ORGANOMETALLICS

Functionalization of Carbon Dioxide with Ethylene at Molybdenum Hydride Complexes

Yuanyuan Zhang,[†] Brian S. Hanna,[†] Andrew Dineen,[‡] Paul G. Williard,[†] and Wesley H. Bernskoetter^{*,†}

[†]Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

[‡]The Charles Stark Draper Laboratory, Inc., Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: The molybdenum tetrahydride species $(Triphos)MoH_4PPh_3$ (Triphos = PhP(CH₂CH₂PPh₂)₂) generated from sodium triethylborohydride addition to (Triphos)MoCl₃ was found to promote CO₂ functionalization to afford acrylate, propionate, and formate species. The formation of (Triphos)MoH₄PPh₃ occurs via a (Triphos)Mo(H)Cl(PPh₃) intermediate followed by dismutation of an unobserved six-coordinate molybdenum(II) dihydride complex. Addition of



dihydrogen to the dismuation product mixture affords a nearly quantitative yield of (Triphos)MoH₄PPh₃. The molybdenum tetrahydride species facilitates CO₂ insertion into a metal hydride to produce a formate complex, (Triphos)Mo(H)(κ^2 -CHO₂)(PPh₃), with an observed rate constant of [2.9(2)] × 10⁻⁴ s⁻¹ (25 °C), which is independent of CO₂ pressure. Selective formation of acrylate and propionate carbon dioxide–ethylene coupling products, (Triphos)Mo(H)(κ^2 -C₃H₃O₂)(PPh₃) and (Triphos)Mo(H)(κ^2 -C₃H₅O₂)(PPh₃), was achieved by sequential addition of olefin and heterocumulene to (Triphos)-MoH₄PPh₃. A formally zerovalent TriphosMo(η^2 -C₂H₄)₃ intermediate was characterized by NMR spectroscopy and computational analysis along the pathway for carbon dioxide–ethylene coupling.

INTRODUCTION

The rising cost and environmental impact of fossil fuel utilization has renewed interest in carbon dioxide functionalization for use in carbon-neutral energy supplies and commodity chemical production.^{1,2} The reduction of CO₂ to fuels, such as methane, methanol, and formate, has received substantial investigation, with many notable successes in activating CO₂ with hydrogen equivalents.³ Analogous reductions of CO₂ to commodity chemicals have been less explored, despite the potential to leverage a renewable and inexpensive C1 chemical feedstock.⁴ The contrasting scope of examination between these two endeavors is no doubt influenced by the higher consumption of petroleum as a fossil fuel than as an industrial chemical precursor. Nevertheless, the ability to convert CO2 into industrially desirable chemicals would still contribute significantly to harnessing one of the world's most underutilized renewable resources.⁵ Additionally, transition-metal-mediated CO₂ reduction pathways toward fuels and commodity chemicals likely share many elementary reaction features and could be pursued in unison.^{1,2}

Currently the chemical functionalization of carbon dioxide in commercial processes is limited to a small collection of products, including urea, salicylic acids, and carbonates,⁶ though many other thermodynamically viable products have been proposed and studied.^{2–4,7} Our laboratory has recently become interested in the reductive functionalization of CO_2 using ethylene and other small molecules which could furnish valuable acrylates and propionates used in applications ranging from polymeric materials to food preservatives.⁸ Inspired by seminal reports of carbon dioxide–ethylene coupling from Hoberg and Carmona in the 1980s,⁹ our laboratory has

examined the mechanism and product extrusion pathway for similar reactions at group VI metals using PhP(CH₂CH₂PPh₂)₂ (Triphos) and other ligand platforms.¹⁰ These investigations suggested that the (Triphos)Mo fragment could be useful in other CO₂ functionalization reactions which also incorporate hydrogen (or hydride) reducing agents, a potential step for accessing either fuels or commodity chemicals from CO₂. Herein we report the reductive functionalization of CO₂ to acrylate, proprionate, and formate by a single, easily accessed molybdenum polyhydride species. Multiple intermediates along these stoichiometric CO₂ activation routes have been characterized and the pathways for the reactions examined.

RESULTS AND DISCUSSION

Synthetic Utility of (Triphos)MoCl₃ Reduction with NaEt₃BH. Traditional synthetic routes to obtain low-valent molybdenum– and tungsten–phosphine complexes used in CO₂ functionalization reactions apply alkali-metal sources (e.g., sodium amalgam, potassium graphite) to metal chloride precursors in the presence of modest stabilizing ligands (e.g., dinitrogen, phosphines).¹¹ These alkali-metal reduction methods work well but are challenging to perform on a large scale, require the use of toxic mediators (e.g., mercury), and present significant safety hazards. Homogeneous hydride reducing agents offer a relatively mild and convenient alternative to accessing lower valent metals, by either direct reduction of a metal halide precursor or reductive elimination from intermediate metal–hydride species.¹² Given our interest in

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incorporating hydrogen atom sources into CO_2 activation reactions at low valent molybdenum, the use of organic soluble hydride reducing agents, such as sodium triethylborohydride (NaEt₃BH), seemed a reasonable starting point for investigation. Gratifyingly, treatment of a tetrahydrofuran suspension of (Triphos)MoCl₃ (1-Cl₃) with 2 equiv of NaEt₃BH in the presence of triphenylphosphine rapidly afforded a molybdenum(II) species, (Triphos)Mo(H)Cl(PPh₃) (2-HCl), as a deep green solid in excellent yield (eq 1). The pathway for



this transform likely proceeds via well-precedented hydride for chloride substitution and dinuclear reductive elimination of H₂, though the mechanistic details of this reaction have not been examined here.¹³ Complex 2-HCl was characterized by a combination of NMR spectroscopy, combustion analysis, and X-ray diffraction, as well as by comparison to a closely related molybdenum(II) hydrido chloride species isolated by George and co-workers during protonolysis of molybdenum dinitrogen compounds.¹⁴ The ¹H NMR spectrum of diamagnetic 2-HCl exhibited a characteristically upfield shifted Mo-H resonance at -2.42 ppm with a multiplicity consistent with coupling to an $A_2BC \ {}^{31}P$ spin system. Three corresponding peaks with a 2:1:1 integration ratio were observed in the ³¹P{¹H} NMR spectrum at 132.2 (dd), 100.1 (dt), and 47.5 (dt) ppm and assigned to the PPh₂, PPh, and PPh₃ fragments, respectively. The molecular structure of 2-HCl was also confirmed by single-crystal X-ray diffraction (Figure 1), with relevant metrical parameters for this and all subsequent crystal structures given in the Supporting



Figure 1. Molecular structure of $(Triphos)Mo(H)Cl(PPh_3)$ (**2-HCl**) with ellipsoids at the 30% probability level. All hydrogen atoms, except that attached to molybdenum, all phenyl carbons, except those attached to phosphorus, and a cocrystallized diethyl ether molecule are omitted for clarity.

