited a doublet resonance at 64.7 ppm and a triplet resonance at 95.3 ppm (${}^{2}J_{P-P} = 6.1 \text{ Hz}$) in the ${}^{31}P{}^{1}H$ 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 $(Triphos)Mo(C_2D_4)(CO_2)$ (4-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 decoalese this signal (limited solubility of complex 4 at lower temperatures prohibited further variable-temperature study), suggesting either that the interchange of the two ethylene CH₂ units is 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,^{17c} with the proton signal in **4** 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 model³² or the variation in metal coordination number.³³

Further spectral analysis of the reaction intermediate was obtained by preparation of $(\text{Triphos})\text{Mo}(\text{C}_2\text{H}_4)(^{13}\text{CO}_2)$ (**4**-^{*I3*}**C**) from addition of excess $^{13}\text{CO}_2$ to **1**. Incorporation of the ^{13}C label resulted in an enhanced doublet of triplets signal at 193.6 ppm in the ^{13}C NMR spectrum with coupling constants of 14.9 and 27.7 Hz (Figure 4). The magnitude of this coupling is similar to the $^2J_{\text{C}-\text{P}} = 17.5$ Hz coupling reported for *trans*-(PMe_3)_4Mo($^{13}\text{CO}_2$)_2³⁴ and significantly greater than the $^3J_{\text{C}-\text{P}} < 6$ Hz couplings reported for more commonly isolated metallalactone complexes.^{12,35} The labeling

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Figure 4. Partial (a) ${}^{31}P{}^{1}H$ NMR and (b) ${}^{13}C{}^{1}H$ NMR spectra of 4- ${}^{13}C$. Asterisk denotes minor formation of labeled 2.

experiment also alters the ³¹P{¹H} NMR spectrum, with $4-^{13}C$ splitting the two signals into a doublet of triplets (PPh) and a doublet of doublets (PPh₂), indicating only one ${}^{13}CO_2$ molecule is incorporated into the intermediate (Figure 4). Infrared spectroscopy confirms the presence of a C=O fragment with a band at 1700 cm⁻¹ for 4 in KBr, which shifts to 1654 cm⁻¹ for 4-¹³C, though the IR bands for transition metal carbon dioxide complexes and metallalactones do not have characteristically distinguishing frequencies.^{7,9–14,34} Notably, no strong bands were observed for either isotopologue of 4 from 2200 to 1800 cm^{-1} , suggesting both dinitrogen ligands of 1 dissociate when binding carbon dioxide. The observation of a pseudo-five-coordinate molybdenum(0) complex was unexpected, given that 4 may be observed in the presence of additional carbon dioxide, ethylene, dinitrogen, and triphenylphoshine. However no spectroscopy signals indicative of a bound sixth ligand were observed, and the use of relatively noncoordinating solvent (benzene) tentatively supports assignment of the coordiatively unsaturated intermediate.33

The mechanism of carbon dioxide substitution with 1 was briefly explored using a series of parallel NMR tube experiments. The coordinative saturation of complex 1 implies that the substitution process to form 4 is dissociative in nature;³⁶ however, the concentration of CO_2 or N_2 may influence the reaction rate if ligand dissociation is reversible. Parallel experiments with stock solutions of 1 were used to investigate these possibilities, as this technique reduces complications from gases mixing into solution. To assess the influence of CO_2 on the formation of 4, two degassed samples of 1 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 min, a 36% greater conversion to 4 (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 4 in the presence of N₂.³⁷ More significantly, upon formation of complex 4, removal of excess CO_2 and introduction of a dinitrogen atmosphere at ambient temperature did not result in reversion to 1 prior to formation of the acrylate hydride species 2. These experiments are consistent with formation of intermediate 4 by reversible dinitrogen loss from 1 followed by slow, effectively irreversible, binding of carbon dioxide with loss of a second N_2 ligand (Figure 5).

Mechanistic Considerations of Acrylate Formation. The observation of **4** 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 precoordination for transition metal mediated metallalactone or acrylate formation is an area that has been investigated computationally for many years with inconsistent conclusions.^{18,19} Early calculations by Dedieu^{18a} and others^{18d,e} concluded that nickelalactone formation proceeds without coordination of ethylene, instead occurring

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Figure 5. Proposed mechanism of CO₂ substitution with 1.