Information. The data were of sufficient quality such that all hydrogens, including that attached to molybdenum, were located and refined from the Fourier map. The solid-state structure of 2-HCl exhibits a coordination environment highly distorted from octahedral symmetry. This feature is probably induced by the strong trans influence ligand and the steric congestion of the multiple phenylphosphine substituents. This distortion is particularly evident in the Cl(1)-Mo(1)-H(1)and P(3)-Mo(1)-P(4) angles of 157(2) and 107.49(2)°, respectively, which draw the PPh₂ groups down toward the relatively open molybdenum-hydride pocket. The diamagnetism of 2-HCl is likely a consequence of the hydride-induced distortion, as the corresponding molybdenum(II) dichloride complex (Triphos)MoCl₂(PPh₂) and related species with octahedral symmetry exhibit the expected magnetic moments for S = 1 metals.¹⁵

Complex 2-HCl has proven a useful synthetic precursor to several new molybdenum species relevant to our studies in CO₂ functionalization (vide infra), as well as zerovalent molybdenum complexes our laboratory has previously employed in the preparation of acrylate from CO₂ and ethylene coupling. Prior studies demonstrate that both *trans*-(Triphos)Mo(N₂)₂(C₂H₄) (1-N₂) and *trans*-(Triphos)Mo(N₂)₂PPh₃ (2-N₂) are capable of functionalizing CO₂ with ethylene to afford mono- and dimeric forms of molybdenum(II) acrylate hydride species (Figure 2).^{10a} Vinylation of 2-HCl can provide alternate access to these



Figure 2. Acrylate formation from CO_2 and ethylene promoted by 1- N_2 and 2- N_2 .

same active species without the sodium amalgam reductions employed previously.^{10a,11b} Addition of vinylmagnesium chloride to a tetrahydrofuran solution of **2-HCl** in the presence of dinitrogen immediately afforded **1-N**₂ and free PPh₃. Subsequent substitution of ethylene by PPh₃ to yield **2-N**₂ required at least 30 min at ambient temperature to give concentrations detectable by NMR spectroscopy (Figure 3).¹⁶ However, it should be noted that quick isolation and multiple recrystallizations are often necessary to purify samples of **1-N**₂ from free triphenylphosphine and the resultant magnesium halide salts. These issues have been resolved through an improved synthesis of **1-N**₂, as described in the Experimental Section.

The molybdenum(II) hydrido chloride species provided more convenient access to $1-N_2$ for CO₂-ethylene coupling reactions but also opened an attractive synthetic route directly



Figure 3. Preparation of $1-N_2$ and $2-N_2$ via vinylation of a molybdenum(II) hydrido chloride species.

to **2-acrylate**, via treatment with silver acrylate (eq 2). This method does not derive the acrylate from CO_2 and ethylene



but afforded substantial quantities of **2-acrylate** with relative ease and permitted isolation of crystals suitable for X-ray diffraction. The molecular structure of **2-acrylate** (Figure 4)



Figure 4. Molecular structure of (Triphos)Mo(H)(κ^2 -C₃H₃O₂)(PPh₃) (**2-acrylate**) with ellipsoids at 30% probability. All hydrogen atoms, except that attached to molybdenum, and all phenyl carbons, except those attached to phosphorus, are omitted for clarity.

confirms the characterization previously reported using NMR and IR spectroscopy. The data reveal an approximate pentagonal-bipyramidal geometry about the molybdenum, with P(1)-Mo(1)-P(2) (173.99(7)°) constituting the axis and the metal-hydride, carboxylate oxygens, and other phosphines comprising the equatorial pentagon. The data were again of sufficient quality such that all hydrogens, including that attached to molybdenum, were located and refined from the Fourier map. As with 2-HCl, the Triphos PPh₂ groups in 2-acrylate are drawn toward the molybdenum–hydride site with a P(3)-Mo(1)-P(4) bond angle of 110.90(6)°. The structure also illustrates the κ^2 coordination

of the acrylate ligand, which retains a carbon–carbon double bond, indicated by the C(2)–C(3) bond length of 1.36(2) Å.

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Formation of (Triphos)MoH₄PPh₃. Having successfully employed 2-HCl in the synthesis of complexes which couple CO_2 and ethylene to acrylate, additional pathways for CO_2 functionalization were sought from this platform. To induce further reactivity, the remaining chloride ligand in 2-HCl was substituted for hydride using 1 equiv of NaEt₃BH (Figure 5).



Figure 5. Hydride substitution and dismutation from 2-HCl.

Interestingly, pale yellow crystals of (Triphos)MoH₄PPh₃ (2-H₄) were isolated from the reaction mixture instead of the expected molybdenum(II) dihydride species. Complex 2-H₄ may also be obtained by addition of 3 equiv of NaEt₃BH directly to 1-Cl₃.^{17,18} Similar eight-coordinate molybdenum polyhydride species have been reported which, along with variable-temperature NMR spectroscopy and X-ray crystallography, aided in the characterization of 2-H4.19 The 1H NMR spectrum of $2-H_4$ in benzene- d_6 at ambient temperature featured a broad metal-hydride signal at -3.49 ppm with an integration corresponding to four hydrogens. Three resonances comprising an A2BC spin system were also observed in the ${}^{31}P{}^{1}H{} NMR$ spectrum at 119.8, 84.1, and 74.4 ppm. Cooling tetrahydrofuran- d_8 solutions of 2-H₄ to -70 °C produced virtually no change in the ³¹P NMR signals but resulted in decoalescence of the Mo-H signal in the ¹H NMR spectrum.²⁰ At low temperature, the hydride resonances appear as three sharp but complex multiplets centered at -2.71, -4.03, and -5.44 ppm with a 1:2:1 integration ratio (Figure 6). This variable-temperature behavior indicates the four hydrogens attached to the metal interchange rapidly at ambient temperature through either geometric rearrangement or reversible dihydride-dihydrogen equilibria.²¹ Due to the exchange of the metal-hydride positions and the inability to obtain spectra at lower temperatures, measurement of true $T_1(\min)$ values for each resonance was obviated, though a T_1 value of 780 ms (400 MHz) was measured for the three peaks at -70 °C. Detailed prior studies on closely related molybdenum and tungsten polyhydride complexes imply 2-H4 may best be described as a classical tetrahydride molybdenum(IV) structure.²²

The solid-state structure of $2-H_4$ was confirmed by X-ray diffraction (Figure 7) and was consistent with the symmetry expected from low-temperature NMR spectra. Despite the incorporation of an isotropic, disordered solvent molecule with no hydrogens which could be located and refined, the data for



Figure 6. Partial ¹H NMR (top) and ¹H 31 P} NMR (bottom) spectra of 2-H₄ at -70 °C in tetrahydrofuran-d₈.



Figure 7. Molecular structure of $(Triphos)MoH_4PPh_3$ (2-H₄) with ellipsoids at the 30% probability level. All hydrogen atoms, except those attached to molybdenum, all phenyl carbons, except those attached to phosphorus, and a cocrystallized solvent molecule are omitted for clarity.

2-H₄ did permit refinement of four hydrogens attached to molybdenum from the Fourier map. Complex $2-H_4$ exhibits a generalized dodecahedral structure consisting of two interpenetrating tetrahedra of MoH₄ and MoP₄ fragments, with the MoP₄ fragment significantly distorted toward planarity. These structural attributes are similar to those reported for MoH₄(PMePh₂)₄ and MoH₄(dppe)₂.²³ Though not crystallographically equivalent, H(97) and H(98) bisect an idealized mirror plane passing through P(1)-P(2)-H(95)-H(96). This feature accounts for the two equivalent (H(97) and H(98))and inequivalent (H(95) and H(96)) hydride environments in the solution NMR spectra (vide supra). The X-ray diffraction data show long H-H interaction distances (>1.80(6) Å) consistent with a dominantly molybdenum(IV) tetrahydride ground state, though caution must be exercised when using these X-ray-determined distances in dihydride-dihydrogen structural determinations.²¹

Isolation of $2-H_4$ from the combination of 2-HCl and NaEt₃BH cannot account for the full mass balance of the reaction and motivated in situ monitoring by NMR spectros-

copy in the presence of an internal integration standard. Treatment of a tetrahydrofuran solution of 2-HCl with 1 equiv of NaEt₃BH immediately bleached the dark green color from the solution and afforded 2-H₄ as the only diamagnetic product (neglecting minor amounts of free PPh_3) in approximately 33% yield based on molybdenum. The low yield suggested that twothirds of the molybdenum was converted to a paramagnetic product (Figure 5). Examination of the ¹H NMR spectrum revealed no signals between 150 and -150 ppm assignable to a paramagnetic molybdenum species. Conducting the NMR experiment with a ferrocene standard confirmed the presence of a paramagnetic product by the Evans method,²⁴ but without a reliable magnetic susceptibility measurement, given the mixture of products. Despite this frustration in characterizing the paramagnetic product, exposure of the in situ reaction mixture to 1 atm of dihydrogen induced growth in the NMR signals of $2-H_4$ equivalent to a >90% total yield. No additional organic or molybdenum species were observed upon H₂ addition, and control experiments using greater amounts of NaEt₃BH did not change the initial yield of 2-H₄.

The limited data regarding the paramagnetic product of the 2-HCl and NaEt₃BH reaction prevented definitive characterization, but several features regarding the species may be inferred from its reactivity and stoichiometry. The 1:2 product ratio between 2-H₄ and the uncharacterized species suggests a molybdenum(I) oxidation state. Additionally, the ability to form 2-H₄ without extrusion of other detectable organics during hydrogenation implies that the species has only phosphine and hydride ligands. One pathway that fits the observations is hydride dismutation from an unstable (Triphos)MoH₂PPh₃ intermediate.²⁵ (Triphos)MoH₂PPh₃ was initially the expected product from 2-HCl and NaEt₃BH, but in fact, examples of six-coordinate molybdenum(II) dihydride species are exceptionally rare,²⁶ especially in comparison to the corresponding molybdenum tetrahydride complexes.^{19,22,23,27} This hypothesis leads to a speculative assignment of (Triphos)Mo(H)PPh3 for the paramagnetic species. However, the relevance of this paramagnetic species to the CO₂ functionalization studies described below is minimized by the ability to hydrogenate this uncharacterized species to 2-H₄ and recrystallize with elemental purity.

Carbon Dioxide Functionalization. The molybdenum-(IV) tetrahydride complexes isolated from sodium triethylborohydride addition to 2-HCl exhibited a higher valence state than our laboratory initially sought for CO_2 functionalization



Figure 8. CO₂ reductive functionalization from 2-H₄.

with ethylene, but 2-H₄ was nevertheless examined for reactivity. Treatment of 2-H₄ with 1 atm of a 5:1 ethylene to carbon dioxide mixture produced what initially appeared to be an intractable mixture of products. However, subsequent experiments which altered the ratio and sequence of ethylene and carbon dioxide addition permitted isolation of (Triphos)- $Mo(H)(\kappa^2-CHO_2)(PPh_3)$ (2-formate), (Triphos)Mo(H)(κ^2 - $C_3H_5O_2$ (PPh₃) (2-propionate), and 2-acrylate, three distinct CO₂ activation products (Figure 8). Application of a 5:1 ethylene to carbon dioxide mixture to 2-H₄ produced 2formate as the major product of CO₂ functionalization; however, increasing the carbon dioxide fraction to a 1:1 mixture gave virtually quantitative formation of the molybdenum(II) formate hydride species over 2 h, as judged by NMR spectroscopy. In preparative-scale experiments, 2formate was isolated in good yield by treating 2-H₄ with an atmosphere of pure CO₂.

The complex 2-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 2-formate bear several similarities to those reported for 2-acrylate, 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 in 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, with bands at 1550 and 1362 cm⁻¹ for 2-formate being red-shifted down to 1511 and 1340 cm⁻¹ for the labeled isotopologue.