Figure 6. Proposed mechanism for the formation of acrylate.

via nucleophilic attack by incoming C_2H_4 on a bound carbon dioxide ligand. Later, Sakaki^{18b,c} and co-workers 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.¹⁹ The characterization of the carbon dioxide ethylene complex **4** provides the first direct evidence that precoordination 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 4 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 4 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 1 with 12 equiv of CO_2 .³⁸ Monitoring the decay of the signal for complex 4 versus an internal standard in the ${}^{1}P{}^{1}H{}$ NMR spectrum at 23 °C afforded an observed rate constant of $3.8(3) \times 10^{-5} \text{ s}^{-1}$ 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 4 to 2. Previous computational studies of acrylate formation from $(PMe_3)_4Mo(\tilde{C}_2H_4)_2$,¹⁹ as well as the experimental observation of numerous metallalactones,7,9-14 suggest the formation of 2 proceeds from complex 4 by formally oxidative C-C bond formation between bound CO_2 and ethylene,³⁹ followed by β -hydride elimination from the resulting metallocycle, and finally a dimerization of the Triphos molybdenum acrylate hydride complex (Figure 6). Unfortunately, the DFT analysis could not distinguish the rate-limiting step of acrylate formation from (PMe₃)₄Mo- $(C_2H_4)_2$ and CO_2 as the computed barriers of several steps were quite similar in energy.¹⁹ Given the importance of deter-



Figure 7. Isotope effect for acrylate formation for C_2H_4 vs C_2D_4 . Asterisks denote deuterium sites.

mining the rate-limiting step for rationally optimizing metal complexes for CO_2 -ethylene coupling, we proceeded to further probe the kinetics of acrylate formation.

The modest stability of 4 as an intermediate during carbon dioxide reduction, along with the absence of any other detectable intermediates during formation of 2, implicates two likely kinetic profiles for acrylate production. In one case complex 4 is favored in a rapid equilibrium with the metallalactone species followed by rate-limiting β -hydride elimination and fast dimerization to afford 2. An alternative kinetic profile is rate-limiting oxidative C-C bond coupling from **4** followed by rapid β -hydride elimination and dimerization.40 An isotope effect experiment was employed to differentiate between these two reaction profiles by comparing the rates of acrylate formation from 4 and $4-d_4$ (Figure 7). 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 metallacylic complex, which is expected to produce a significant primary isotope effect.⁴¹

The activation parameters for acrylate formation from complex **4** were also examined by measuring the observed

⁽³⁸⁾ Less than 15% formation of 2 was observed prior to complete conversion of 1 to 4.

⁽³⁹⁾ The C-C bond forming event may also be viewed as a nucleophilic attack by ethylene on the electrophilic carbon dioxide.

⁽⁴⁰⁾ 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-acylate hydride monomer, both of which must favor the reactants. This possibility is also excluded on the basis of the measured KIE and activation entropy.

^{(41) (}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.



Figure 8. Eyring plot for the conversion of 4 to 2.

 Table 1. Temperature Dependence of Rate Constants for Acrylate

 Formation^a

$k (s^{-1})$	<i>T</i> (K)	
$\begin{array}{c} 1.3(4) \times 10^{-3} \\ 4.1(4) \times 10^{-4} \\ 2.1(3) \times 10^{-4} \\ 3.8(3) \times 10^{-4} \\ 6.2(3) \times 10^{-6} \end{array}$	322.2 313.9 308.7 298.2 282.0	

 a Rate constants measured for 0.030 M benzene- d_6 solutions of 4 with 12 equiv of CO_2.

rate constant for the reaction over a 40 °C temperature range. The effect of temperature on the rate of molybdenum acrylate hydride formation is depicted in Figure 7, and the rate constants are reported in Table 1. From the Eyring plot an activation entropy (ΔS^{\ddagger}) of 1(7) eu and an activation enthalpy (ΔH^{\ddagger}) of 24(3) kcal/mol were computed. The near zero ΔS^{\ddagger} 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. Ratelimiting C–C bond formation for CO_2 –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. Our findings suggest that efforts to engender electron-rich early transition metal centers may enhance the rate of acrylate formation. 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,⁴² and the chelation mode of the ancillary ligand.^{17c}

Concluding Remarks

A new $(Ph_2PCH_2CH_2)_2PPh$ -supported bis(dinitrogen) molybdenum ethylene complex has been prepared and found to promote C-C bond coupling with carbon dioxide to afford a binuclear acrylate hydride species. The reduction of CO_2 by 1, although qualitatively slower than the handful of similar transformations inspired by Carmona over two decades ago, provided a platform for the first experimental examination of the mechanism for this intriguing carbon dioxide functionalization. Monitoring the conversion of 1 to acrylate hydride complex 2 afforded direct characterization of an intermediate molybdenum carbon dioxide ethylene adduct 4, establishing precoordination of both substrates as a likely requirement for CO_2 functionalization by ethylene at early transition metals. Kinetic analysis of the conversion of 4 to 2 revealed an isotope effect of 1.2(2) for functionalization with C₂H₄ versus C₂D₄ 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. Further investigations to leverage this new mechanistic data toward enhanced CO₂-ethylene coupling as well as to elucidate the influences of other coordination chemistry factors are currently ongoing in our laboratory. Development of improved methods for acrylate formation may lead to new routes for carbon dioxide functionalization and further our efforts to liberate acrylate-containing products from the metal in a catalytically viable manner.

Experimental Section

General Considerations. 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. Solvents were dried and deoxygenated using literature procedures.⁴³

¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker DRX 400 Avance and 300 Avance MHz spectrometers. ¹H and ¹³C chemical shifts are referenced to residual protio solvent signals; ³¹P chemical shifts are referenced to an external standard of H₃PO₄. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.⁴⁴ 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.

Preparation of [(Ph₂PCH₂CH₂)₂PPh]Mo(C₂H₄)(N₂)₂ (1). A heavy-walled glass reaction vessel was charged with 9.36 g (2.04 mmol) of 0.5% sodium amalgam, 0.150 g (0.204 mmol) of $[(Ph_2PCH_2CH_2)_2PPh]MoCl_3$ ²¹ and approximately 10 mL of tetrahydrofuran. On a vacuum line approximately 4 equiv of ethylene and 1 atm of dinitrogen were added at -196 °C. The resulting reaction mixture was stirred at ambient temperature for 18 h. The volatiles were removed in vacuo from the green reaction mixture. The residue was extracted with toluene, filtered through Celite, concentrated to approximately 5 mL, and recrystallized at -35 °C to afford 0.135 g (93%) of 1 as a yellow powder. Anal. Calcd for C₃₆H₃₇MoN₄P₃·0.5(C₇H₈): C, 62.37; H, 5.43; N, 7.37. Found: C, 62.02; H, 5.39; N, 6.82. ¹H NMR (23 °C, C₆D₆): δ 1.44 (br s, 4H, C₂H₄), 1.70 (m, 2H, PCH₂), 2.03 (m, 2H, PCH₂), 2.62 (m, 2H, PCH₂), 2.82-3.03 (m, 2H, PCH₂), 6.87-7.04 (m, 12H, C₆H₅), 7.08 (t, 7.7 Hz, 8H, C₆H₅), 7.32 (t, 7.7 Hz, 2H, C₆H₅), 7.46 (t, 8.0 Hz, 1H, C₆H₅), 7.65 (t, 7.7 Hz, 2H, C_6H_5). $^{13}C{^{1}H}$ NMR (23 °C, C_6D_6): δ 30.17 (PCH₂), 34.21 (PCH₂), 38.76 (C₂H₄), 129.66, 129.72, 131.77, 131.97, 132.13,

⁽⁴²⁾ 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.

⁽⁴³⁾ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518.

⁽⁴⁴⁾ Sandström, J. Dynamic NMR Spectroscopy; Academic Press: New York, 1982.

133.60, 139.05, 140.81(aryl). ³¹P{¹H} NMR (23 °C, C₆D₆): δ 75.0 (d, 16.8 Hz, 2P, PPh₂), 92.7 (t, 16.8 Hz, 1P, PPh). IR (KBr): $\nu_{N=N} = 2051$, 1981 cm⁻¹ (approximately 1:2 relative intensity).