The insertion of carbon dioxide into transition metalhydride bonds is a key step in the hydrogenation of CO₂ to formate and has previously been observed for other molybdenum complexes.^{19a,26a,28} 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.^{3d,e,29} The insertion of carbon dioxide into 2-H4 occurred with loss of dihydrogen (detected by ¹H NMR spectroscopy) and no evidence of organic formate products. Previous studies in the field have concluded that CO₂ insertion into a metal-hydride may occur without precoordination of the heterocumulene.³⁰ Thus, it is reasonable to consider the direct insertion of CO2 into 18electron 2-H₄, followed by reductive H₂ elimination, as a possible route to 2-formate. However, monitoring the conversion of 2-H₄ to 2-formate over a range of CO₂ pressures (Table 1) showed no influence on the observed rate constant of the reaction. The persistent $[2.9(2)] \times 10^{-4} \text{ s}^{-1} (25 \text{ °C})$ rate constant indicates that incorporation of CO₂ occurs after the rate-limiting step and suggests that elimination of dihydrogen

Table 1. Pressure Dependence of Rate Constants for Formation of 2-formate from $2-H_4^{\ a}$

P _{CO2} (atm)	$k_{\rm obs}~(10^{-4}~{\rm s}^{-1})$
0.5	2.7(2)
1.0	2.9(2)
1.5	2.9(2)
2.0	2.8(2)
2.5	3.0(2)

"Rate constants measured at 25 $\,^{\circ}\mathrm{C}$ in well-mixed tetrahydrofuran solutions.

precedes CO_2 insertion (Figure 9).³¹ An alternative route necessitating dissociation of a chelating phosphine ligand could



Figure 9. Proposed pathway for CO₂ insertion into 2-H₄.

also account for a lack of CO_2 dependence but was deemed less likely, given the relative affinity of carbon dioxide and phosphine for molybdenum. Attempts to experimentally distinguish these routes by rate inhibition from excess dihydrogen were obviated by further reaction of **2-formate** with H₂, which afforded an intractable mixture of products. The reversibility of carbon dioxide insertion was evidenced by isotopic scrambling of **2-formate** and 1 atm of ¹³CO₂ at ambient temperature over 18 h.

Completing the characterization of 2-formate shifted our focus toward selective synthesis of the CO_2 functionalization products which incorporated ethylene, 2-propionate, and 2-acrylate. The formation of 2-formate, 2-propionate, and 2-acrylate in the same reaction suggested that at least two distinct CO_2 reduction pathways from 2-H₄ were competitive. Divergence between the formate and acrylate/propionate production routes could be influenced by the relative rates of 2-H₄ (or species derived from 2-H₄) reacting with carbon dioxide versus ethylene. However, the observation that addition of a 5:1 ethylene to carbon dioxide mixture to 2-H₄ still afforded 2-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 $2-H_4$ with 1 atm of ethylene for 5 h followed by addition of 0.1 atm of CO₂ and stirring for a further 14 h afforded an approximately 7:1 mixture of 2-propionate and 2acrylate with no detectable formation of 2-formate. Previously reported characterization data for 2-acrylate were used to differentiate the signals corresponding to 2-propionate.^{10a} Many of the NMR signals for 2-propionate closely resemble those of 2-acrylate, including ${}^{31}P{}^{1}H{}$ 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 ppm 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 ${}^{13}CO_2$. 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 2-propionate were red-shifted to 1486 and 1414 cm⁻¹ upon ¹³C labeling.

The origin of **2-propionate** was initially hypothesized as CO_2 insertion into a transient molybdenum ethyl complex, but subsequent observations suggested that the complex more likely derives from hydrogenation of 2-acrylate. Repeated syntheses of the 2-propionate and 2-acrylate mixture were found to increasingly favor 2-propionate at the expense of 2acrylate over longer time courses. This is consistent with 2acrylate serving as an intermediate to 2-propionate. Additionally, several previous reports of CO₂ insertion indicate that the rates of reactivity with metal-hydrides outpace those of metalalkyls in carboxylate formation.^{30b,32} 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 2-propionate was confirmed by addition of dihydrogen to the 2-propionate and 2-acrylate mixture, which completed the conversion to 2-propionate. Identical observations were made upon addition of an atmosphere of dihydrogen to isolated samples of 2-acrylate (eq 3). During CO_2 functionalization reactions, the dihydrogen



probably originates from $2-H_4$ 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.³³

Interest in these remarkable CO_2 reductive functionalization pathways motivated further investigation by in situ NMR

monitoring of the reaction of $2-H_4$, ethylene, and CO_2 . Exposure of a tetrahydrofuran- d_8 solution of 2-H₄ to 3 atm of ethylene resulted in complete decay of the molybdenum tetrahydride complex over 4 h at ambient temperature.³⁴ The ${}^{31}P{}^{1}H$ NMR spectrum displayed a new doublet and triplet at 76.4 and 105.9 ppm, respectively, along with a large peak corresponding to free PPh₃. The ¹H NMR spectrum revealed six new signals arrayed between -1.32 and 2.13 ppm along with dissolved ethane and peaks from the Triphos ligand. These resonances appear broad in the ambient-temperature ¹H NMR spectrum but sharpen considerably upon ${}^{31}P$ decoupling and cooling to -20 °C (Figure 10). ${}^{1}H^{-13}C$ HSQC NMR spectroscopy indicated that these six equal integration signals corresponded to a total of four methylene ¹³C NMR resonances, with two of the methylene carbons bearing inequivalent hydrogens.²⁰ The ¹H COSY NMR spectrum also indicated three pairwise ${}^{1}H-{}^{1}H$ coupling interactions among the six resonances. These data support the assignment of the immediate product from $2-H_4$ and ethylene reaction as a formally zerovalent molybdenum tris(ethylene) complex, (Triphos)Mo(η^2 -C₂H₄)₃ (**1**-C₂H₄) (Figure 11). Computational analysis of $1-C_2H_4$ indicated the lowest energy geometry orients the mutually trans ethylene ligands such that the C-C bonds are nearly perpendicular to each other with the third ethylene C-C bond approximately coplanar with the Triphos chelate (Figure 12). This geometry is consistent with the number of ethylene ¹³C and ¹H NMR resonances observed for $1-C_2H_4$ as well as the correlations in the 2D NMR spectra.² Attempts to isolate $1-C_2H_4$ were unsuccessful, as the species was moderately unstable in the absence of an ethylene atmosphere.35

The pathway for formation of $1-C_2H_4$ from $2-H_4$ likely involves a sequence of reductive H_2 elimination followed by ethylene hydrogenation. Although dissolved dihydrogen could not be detected by ¹H NMR spectra in the presence of an excess of ethylene, earlier experiments (vide supra) which altered the subsequent 2-propionate:2-acrylate ratio by evacuating the reaction head space strongly support the presence of H_2 . Additionally, the ethylene hydrogenation (confirmed by the presence of ethane) would necessitate a coordination vacancy to allow ethylene to bind, insert, and reductively eliminate in the ubiquitous olefin hydrogenation sequence. Unlike insertion of CO₂, there is little evidence for direct olefin insertion of ethylene into 18-electron transitionmetal—hydride complexes such as 2-H₄.³⁶

In situ monitoring of the reaction by NMR spectroscopy was continued following addition of an atmosphere of CO₂ to the $1-C_2H_4$ solution. After 30 min the resonances of $1-C_2H_4$ had completely disappeared from the ³¹P{¹H} NMR spectrum and were replaced by minor amounts of 2-propionate and 2acrylate along with more significant doublet and triplet signals at 64.9 and 95.5 ppm, respectively. These resonances match those previously reported for $(Triphos)Mo(CO_2)(C_2H_4)$, a transient intermediate observed in kinetic studies of CO2ethylene coupling to acrylate (Figure 11).^{10a} Over the next 8 h the ³¹P NMR resonances of 2-propionate and 2-acrylate continued to grow at the expense of $(Triphos)Mo(CO_2)$ - (C_2H_4) . Over the first 2 h following CO₂ addition, 2-acrylate was observed as the major CO₂ functionalization product. However, over longer time courses, 2-propionate became the major product while the resonances for 2-acrylate diminished. After 12 h, all $(Triphos)Mo(CO_2)(C_2H_4)$ was consumed, leaving an approximate 1:3 ratio of 2-acrylate to 2-propionate.



Figure 10. Partial ${}^{1}H{}^{31}P{}$ NMR spectrum of $1-C_{2}H_{4}$ at -20 °C in tetrahydrofuran- d_{8} .



Figure 11. Observed pathway for the coupling of carbon dioxide and ethylene from $2-H_4$.



Figure 12. Geometry optimized structure for 1-C₂H₄.

The lack of complete hydrogenation of **2-acrylate** may originate from loss of H_2 into the reaction headspace or through ethylene hydrogenation. These observations create a partial description of the reaction sequence for CO_2 functionalization with ethylene from **2-H**₄ (Figure 11). Our laboratory is currently engaged in studies to transfer this reaction pathway to a broader array of substrates for CO_2 olefin coupling and examine the prospects for catalytic versions of these reactions. Additionally, we hope to apply the in situ NaEt₃BH reduction procedure in pursuing a wider survey of ligand-Mo architectures for CO_2 functionalization without the restriction of isolating suitable zerovalent metal complexes.

CONCLUSIONS

The wealth of CO₂ functionalization chemistry obtained from 2-H₄ highlights the relationship between CO_2 reduction efforts toward molecular energy targets and renewable commodity chemicals. In the case of the (Triphos)Mo platform, reactions progressing toward each of these goals occur from a single molybdenum polyhydride species. The reactive $2-H_4$ complex appears to form, in part, by dismutation of an unstable sixcoordinate molybdenum(II) dihydride complex produced by treating 2-HCl with NaEt₃BH. Complete conversion of the dismutation reaction mixture to 2-H₄ may be induced by dihydrogen addition. Our findings demonstrate that CO₂ functionalization from 2-H₄ most likely occurs via this same transient molybdenum(II) dihydride complex, with competitive insertion of ethylene and carbon dioxide ultimately leading to formate, acrylate, and propionate products. The CO₂ functionalization pathways to produce formate and acrylate/ propionate may be selected by utilizing specific reaction conditions with sequential addition of carbon dioxide and ethylene. The observed rate constant of formate formation from 2-H₄, [2.9(2)] × 10⁻⁴ s⁻¹ (25 °C), was found to be independent of CO_2 pressure (0.5–2.45 atm). The pathway for CO₂ functionalization with olefin proceeds via a formally zerovalent molybdenum tris(ethylene) complex, $1-C_2H_4$, which as characterized by in situ NMR spectroscopy and computational analysis. Coupling of carbon dioxide to $1-C_2H_4$ affords an acrylate product which may then be rapidly hydrogenated to produce propionate. In addition, the remarkable array of CO₂ functionalization chemistry observed herein may be accessed by use of a convenient and mild reducing agent, obviating the harsh alkali-metal reductions commonly employed to prepare zerovalent group IV metal complexes. This observation suggests that screening a wider landscape of supporting ligands for improved rates and selectivity in CO₂ functionalization may be approached by rapid in situ generation of group VI metal hydrides or other low-valent species.

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. [(Ph₂PCH₂CH₂)₂PPh]MoCl₃ was obtained as previously described.³⁷ All other chemicals were purchased from Aldrich, Fisher, VWR, Strem, or Cambridge Isotope Laboratories. Solvents were dried and deoxygenated using literature procedures.³⁸

¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker DRX 400 MHz Avance, 300 MHz Avance, and 600 MHz Avance 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.³⁹ IR spectra were recorded on Jasco 4100 FTIR and Mettler Toledo React IR spectrometers. X-ray crystallographic data were collected on Bruker Smart Apex I and D8 QUEST diffractometers. Samples were collected in inert oil and quickly transferred to a cold gas stream. The structures were solved by direct methods and Fourier syntheses and refined by full-matrix leastsquares procedures with anisotropic thermal parameters for all nonhydrogen atoms. Crystallographic calculations were carried out using SHELXTL. Crystal structure data have been deposited with the CCDC under reference numbers 936630, 936631, and 936632. Elemental analyses were performed at Atlantic Microlab, Inc., in Norcross, GA.