Preparation of {[(Ph₂PCH₂CH₂)₂PPh]Mo(CO₂CH=CH₂)}₂ (2). A heavy-walled glass reaction vessel was charged with 0.108 g (0.152 mmol) of 1 and approximately 5 mL of toluene. On a vacuum line 12 equiv of carbon dioxide (335 Torr in 101 mL) was added at -196 °C. The resulting reaction mixture was stirred at ambient temperature for 25 h. The volatiles were removed in vacuo from the brown reaction mixture. The residue washed with pentane and dried to afford 0.096 g (90%) of **2** as a red-brown solid, which was characterized without further purification. Anal. Calcd for C₃₇H₃₇MoO₂P₃: C, 63.25; H, 5.31. Found: C, 62.99; H, 5.50. Spectral data for combined isomers: ¹H NMR (25 °C, C₆D₆): δ -7.15 (ddd, 13.2, 54.0, 96.0, Mo-H), -6.73 (ddd, 13.2, 64.9, 94.4 Hz, Mo-H), 1.12-3.20, 3.70, 3.99 (m, PCH₂ and CH=CH₂), 6.86, 6.95–7.34, 7.40, 7.61, 7.69, 8.15, 8.24 (m, C₆H₅). ³¹P{¹H} NMR (23 °C, C₆D₆): δ 80.2 (dd, 14.5, 27.6 Hz), 81.0 (dd, 15.3, 28.5 Hz), 90.3 (m), 92.8 (dd, 16.8, 28.4 Hz), 96.0 (m), 100.3 (m). IR (KBr): $\nu_{C=0} = 1512 \text{ cm}^{-1}$ **2-**¹³C₂: Partial ¹³C{¹H} NMR (23 °C, C₆D₆): δ 189.9, 192.3 $(CO_2CH=CH_2).$

Preparation of (Triphos)Mo(H)(PPh₃)(CO₂CH=CH₂) (3). Method A: A heavy-walled glass reaction vessel was charged with 1.54 g (0.330 mmol) of 0.5% sodium amalgam, 0.075 g (0.010 mmol) of $[(Ph_2PCH_2CH_2)_2PPh]MoCl_3$,²¹ 0.029 g (0.011 mmol) of triphenylphosphine, and approximately 10 mL of tetrahydrofuran. On a vacuum line 4 equiv of ethylene (260 Torr in 28.9 mL) and 1.2 equiv of carbon dioxide (78 Torr in 28.9 mL) were added via calibrated gas bulb at -196 °C. The resulting reaction mixture was stirred at ambient temperature for 18 h. The volatiles were removed in vacuo from the red-orange reaction mixture. The residue was washed with pentane to remove residue PPh₃, extracted with toluene, filtered through Celite, concentrated to approximately 3 mL, and recrystallized at -35 °C to afford 0.042 g (43%) of 3 as a microcrystalline red powder. Method B: A J. Young NMR tube was charged with 0.015 mg of *trans*-(Triphos)Mo(N_2)₂PPh₃²² and approximately 500 μ L of benzene- d_6 . On a vacuum line, 6 equiv (61 Torr in 28.9 mL) of both carbon dioxide and ethylene were admitted to the sample via calibrated gas bulb at -196 °C. The tube was warmed to ambient temperature and agitated overnight. Analysis by ¹H and ³¹P{¹H} NMR spectroscopy revealed conversion to 3 (>85% yield) along with a small quantity of free PPh₃ Method C: A J. Young NMR tube was charged with 0.008 g of 2 and approximately 500 μ L of benzene- d_6 . Addition of excess triphenylphosphine (\sim 5 equiv) afforded **3** as the only observable organometallic product by ¹H and ³¹P{¹H} NMR spectroscopy. Anal. Calcd for C55H52MoO2P4: C, 68.47; H, 5.43. Found: C, 68.21; H, 5.71. ¹H NMR (23 °C, C₆D₆): δ -4.71 (tdd, 74.0, 42.4, 14.0 Hz, 1H, Mo-H), 1.20 (m, 2H, PCH₂), 1.49 (m, 2H, PCH₂), 1.94 (m, 2H, PCH₂), 2.51-2.64 (m, 2H, PCH₂), 4.68 (dd, 2.0, 10.4 Hz, CH=CH₂), 5.15 (dd, 10.4, 17.2 Hz, CH=CH₂), 5.48 $(dd, 2.0, 17.2 Hz, CH=CH_2), 6.77 (m, 6H, C_6H_5), 6.85 (m, 6H,$ C_6H_5), 6.90–7.20 (m, 12H, C_6H_5), 7.30 (m, 7H, C_6H_5), 7.38 (m, 3H, C_6H_5), 7.58 (m, 4H, C_6H_5), 7.79 (t, 7.6 H, C_6H_5). ¹³C{¹H} NMR (23 °C, C₆D₆): δ 26.24 (PCH₂), 34.77 (PCH₂), 123.15