Preparation of [(Ph2PCH2CH2)2PPh]Mo(H)(PPh3)(Cl) (2-HCl). A 20 mL scintillation vial was charged with 0.075 g (0.10 mmol) of 1-Cl₃, 0.025 g (0.10 mmol) of PPh₃, and approximately 5 mL of tetrahydrofuran. Then 204 μ L (0.20 mmol) of NaEt₃BH solution (1 M in toluene) was added to the suspension, resulting in a rapid color change from yellow to dark blue-green. After the mixture was stirred at ambient temperature for 1 h, the volatiles were removed in vacuo to afford a dark residue. The residue was washed with pentane to remove free PPh3 and extracted with toluene, and the extract was dried to afford 91 mg (97%) of 2-HCl as a dark blue-green solid of good purity, which can be used in subsequent procedures without further purification. Analytically pure material can be obtained by recrystallization at -35 °C from toluene solution by layering with diethyl ether. Anal. Calcd for C₅₂H₄₉MoP₄Cl + C₄H₁₀O (one cocrystallized diethyl ether): C, 67.13; H, 6.09. Found: C, 67.30; H, 6.12. ¹H NMR (25 °C, C₆D₆): δ -2.42 (tdd, 75.04, 42.02, 12.01 Hz, 1H, Mo-H), 0.79 (m, 2H, PCH₂), 1.30 (m, 2H, PCH₂), 1.56–1.79 (m, 2H, PCH₂), 2.42– 2.65 (m, 2H, PCH₂), 6.74 (m, 6H, C₆H₅), 6.87 (m, 7H, C₆H₅), 6.93-7.04 (m, 13H, C_6H_5), 7.20 (m, 5H, C_6H_5), 7.37 (m, 3H, C_6H_5), 7.77 (m, 4H, C_6H_5), 7.95 (t, 2H, C_6H_5). ¹³C{¹H} NMR (23 °C, C_6D_6): δ 27.86 (PCH₂), 35.91 (PCH₂), 127.88, 128.27, 128.49, 128.81, 129.60, 131.41 133.24, 134.31, 135.33, 137.31, 137.61, 141.32, 147.80 (Ar), three quaternary signals not located. ³¹P{¹H} NMR (23 °C, C_6D_6): δ 47.5 (dt, 12.1, 163.4 Hz, 1P, PPh3), 100.1 (dt, 24.3, 163.4 Hz, 1P, PPh), 132.2 (dd, 12.1, 24.3 Hz, 2P, PPh₂).

Preparation of [(Ph₂PCH₂CH₂)₂PPh]MOH₄PPh₃ (2-H₄). *Method A*. A heavy-walled glass reaction vessel was charged with 0.15 g (0.20 mmol) of 1-Cl₃, 0.05 g (0.20 mmol) of PPh₃, and approximately 10 mL of tetrahydrofuran. Then 610 μ L (0.30 mmol) of a NaEt₃BH solution (1 M in THF) was added to the suspension, resulting in a rapid color change from yellow to dark green over the first few minutes and finally to red- orange over 30 min. After addition of 1 atm of hydrogen gas, the reaction mixture was stirred a further 14 h at ambient temperature. The volatiles were removed in vacuo, the residue was extracted with toluene, and the filtrate was concentrated to approximately 4 mL. Careful layering of pentane onto the toluene solution and chilling at -35 °C afforded 164 mg (90%) of 2-H₄ as yellow crystals.

Method B. A heavy-walled glass reaction vessel was charged with 75 mg (0.08 mmol) of **2-HCl** and approximately 5 mL of tetrahydrofuran.

Then 81 μ L (0.08 mmol) of a NaEt₃BH solution (1 M in THF) was added to the suspension, resulting in a color change from dark green to red-orange over 30 min. After addition of 1 atm of hydrogen gas, the reaction mixture was stirred a further 14 h at ambient temperature. The volatiles were then removed in vacuo, the residue was extracted with toluene, and the filtrate was concentrated to approximately 3 mL. Careful layering of pentane onto the toluene solution and chilling at -35 °C afforded 76 mg (92%) of 2-H₄ as a yellow powder. Anal. Calcd for $C_{52}H_{52}MoP_4 + C_7H_8$ (one cocrystallized toluene): C, 71.65; H, 6.11. Found: C, 71.32; H, 6.05. ¹H NMR (25 °C, C₆D₆): δ -3.49 (br m, 4H, Mo-H), 1.07 (m, 2H, PCH₂), 1.63 (m, 2H, PCH₂), 2.12 (m, 2H, PCH₂), 2.49–2.77 (m, 2H, PCH₂), 6.74–6.82 (m, 6H, C₆H₅), 6.87 (m, 10H, C₆H₅), 7.20-7.25 (m, 13H, C₆H₅), 7.69 (m, 6H, C_6H_5), 8.14 (m, 3H, C_6H_5), 8.28 (t, 2H, C_6H_5). ¹H NMR (-70 °C, THF- d_8): δ -5.44 (m, 1H, Mo-H), -4.03 (m, 2H, Mo-H), -2.71 (m, 1H, Mo-H), 1.10 (m, 2H, PCH₂), 1.26 (m, 2H, PCH₂), 2.46-2.57 (m, 2H, PCH₂), 2.86–2.99 (m, 2H, PCH₂), 6.88 (q, 8H, C₆H₅), 6.96–7.03 (m, 8H, C_6H_5), 7.20–7.23 (m, 3H, C_6H_5), 7.30 (t, 5H, C_6H_5), 7.39– 7.43 (m, 11H, C_6H_5), 8.23 (m, 3H, C_6H_5), 8.32 (t, 2H, C_6H_5). ¹³C{¹H} NMR (23 °C, C₆D₆): δ 30.62 (PCH₂), 38.12 (PCH₂), 127.53, 127.84, 128.09, 128.31, 128.68, 129.41 132.44, 134.46, 134.55, 135.34, 141.30, 143.28, 144.56 (Ar), three quaternary signals not located. ³¹P{¹H} NMR (23 °C, C₆D₆): δ 74.4 (dt, 20.7, 47.4 Hz, 1P, PPh₃), 84.1 (d, 20.7 Hz, 2P, PPh₂), 119.8 (d, 47.4 Hz, 1P, PPh).

Preparation of [(Ph₂PCH₂CH₂)₂PPh]Mo(H)(PPh₃)($\kappa^2 O$,O-CHO₂) (2-formate). *Method A*. A heavy-walled glass reaction vessel was charged with 0.060 g (0.067 mmol) of 2-H₄ and approximately 4 mL of tetrahydrofuran. On a high-vacuum line, 10 equiv of carbon dioxide (460 Torr in 28.9 mL) was admitted to the reaction mixture at -196 °C via a calibrated gas bulb. After the mixture was stirred for 2 h at ambient temperature, the volatiles were removed in vacuo, the residue was extracted with diethyl ether, and the extract was filtered through Celite and dried to afford 57 mg (99%) of 2-formate as a redorange solid with excellent purity. Crystalline material may be obtained through layering pentane on a concentrated diethyl ether solution and chilling at -35 °C.

Method B. A heavy-walled glass reaction vessel was charged with 0.075 g (0.10 mmol) of 1-Cl₃, 0.025 mg (0.10 mmol) of PPh₃, and approximately 5 mL of tetrahydrofuran. Then 305 μ L (0.30 mmol) of NaEt₃BH solution (1 M in toluene) was added to the suspension and stirred for 30 min. On a high vacuum line, 10 equiv of carbon dioxide (187 Torr in 101 mL) was admitted to the reaction mixture at -196 °C via a calibrated gas bulb. After the mixture was stirred for a further 18 h at ambient temperature, the volatiles were removed in vacuo, the residue was extracted with diethyl ether, and the extract was filtered through Celite and dried to afford 83 mg (87%) of 2-formate as a redorange solid which contained minor amounts of free PPh₃. The crude product may be redissolved in diethyl ether, and this solution may be concentrated to approximately 3 mL, layered with pentane, and chilled at -35 °C to afford 72 mg of 2-formate as analytically pure red crystals in 75% yield based on molybdenum. Anal. Calcd for C₅₃H₅₀MoP₄O₂: C, 67.81; H, 5.37. Found: C, 68.00; H, 5.49. ¹H NMR (25 °C, C₆D₆): δ –4.74 (tdd, 74.02, 44.01, 14.00 Hz, 1H, Mo-H), 1.22 (m, 2H, PCH₂), 1.43 (m, 2H, PCH₂), 1.94 (m, 2H, PCH₂), 2.46–2.65 (m, 2H, PCH₂), 6.80 (t, 6H, C_6H_5), 6.88 (t, 3H, C_6H_5), 7.07 (m, 17H, C₆H₅), 7.11 (s, 1H OCHO), 7.14 (m, 2H, C₆H₅) 7.30 (m, 6H, C_6H_5), 7.55 (m, 4H, C_6H_5), 7.80 (t, 2H, C_6H_5). ¹³C{¹H} NMR (23 °C, C_6D_6): δ 26.15 (PCH₂), 34.52 (PCH₂), 127.72, 127.92, 128.30, 128.66, 128.78, 131.57, 133.57, 133.83, 135.36, 137.78, 141.52, 143.86, 144.66 (Ar), 169.13 (s, OCHO), three quaternary signals not located. IR (KBr): $\nu_{\rm C-O}$ 1550, 1362 cm⁻¹. ³¹P{¹H} NMR (23 °C, C₆D₆): δ 50.1 (dt, 11.5, 151.9 Hz, 1P, PPh₃), 103.5 (dt, 20.0, 151.9 Hz, 1P, PPh), 112.6 (dd, 1.5, 20.0 Hz, 2P, PPh₂). Partial spectral data for 2-formate labeled with $^{13}\text{CO}_2$ are as follows. $^{13}\text{C}\{^1\text{H}\}$ NMR (23 °C, C₆D₆): δ 169.13 (s, OCHO). IR (KBr): ν^{13} _{C-O} 1511, 1340 cm

Preparation of $[(Ph_2PCH_2CH_2)_2PPh]Mo(H)(PPh_3)(\kappa^2O,O-C_3H_5O_2)$ (2-propionate). *Method A*. A 50 mL heavy-walled glass reaction vessel was charged with 137 mg of 2-H₄ and approximately 5 mL of tetrahydrofuran. On a high-vacuum line, 3 atm of ethylene was added to the reaction mixture at -196 °C via a calibrated gas bulb.

After the mixture was stirred for 3 h at ambient temperature, the ethylene was partially removed and 4 equiv of carbon dioxide was added via a calibrated gas bulb (393 Torr in 28.9 mL) followed by 0.25 atm of dihydrogen at -196 °C. After the mixture was stirred for a further 14 h at ambient temperature, the volatiles were removed in vacuo, the residue was extracted with diethyl ether, and the extract was filtered through Celite and dried to afford 64 mg (43%) of **2**-**propionate** as a red-orange solid.

Method B. A heavy-walled glass reaction vessel was charged with 0.075 g (0.10 mmol) of 1-Cl₃, 0.025 g (0.10 mmol) of PPh₃, and approximately 5 mL of tetrahydrofuran. Then 305 μ L (0.3 mmol) of a NaEt₃BH solution (1 M in THF) was added to the suspension and the mixture stirred for 6 h. On a high-vacuum line, 25 equiv of ethylene (470 Torr in 101 mL) was admitted to the reaction at -196 °C via a calibrated gas bulb. After the mixture was stirred for 30 h at ambient temperature, an additional 4 equiv of carbon dioxide (75 Torr in 101 mL) was admitted to the reaction mixture at -196 °C via a calibrated gas bulb. After the mixture was stirred for a further 18 h at ambient temperature, the volatiles were removed in vacuo, the residue was extracted with diethyl ether, the extract was filtered through Celite, and the filtrate was concentrated to approximately 3 mL. The solution was layered with pentane and chilled at -35 °C to afford 41 mg (41%) of **2-propionate** as red crystals. Anal. Calcd for $C_{55}H_{54}MoO_2P_4 + C_5H_{12}$ (one cocrystallized pentane): C, 69.36; H, 6.40. Found: C, 69.20; H, 6.37. ¹H NMR (25 °C, C₆D₆): δ –4.70 (tdd, 71.97, 43.98, 14.00 Hz, 1H, Mo-H), 0.47 (t, 7.47 Hz, 3H, CH₃), 1.10 (br q, 7.34 Hz, 2H, CH₂), 1.21 (m, 2H, PCH₂), 1.51 (m, 2H, PCH₂), 1.97 (m, 2H, PCH₂), 2.51-2.65 (m, 2H, PCH₂), 6.80 (t, 6H, C₆H₅), 6.89 (t, 4H, C₆H₅), 7.02 (m, 7H, C_6H_5), 7.09–7.14 (m, 11H, C_6H_5) 7.32 (m, 6H, C_6H_5), 7.58 (m, 4H, C_6H_5), 7.81 (t, 2H, C_6H_5). ¹³C{¹H} NMR (23 °C, C_6D_6): δ 8.85 (OCOCH₂CH₃), 26.16 (PCH₂), 30.43 (OCOCH₂CH₃), 34.57 (PCH₂), 127.70, 127.85, 128.31, 128.47, 128.68, 131.53, 133.64, 133.88, 135.40, 138.21, 142.68, 144.25, 144.78 (P-Ar), 182.67 (s, OCOCH₂CH₃), three quaternary signals not located. ³¹P{¹H} NMR (23 °C, C₆D₆): δ 48.2 (dt, 30.4, 392.1 Hz, 1P, PPh₃), 101.5 (dt, 48.0, 392.1 Hz, 1P, PPh), 110.9 (dd, 30.4, 48.0 Hz, 2P, PPh₂). IR (KBr): ν_{C-O} 1514, 1445 cm⁻¹. Partial spectral data for **2**-propionate labeled with ¹³CO₂ are as follows. ¹H NMR (25 °C, C_6D_6): δ 0.47 (td, ${}^{3}J_{H-H} = 7.47$; ${}^{3}J_{C-H} = 5.20$ Hz, 3H, CH₃), ${}^{13}C-{}^{1}H$ coupling to methylene group obscured by signal broadening. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (25 °C, C₆D₆): 182.64 (s, CO₂Et). IR (KBr): ν¹³C-O 1486, 1414 cm^{-1}