(CH=CH₂), 131.75 (CH=CH₂) 123.48, 127.74, 127.90, 128.53, 128.91 131.53, 131.60, 133.61, 133.87, 134.54, 135.33, 135.44, 137.84, 138.39 (aryl) two quaternary signals not located. ³¹P-{¹H} NMR (23 °C, C₆D₆): δ 47.7 (dt, 12.1, 155.5 Hz, 1P, PPh), 99.4 (dt, 20.6, 155.5 Hz, 1P, PPh₃), 109.7 (dd, 12.1, 20.6 Hz, 2P, PPh₂). IR (KBr): $\nu_{C=O} = 1519 \text{ cm}^{-1}$.

Observation of $[(Ph_2PCH_2CH_2)_2PPh]Mo(CO_2)(C_2H_4)$ (4). A J. Young NMR tube was charged with 0.015 g (0.021 mmol) of 1 and approximately 400 μ L of benzene- d_6 . On a vacuum line, 12 equiv of carbon dioxide was admitted at -196 °C via calibrated gas bulb (162 Torr in 28.9 mL). The full conversion of 1 to 4 was monitored by NMR spectroscopy and occurred in approximately 20 min at 23 °C. ¹H NMR (25 °C, C₆D₆): δ 0.21 (m, 4H, C₂H₄), 2.21 (m, 2H, PCH₂), 2.62 (m, 2H, PCH₂), 3.16–3.34 (m, 2H, PCH₂), 3.59 (m, 2H, PCH₂), 6.91 (m, 2H, C₆H₅), 7.07–7.20 (m, 17H, C₆H₅), 7.25 (m, 4H, C₆H₅), 7.81 (m, 2H, C₆H₅). ³¹P{¹H} NMR (23 °C, C₆D₆): δ 64.7 (d, 6.1 Hz, 2P, PPh₂), 95.3 (t, 6.1 Hz, 1P, PPh). IR (KBr): $\nu_{C=O} = 1700$ cm⁻¹. Partial ¹³C NMR from ¹H–¹³C HSQC: δ 27.72 (PCH₂), 33.81 (PCH₂), 41.60 (C₂H₄). Spectral data for 4-¹³C. ³¹P{¹H} NMR (23 °C, C₆D₆): δ 64.7 (dd, 6.1, 14.9, Hz, 2P, PPh₂), 95.3 (dt, 6.1, 27.7 Hz, 1P, PPh). ¹³C{¹H} NMR (23 °C, C₆D₆): δ 193.6 (dt, 14.9, 27.7 Hz, CO₂). IR (KBr): $\nu_{13C=O} = 1654$ cm⁻¹.

General Procedure for the Determination of Kinetics of Acrylate Formation. 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 was 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 monitored by ³¹P NMR spectroscopy over greater than 2 half-lives beginning after all observable quantities of 1 had converted to 4. The decay of the resonances for 4 was converted to concentration and fitted to a first-order plot of ln [4] versus time, which gave observed rate constants as the slope. Example graphs may be found in the Supporting Information.

General Procedure for Determination of Carbon Dioxide Influence on Formation of 4. Two J. Young NMR tubes were charged in parallel with a stock solution of 300 mg of a benzene d_6 solution of 1 of known concentration (ca. 0.07 M). Then 4 and 12 equiv of carbon dioxide were added via calibrated gas bulb at -196 °C, respectively. The reactions were thawed and shaken in parallel for 10 min. The reactions were then frozen at -196 °C and analyzed in series by ³¹P NMR spectroscopy.

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Supporting Information Available: Sample kinetic data and NMR spectra. These data are available free of charge via the Internet at http://pubs.acs.org.