Observation of $[(Ph_2PCH_2CH_2)_2PPh]Mo(\eta^2-C_2H_4)_3$ (1-C₂H₄) from the Reaction of 2-H₄ with Ethylene. Method A. A J. Young NMR tube was charged with 0.010 g (0.011 mmol) of 2-H₄, approximately 0.5 mL of tetrahydrofuran- d_8 , and 25 equiv (180 Torr in 28.9 mL) of ethylene. The reaction was monitored by NMR spectroscopy, showing complete conversion to a yellow solution of 1-C₂H₄ after 4 h. 1-C₂H₄ proved unstable in the absence of an ethylene atmosphere. The product was characterized by ¹H, ³¹P{¹H}, ¹H-¹³C HSQC, and ¹H-¹H COSY NMR spectroscopy without isolation.

Method B. A J. Young NMR tube was charged with 0.015 g (0.02 mmol) of 1-Cl₃ and approximately 0.5 mL of tetrahydrofuran. Then 61 μ L (0.30 mmol) of a NaEt₃BH solution (1 M in THF) was added to the suspension, and the mixture was thawed, shaken, and allowed to stand for 1 h. Then 25 equiv of ethylene was added via a calibrated gas bulb (328 Torr in 28.9 mL) at -196 °C on a high-vacuum line. After 6 h at ambient temperature conversion to 1-C₂H₄ was complete. Partial ¹H NMR (25 °C, THF-*d*₈): δ -1.32 (br, 2H, CH₂==CH₂), -0.22 (br, 2H, CH₂==CH₂), 0.28 (br, 2H, CH₂==CH₂), 0.47 (br, 2H, CH₂==CH₂), 1.10 (br, 2H, CH₂==CH₂), 2.12 (br, 2H, CH₂==CH₂), 2.32 (m, 2H, PCH₂). ³¹P{¹H} NMR (23 °C, THF-*d*₈): δ 75.5 (d, 9.7 Hz, 2P, PPh₂), 105.3 (t, 9.7 Hz, 1P, PPh). Partial ¹³C NMR taken from ¹H-1³C HSQC (25 °C, THF-*d*₈): δ 27.16 (PCH₂), 34.08 (PCH₂), 36.87, 38.58, 41.93, 46.52 (CH₂==CH₂).

Alternative Preparation of $[(Ph_2PCH_2CH_2)_2PPh]Mo(H)(PPh_3)-(\kappa^2O,O-C_3H_3O_2)$ (2-acrylate). A 20 mL scintillation vial was charged with 0.256 g (0.28 mmol) of 2-HCl and 0.050 g (0.28 mmol) of silver

acrylate. The solids were dissolved in approximately 5 mL of a 3:1 diethyl ether to toluene mixture, and the mixture was stirred at ambient temperature for 1 h. The dark reaction mixture was then filtered through Celite, which was further washed with 3 mL of toluene. The solvent was then removed by vacuum and the resulting red powder suspended in 10 mL of a 1:1 diethyl ether to pentane mixture. A red-orange powder was obtained by filtration of the suspension, affording 134 mg of **2-acrylate**. Concentration of the filtrate and cooling to -35 °C afforded a further 49 mg of **2-acrylate** as red crystals, for a total yield of 67% based on molybdenum. The material from both crops was examined by NMR spectroscopy and found to be identical with the previously reported characterization data.^{10a}

Improved Preparation of trans-[(Ph₂PCH₂CH₂)₂PPh]Mo(η^2 - $(C_2H_4)(N_2)_2$ (1-N₂). A heavy-walled glass reaction vessel was charged with 0.300 g (0.41 mmol) of 1-Cl₃ and approximately 10 mL of tetrahydrofuran. Then 1.22 mL (1.22 mmol) of NaEt₃BH solution (1 M in THF) was added to the suspension at room temperature, resulting in an immediate color change from yellow to red-orange. After addition of 1 atm of dihydrogen gas, the reaction mixture was stirred at ambient temperature for 14 h. The excess dihydrogen gas was removed in vacuo and replaced with approximately 1/2 atm of ethylene and stirred a further 3 h, affording a color change to yellow. The volume of the reaction mixture was then concentrated by half in vacuo, and the vessel was placed under an atmosphere of dinitrogen. After the mixture was stirred for 1 h, the remaining solvent was removed in vacuo over 15 min with five periodic reintroductions of N₂ for several seconds to avoid decomposition. The residue was then extracted with toluene, and the filtrate was concentrated to approximately 2 mL, layered with pentane, and chilled at -35 °C to afford 221 mg (76%) of $1-N_2$ as a yellow powder, as previously characterized.^{10a} Unlike the previously reported synthesis of $1-N_2$, the above method circumvents the use of mercury and was found to work better on larger scale syntheses.

General Procedure for the Determination of Kinetics of 2-Formate Formation. A J. Young NMR tube was charged with 500 μ L of a tetrahydrofuran solution of 2-H₄ of known concentration (ca. 0.02 M) and a capillary of triethyl phosphite for use as an integration standard. Then varying amounts of carbon dioxide were added via a calibrated gas bulb at -196 °C. The reaction mixture was thawed, shaken, and inserted into a temperature-controlled NMR probe. The sample was quickly ejected from the NMR probe and shaken between measurements to ensure complete mixing of the carbon dioxide into solution. The reaction progress was monitored by ³¹P NMR spectroscopy over greater than 2 half-lives. The decays of the resonances for 2-H₄ were converted to concentrations and fitted to a first-order plot of ln [2-H₄] versus time, which gave the observed rate constant as the slope. Example graphs may be found in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving crystallographic data for 2-HCl, 2-acrylate, and 2-H₄, selected spectral data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*e-mail: wb36@brown.edu.

Notes

The authors declare no competing financial interest.

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